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Surface effects on phase transitions of modulated phases and at Lifshitz points: A mean field theory of the ANNNI model

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Abstract. The semi-infinite axial next nearest neighbor Ising (ANNNI) model in the disordered phase is treated within the molecular field approximation, as a prototype case for surface effects in systems undergoing transitions to both ferromagnetic and modulated phases. As a first step, a discrete set of layerwise mean field equations for the local order parameter m_n in the nth layer parallel to the free surface is derived and solved, allowing for a surface field H_1 and for interactions J_S in the surface plane which differ from the interactions J_0 in the bulk, while only in the z-direction perpendicular to the surface competing nearest neighbor ferromagnetic exchange (J_1) and next nearest neighbor antiferromagnetic exchange (J_2) occurs. We show that for $\kappa \equiv -J_2/J_1 < \kappa_{\rm L} = 1/4$ and temperatures in between the critical point of the bulk ($T_{\rm cb}(\kappa)$) and the disorder line ($T_{\rm d}(\kappa)$) the decay of the profile is exponential with two competing lengths ξ_+, ξ_- with $\xi_+ \propto [T/T_{\rm cb}(\kappa)-1]^{-1/2}$ while ξ_- stays finite at $T_{\rm cb}$. The amplitudes of these exponentials $\exp(-na/\xi_\pm)$ (a is the lattice spacing) are obtained from boundary conditions that follow from the molecular field equations. For $\kappa < \kappa_{\rm L}$ but $T > T_{\rm d}(\kappa)$, as well as at the Lifshitz point ($\kappa = \kappa_{\rm L} = 1/4$) and in the modulated region ($\kappa > \kappa_{\rm L}$), we obtain a modulated profile $m_{n+1} = A\cos(naq + \psi){\rm e}^{-na/\xi}$, where again the amplitude A and the phase Ψ can be found from the boundary conditions. As a further step, replacing differences by differentials we derive a continuum description, where the familiar differential equation in the bulk (which contains both terms of order $\partial^2 m/\partial z^2$ and $\partial^4 m/\partial z^4$ here) is supplemented by two boundary conditions, which both contain terms up to order $\partial^2 m/\partial z^2$. It is shown that the solution of the continuum theory reproduces the lattice model only when both the leading correlation length (ξ^+ or ξ, respectively) *and* the second characteristic length (ξ_- or the wavelength of the modulation $\lambda = 2\pi/q$, respectively) are very large. We obtain for $J_{\rm s} > J_{\rm sc}(\kappa)$ a surface transition, with a two-dimensional ferromagnetic order occurring at a transition $T_{\rm cs}(\kappa)$ exceeding the transition of the bulk, and calculate the associated critical exponents within mean field theory. In particular, we show that at the Lifshitz point $T_{\rm cs}(\kappa_{\rm L}) - T_{\rm cb}(\kappa_{\rm L}) \propto (J_{\rm s} - J_{\rm sc})^{1/\phi_{\rm L}}$ with $\phi_{\rm L} = 1/4$ while for $\kappa \neq \kappa_{\rm L}$ the crossover exponent is $\phi = 1/2$. We also consider the "ordinary transition" ($J_{\rm s} < J_{\rm sc}(\kappa)$) and obtain the critical exponents and associated critical amplitudes (the latter are often singular when $\kappa \to \kappa_{\rm L}$). At the Lifshitz point, the exponents of the surface layer and surface susceptibilities take the values $\gamma_{11}^{\rm L} = -1/4$, $\gamma_1^{\rm L} = 1/2$, $\gamma_{\rm s}^{\rm L} = 5/4$, while from scaling relations the surface "gap exponent" is found to be $\Delta_1^{\rm L} = 3/4$ and the surface order parameter exponents are $\beta_1^{\rm L} = 1$, $\beta_{\rm s}^{\rm L} = 1/4$. Open questions and possible applications are discussed briefly.

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1 Introduction

Spatially modulated periodic structures occur in a variety of condensed matter systems, and find increasing interest [1–15], including helimagnetic structures [1,4,6, 7], magnetic layers [8], dielectric materials [3,9], ordered metallic alloys [2,10,11], Langmuir films [12], amphiphilic systems [13], diblock copolymers [14,15], for instance. This selforganization can result from competing interactions, and a generic model to describe this competition in the simplest terms is the axial next nearest neighbor Ising (ANNNI) model [1,4,6,16]. In this model, sites i of a (hyper)cubic d-dimensional lattice carry Ising spins $S_i = \pm 1$, which interact with a (ferromagnetic) nearest neighbor interaction $J_1 > 0$, while in one lattice direction (the z-direction) a competing antiferromagnetic interaction $J_2 < 0$ is present. If the ratio $\kappa = -J_2/J_1$ exceeds

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a particular value κ_L, the system undergoes a (second order) phase transition from the disordered phase to a modulated phase, characterized by a wavenumber $q(\kappa)$ with $q(\kappa) \propto (\kappa - \kappa_L)^{\beta_q}$ [17,18], β_q being an (universal) exponent characterizing the vanishing of $q(\kappa)$ as one approaches the multicritical value κ_L, at this so-called [17] Lifshitz point. For $\kappa < \kappa_L$, one has a standard phase transition from a paramagnetic phase to a ferromagnetic phase in this Ising spin system as the temperature is lowered. Of course, the mechanism of this competition among interactions differs in the various systems mentioned above. *E.g.*, in block copolymers $(A_f B_{1-f})$, *i.e.* flexible polymer chains where a chain of type A and length $N_A = fN$ is covalently linked to a chain of type B and length $N_B = (1-f)N$, the competition arises between the repulsive interaction between monomers of different kind (which would favor unmixing) and the elastic force keeping A and B parts of the coil closely together.

While the bulk phase behavior of such systems and also interfacial properties (*e.g.* [19]) have received much attention in the literature, the effect of free surfaces on the ordering of modulated phases has been studied much less, with the notable exception of surface effects on block copolymers [20,21]. Although surface effects on the paramagnetic – ferromagnetic phase transition have found longstanding interest [22–25], we are not aware of any previous work addressing surface critical behavior at a Lifshitz point (while surface effects at tricritical points have been early studied [26]).

In the present paper we take a modest first step towards such problems, confining our attention to a molecular field theory of the ANNNI model in the disordered phase for semi-infinite geometry. Similar as in our recent study of the kinetics of surface enrichment in binary mixtures [27], the lattice approach yields a microscopic justification of boundary conditions that apply to the partial differential equation describing the corresponding continuum Ginzburg-Landau type approach in order to include surface effects there. An alternative route using symmetry arguments in the framework of field theory [28] might also be useful but is left to future work. And while we pay attention to describe the expected surface phase diagrams – with a suitable enhancement of interactions in the surface layer, the surface of a ferromagnet may order before the bulk, as is well known, and a surface-bulk multicritical point occurs [22–25] – we do not attempt to describe surface critical phenomena beyond the mean field level here, although close to criticality for a Lifshitz point even stronger deviations from mean field theory are expected than for an ordinary critical point (remembering that the upper critical dimension is $d_u = 4$ for Ising ferromagnets but $d_u = 4.5$ for uniaxial Lifshitz points [17,18]).

In Section 2, we briefly recall the phase behavior of the ANNNI model in the bulk, in the framework of molecular field theory, and of the corresponding Ginzburg-Landau theory. Section 3 then reviews the basic facts and definitions needed to describe surface criticality, considering also the extensions necessary in our context. Section 4 then presents the molecular field treatment of the semi-infinite ANNNI model, and derives its surface phase diagram. Section 5 then presents the derivation of suitable boundary conditions for the corresponding continuum theory, while Section 6 considers the corresponding free energy functional. Our conclusions are summarized in Section 7.

2 Mean field theory of the ANNNI model in the disordered phase: a brief review

2.1 The wavevector-dependent susceptibility

In this section we recall the basic facts about the ANNNI model to the extent that they will be needed later, and also introduce the necessary notation.

A convenient starting point of our discussion is the wavevector-dependent susceptibility $\chi(\mathbf{k})$, which for Ising systems in the limit where the magnetic field H tends to zero becomes [29]

$$\chi(\mathbf{k}) = (k_B T)^{-1}[1 - J(\mathbf{k})/k_B T]^{-1}, \tag{1}$$

where k_B is Boltzmann's constant, T the absolute temperature, and $J(\mathbf{k})$ the Fourier transform of the exchange interactions J_{ij},

$$J(\mathbf{k}) = \sum_{j(\neq i)} J_{ij} \exp[\mathrm{i}\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)] \tag{2}$$

$\mathbf{r}_i$, $\mathbf{r}_j$ being the position vectors of the lattice sites labelled by i, j. We wish to evaluate equations (1, 2) for the ANNNI model, where we choose the nearest neighbor exchange (J_0) isotropic in all lattice directions apart from the z direction, where we have both a nearest neighbor exchange (J_1) and a next nearest neighbor exchange (J_2),

$$\mathcal{H} = -J_0 \sum_{\substack{\langle i,j \rangle \\ \text{same } z}} S_i S_j - J_1 \sum_{\langle i,j \rangle_{\text{nn}}} S_i S_j - J_2 \sum_{\langle i,j \rangle_{nnn}} S_i S_j - H \sum_i S_i, \tag{3}$$

and $S_i = \pm 1$. Denoting the coordination number in the (hyper) plane perpendicular to the z-axis as $z_\parallel$, one finds {writing the wavevector $\mathbf{k}$ as $(\mathbf{k}_\parallel, k_z)$}

$$J(\mathbf{k}) = z_\parallel J_0 \cos(k_\parallel a) + 2J_1 \cos(k_z a) + 2J_2 \cos(2k_z a), \tag{4}$$

a being the lattice spacing. From equation (1) one concludes that the wavevector $\mathbf{k}$ that yields the maximum of $J(\mathbf{k})$ defines the type of ordering (in the case of second-order transitions). This maximum occurs for $\mathbf{k} = (0, q)$ where q satisfies the equation $J_1 \sin(qa) + 2J_2 \sin(2qa) = 0$, which yields a nontrivial result for $\kappa \equiv -J_2/J_1 > \kappa_L = 1/4$,

$$\cos(qa) = (4\kappa)^{-1}, \; q \approx a^{-1}\sqrt{2(\kappa/\kappa_L - 1)} \text{ for } \kappa \to \kappa_L, \tag{5}$$

which exhibits an exponent $\beta_q = 1/2$ in mean field theory. For $\kappa \to \kappa_L$ we have $q = 0$, *i.e.* the ferromagnetic susceptibility diverges as $T \to T_{cb}$,

$$k_B T \chi(\mathbf{k}) = \hat{\Gamma}(1 - T_{cb}/T)^{-\gamma_b}(1 + k_\parallel^2 \xi_\parallel^2 + k_\perp^2 \xi_\perp^2)^{-1}, \tag{6}$$

with $\hat{\Gamma} = 1$, $\gamma_b = \gamma_b^{MF} = 1$ and the standard mean field result for the critical point,

$$k_B T_{cb} = z_\| J_0 + 2J_1 + 2J_2 = z_\| J_0 + 2J_1(1-\kappa). \quad (7)$$

Parallel ($\xi_\|$) and perpendicular ($\xi_\perp$) correlation ranges are defined by

$$\xi_\| = \hat{\xi}_\|(1 - T_{cb}/T)^{-\nu_b},\ \xi_\perp = \hat{\xi}_\perp(1 - T_{cb}/T)^{-\nu_b}, \quad (8)$$

where in mean field theory the critical exponent $\nu_b = 1/2$, and the critical amplitudes $\hat{\xi}_\|$, $\hat{\xi}_\perp$ are given by

$$\begin{aligned}\hat{\xi}_\| &= a\sqrt{J_0/k_B T_{cb}},\\ \hat{\xi}_\perp &= a\sqrt{(J_1+4J_2)/k_B T_{cb}}\\ &= a\sqrt{J_1/k_B T_{cb}}\,(1-\kappa/\kappa_L)^{1/2}. \end{aligned} \quad (9)$$

Note the critical vanishing of $\hat{\xi}_\perp$ as one approaches the Lifshitz point (in general we have $\hat{\xi}_\perp \propto (1-\kappa/\kappa_L)^\phi$ where ϕ is the crossover exponent near the Lifshitz point [18]). Right at the Lifshitz point, equations (1–4) yield (now $T_{cb} = T_L = z_\| J_0 + 3J_1/2$)

$$k_B T \chi(\mathbf{k}) = \hat{\Gamma}(1 - T_{cb}/T)^{-\gamma_b}(1 + k_\|^2 \xi_\|^2 + k_\perp^4 \xi_\perp^4)^{-1}, \quad (10)$$

where $\xi_\|$ is still given by equations (8, 9) but $\xi_\perp$ is now given by

$$\begin{aligned}\xi_\perp &= \xi_\perp^{(L)} = \hat{\xi}_\perp^{(L)}(1 - T_{cb}/T)^{-\nu_L},\\ \nu_L &= \frac{1}{4}, \quad \hat{\xi}_\perp^{(L)} = a(J_1/4)^{1/4}. \end{aligned} \quad (11)$$

In the modulated phase, one finds

$$k_B T \chi(\mathbf{k}) = \hat{\Gamma}(1 - T_{mb}/T)^{-\gamma_b}[1 + k_\|^2 \xi_\|^2 + (k_\perp - q)^2 \xi_\perp^2]^{-1}, \quad (12)$$

with the critical temperature of the modulated phase

$$\begin{aligned}k_B T_{mb} &= z_\| J_0 - 2J_2 - J_1^2/(4J_2)\\ &= k_B T_{cb} + J_1 \frac{\kappa_L}{\kappa}\left(\frac{\kappa}{\kappa_L} - 1\right)^2, \quad \kappa > \kappa_L \end{aligned} \quad (13)$$

i.e. T_{cb} and T_{mb} merge at T_L without a discontinuity in their slope (Fig. 1).

The critical amplitude $\hat{\Gamma} = 1$ again, as well as $\gamma_b = 1$, and in analogy with equation (8) we have

$$\xi_\| = \hat{\xi}_\|(1 - T_{mb}/T)^{-\nu_b}, \quad \xi_\perp = \hat{\xi}_\perp(1 - T_{mb}/T)^{-\nu_b}$$

with $\nu_b = 1/2$, but the critical amplitudes now are given by

$$\begin{aligned}\hat{\xi}_\| &= a\sqrt{J_0/k_B T_{mb}},\\ \hat{\xi}_\perp &= a\sqrt{J_1/k_B T_{mb}}\left[\left(1 - \frac{\kappa_L^2}{\kappa^2}\right)\frac{\kappa}{\kappa_L}\right]^{1/2}, \end{aligned} \quad (14)$$

i.e. again it is evident that $\hat{\xi}_\perp \propto (\kappa/\kappa_L - 1)^\phi$ with $\phi = 1/2$.

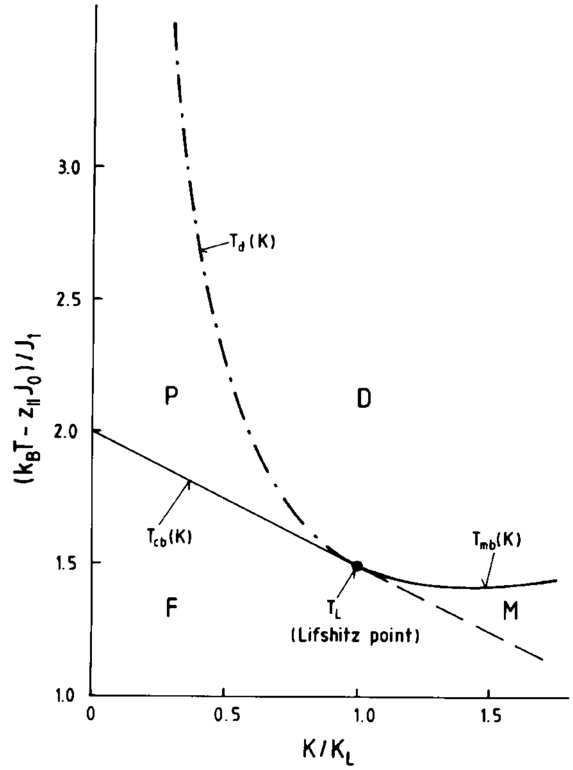

Fig. 1. Phase diagram of the ANNNI model in the bulk in molecular field approximation, in the plane of variables $(k_B T - z_\| J_0)/J_1$ and $\kappa = -J_2/J_1$. The phase transition occurs from a paramagnetic phase (P) (characterized by a monotonously decaying correlation function, to a ferromagnetic phase (F) at $T = T_{cb}(\kappa)$ for $\kappa \le \kappa_L$. The endpoint of this line, $T_L = T_{cb}(\kappa = \kappa_L)$, is the Lifshitz point. For $\kappa > \kappa_L$ one has a transition from a disordered phase (D), where the correlation function exhibits an oscillatory decay, to a phase with modulated periodic order at $T = T_{mb}(\kappa)$. Note that in molecular field approximation $T_{cb}(\kappa)$ and $T_{mb}(\kappa)$ meet tangentially at the Lifshitz point. The disorder line $T_d(\kappa)$ does not mean a thermodynamic phase transition but a crossover of the asymptotic decay of the correlation function from exponentially damped oscillatory (for $T > T_d(\kappa)$) to simple exponential (for $T < T_d(\kappa)$). The disorder line also merges tangentially at T_L with $T_{cb}(\kappa)$. Note that the phase structure of the ordered phase for $\kappa > \kappa_L$ (which is characterized by a devil's staircase of infinitely many high-order commensurate phases [33,34]) is not shown here.

2.2 Solution of the difference equations

For a treatment of the surface effects in the later sections it is important to treat the problem not only in reciprocal space but also in position space. We start from the fact that in mean field theory every spin is aligned by the local field acting on it; this field is written as a sum of the external field and the contribution due to the coupling to the neighboring spins. For the sake of simplicity, only an inhomogeneity in the z-direction is considered. Labeling the lattice planes normal to the z-direction by an index n, we have for the average magnetization M_n of the nth plane, $n \geq 3$

$$M_n = \tanh \frac{1}{k_B T} \Big\{ H + z_\parallel J_0 M_n + J_1(M_{n-1} + M_{n+1}) + J_2(M_{n-2} + M_{n+2}) \Big\}. \quad (15)$$

In the limit $H \to 0$ and in the region of the disordered phase the tanh functions can be linearized, and hence a linear inhomogeneous set of equations result. Setting $M_n = \tilde{M}_n + M_b$, $M_b = H/(k_B T - z_\parallel J_0 - 2J_1 - 2J_2) = \chi_b H$, we recover $\chi_b = \chi(\mathbf{k} = 0)$ and obtain for the deviation $\tilde{M}_n$ a homogeneous equation,

$$(z_\parallel J_0 - k_B T)\tilde{M}_n + J_1(\tilde{M}_{n-1} + \tilde{M}_{n+1}) + J_2(\tilde{M}_{n-2} + \tilde{M}_{n+2}) = 0, \quad (16)$$

which we solve by assuming an exponential decay, $\tilde{M}_n \propto \exp(-na/\xi)$, to find

$$\cosh(a/\xi_\pm) = -\frac{J_1}{4J_2} \pm \frac{1}{8J_2}\Big[4J_1^2 - 16J_2\left(z_\parallel J_0 - k_B T - 2J_2\right)\Big]^{1/2} \quad (17)$$

It is seen that real solutions are found only for temperatures $T < T_d$, $T = T_d(\kappa)$ being the "disorder line" [30–32],

$$k_B T_d(\kappa)/J_1 = z_\parallel J_0/J_1 + (4\kappa)^{-1} + 2\kappa = k_B T_{cb}(\kappa)/J_1 + \frac{\kappa_L}{\kappa}\left(\frac{\kappa}{\kappa_L} - 1\right)^2, \; \kappa < \kappa_L. \quad (18)$$

One sees that the disorder line in mean field theory simply is the continuation of the critical line of the modulated phase $T_{mb}(\kappa)/J_1$, *cf.* equation (13). For $J_2 \to 0$ the disorder line persists to arbitrarily large temperatures, $k_B T_d/J_1 \approx -J_1/4J_2 \to \infty$, which agrees with the exact result for the 1-dimensional case [30], $\cosh(J_1/k_B T_d) = \exp(-2J_2/k_B T_d)$, in leading order of the high temperature expansion. For a more detailed analysis of mean field theories for the ANNNI model we refer to the literature [33,34].

We now discuss the behavior of the correlation lengths ξ_+, ξ_- near $T_{cb}(\kappa)$. From equation (17) one can show that for $T \to T_{cb}(\kappa)$ the length ξ_- indeed stays finite, and is given by

$$\sinh \frac{a}{2\xi_-} = \left(\frac{\kappa_L}{\kappa} - 1\right)^{1/2}, \quad T = T_{cb}(\kappa). \quad (19)$$

The length ξ_- thus diverges as the Lifshitz point is approached, while $\xi_- \to 0$ when $J_2 \to 0$ (the latter finding applies to all temperatures, not only for $T = T_{cb}(\kappa)$). The length ξ_+, on the other hand, diverges for $T \to T_{cb}(\kappa)$ in the whole range $\kappa < \kappa_L$, and one finds readily from equation (17) for $T \to T_{cb}(\kappa)$

$$\xi_+ \approx a\left[\frac{J_1 + 4J_2}{k_B(T - T_{cb}(\kappa))}\right]^{1/2} = a\sqrt{\frac{J_1}{k_B T_{cb}(\kappa)}}\left(\frac{T}{T_{cb}(\kappa)} - 1\right)^{1/2}\left(1 - \frac{\kappa}{\kappa_L}\right)^{1/2}, \quad (20)$$

which precisely coincides with the correlation range $\xi_\perp$, in equations (8, 9), as expected. Somewhat further away from $T_{cb}(\kappa)$, however, $\xi_\perp(\kappa)$ and ξ_+, no longer agree: ξ_+ is the true correlation length, describing the asymptotic decay of the correlation function in real space for large distances, and differs in general from the correlation range obtained from the second moment of the correlation function, as considered in equations (6–9) [35].

We now discuss the behavior in the region where $4J_1^2 - 16J_2(z_\parallel J_0 - k_B T - 2J_2) < 0$, so a naive application of equation (17) would yield complex correlation lengths $\xi_\pm^{(c)}$. Of course, only real M_n make sense, and hence these terms $\exp(-na/\xi^{(c)})$ with complex ξ have to be decomposed into real and imaginary parts and rearranged to give

$$\tilde{M}_n \propto \exp(-na/\xi)\cos(n\varphi), \quad \text{or} \quad \tilde{M}_n \propto \exp(-na/\xi)\sin(n\varphi), \quad (21)$$

where now ξ and φ are real, and for $T \to T_{mb}$ as given by equation (13) we expect to obtain $\varphi = qa$ with q given by equation (5), and $\xi = \hat{\xi}_\perp(1 - T_{mb}/T)^{-1/2}$ with $\xi_\perp$ given by equation (14). Thus when we use equation (21) in equation (16) we find that equation (21) solves equation (16) only if

$$z_\parallel J_0 - k_B T + J_1\Big\{e^{-a/\xi}(\cos\varphi - \tan(n\varphi)\sin\varphi) + e^{a/\xi}(\cos\varphi + \tan(n\varphi)\sin\varphi)\Big\} + J_2\Big\{e^{-2a/\xi}(\cos 2\varphi - \tan(n\varphi)\sin 2\varphi) + e^{2a/\xi}(\cos 2\varphi + \tan(n\varphi)\sin 2\varphi)\Big\} = 0 \quad (22)$$

holds identically for all n. Requiring hence that the coefficient of $\tan(n\varphi)$ vanishes yields

$$\cos\varphi = -(J_1/4J_2)/\cosh(a/\xi) \to (4\kappa)^{-1} \text{ for } \xi \to \infty. \quad (23)$$

Thus $\varphi = qa$, equation (5), is indeed recovered for large ξ. Using equation (23) in equation (22) yields

$$z_\parallel J_0 - k_B T - \frac{J_1^2}{4J_2} - 2J_2 + \frac{J_1^2}{4J_2}\tanh^2(a/\xi) - 4J_2\sinh^2(a/\xi) = 0,$$

which yields $\xi \to \infty$ for $T = T_{mb}$ as given by equation (13), and for T near T_{mb} where $\tanh(a/\xi) \approx \sinh(a/\xi) \approx a/\xi$ can be used. Near T_{mb} we recover the result for $\xi_\perp$ as described by equations (8, 14). Of course, further away from T_{mb} the result for ξ that follows differs from equation (14), as expected. One finds

$$\sinh^2(a/\xi) = \frac{1}{2}\Bigg\{ \left[\frac{\kappa_{\rm L}^2}{\kappa^2} - 1 + \frac{\kappa_{\rm L}}{\kappa}(T - T_{\rm mb})k_{\rm B}/J_1\right] \overset{+}{(-)} \sqrt{\left[\frac{\kappa_{\rm L}^2}{\kappa^2} - 1 + \frac{\kappa_{\rm L}}{\kappa}\frac{(T - T_{\rm mb})k_{\rm B}}{J_1}\right]^2 + \frac{4\kappa_{\rm L}}{\kappa}\frac{(T - T_{\rm mb})k_{\rm B}}{J_1}}\Bigg\}. \quad (24)$$

At the Lifshitz point ($\kappa = \kappa_{\rm L}$) for $T \to T_{\rm mb}(\kappa_{\rm L}) = T_{\rm L}$ the last term under the square root yields the leading behavior, *i.e.* $\sinh^2(a/\xi) \approx \sqrt{(T - T_{\rm L})k_{\rm B}/J_1}$, and hence one recovers the behavior found in equation (11), with $\nu_{\rm L} = 1/4$.

2.3 Continuum theory

Now it is also useful to derive a continuum theory from the lattice model. This can be done by associating a continuous function $m(z)$ to the discrete function $\tilde{M}_n$ with $n = za$ and replacing differences by differentials,

$$\tilde{M}_{n\pm1} = m(z) \pm a{\rm d}m/{\rm d}z + (a^2/2){\rm d}^2m/{\rm d}z^2 \pm (a^3/6){\rm d}^3m/{\rm d}z^3 + (a^4/24){\rm d}^4m/{\rm d}z^4 + ..., \quad (25)$$

and an anologuous expression applies for $\tilde{M}_{n\pm2}$. Then equation (16) has to be replaced by

$$\left[z_\| J_0 - k_{\rm B}T + 2(J_1 + J_2)\right] m(z) + a^2(J_1 + 4J_2){\rm d}^2m/{\rm d}z^2 + (a^4/12)(J_1 + 16J_2){\rm d}^4m/{\rm d}z^4 = 0. \quad (26)$$

We first consider the ferromagnetic side of the phase diagram where the coefficient of the second derivative, $a^2(J_1 + 4J_2) = a^2J_1(1 - \kappa/\kappa_{\rm L})$ is positive. There equation (26) is rewritten, using equation (7)

$$[k_{\rm B}(T_{\rm cb} - T)/J_1]\, m(z) + a^2(1 - \kappa/\kappa_{\rm L}){\rm d}^2m/{\rm d}z^2 + (a^4/12)(1 - 4\kappa/\kappa_{\rm L}){\rm d}^4m/{\rm d}z^4 = 0. \quad (27)$$

Setting as above $m(z) \propto \exp(-z/\xi)$ one obtains a biquadratic equation for ξ, which yields

$$(a/\xi_\pm)^2 = -\frac{6(1 - \kappa/\kappa_{\rm L})}{(1 - 4\kappa/\kappa_{\rm L})} \pm \sqrt{\left[\frac{6(1 - \kappa/\kappa_{\rm L})}{(1 - 4\kappa/\kappa_{\rm L})}\right]^2 - \frac{12k_{\rm B}(T_{\rm cb} - T)/J_1}{(1 - 4\kappa/\kappa_{\rm L})}}. \quad (28)$$

The condition that the argument of the square root is nonnegative then requires that $T_{\rm cb} < T < T_{\rm d}^{\rm cont}(\kappa)$, where the result of the continuum theory for the disorder line is

$$k_{\rm B}T_{\rm d}^{\rm cont}(\kappa)/J_1 = k_{\rm B}T_{\rm cb}(\kappa)/J_1 + 3(\kappa/\kappa_{\rm L} - 1)^2/(4\kappa/\kappa_{\rm L} - 1), \quad \kappa > \kappa_{\rm L}/4. \quad (29)$$

Comparing equations (18, 29) we note agreement to leading order in $(\kappa/\kappa_{\rm L} - 1)^2$ only, while further away from $T_{\rm cb}(\kappa)$ equation (29) deviates from equation (18); in particular, $T_{\rm d}^{\rm cont}(\kappa) \to \infty$ for $\kappa = \kappa_{\rm L}/4 = 1/16$ rather than for $\kappa \to 0$. This discrepancy, of course, must be expected, since the continuum approximation, equations (25–28), reproduces the lattice model only for $T \to T_{\rm cb}$ where $\xi \to \infty$, while for temperatures above $T_{\rm cb}$ where ξ is no longer very large, the lattice and continuum models differ. Therefore we are interested in equation (28) only in the limit $T \to T_{\rm cb}(\kappa)$, and can hence simplify equation (28) by expanding the square root to find (calling the larger length ξ_+ as in Eq. (20))

$$(a/\xi_+)^2 \approx \{k_{\rm B}\,[T - T_{\rm cb}(\kappa)]\,/J_1\}\,/(1 - \kappa/\kappa_{\rm L}), \quad (30)$$

$$(a/\xi_-)^2 \approx 12(1 - \kappa/\kappa_{\rm L})/(4\kappa/\kappa_{\rm L} - 1). \quad (31)$$

While equation (30) is identical to equation (20) for all κ, equation (31) reduces to equation (19) again only in the leading order of $(\kappa/\kappa_{\rm L} - 1)$, as expected, since for κ away from $\kappa_{\rm L}$ ξ_- is a finite length, and can no longer be predicted reliably from the continuum approximation. Note also that throughout the above treatment we have considered decaying solutions only, $\tilde{M}_n \propto \exp(-na/\xi)$ or $m(z) \propto \exp(-z/\xi)$, respectively. Of course exponentially growing solutions, $\tilde{M}_n \propto \exp(na/\xi)$ or $m(z) \propto \exp(z/\xi)$ exist as well, but yield nothing new here, and also we need not consider them for the semiinfinite problem, although we shall need them when we consider thin films.

In full analogy to equation (21) we try for $\kappa \geq \kappa_{\rm L}$ a solution $m(z) \propto \exp(-z/\xi)\cos(qz)$ in equation (27) to find (remember that $T_{\rm cb}(\kappa)$ for $\kappa > \kappa_{\rm L}$ is no longer the critical temperature, since the modulated structure orders at $T_{\rm mb}(\kappa) > T_{\rm cb}(\kappa)$, see Fig. 1).

$$\exp(-z/\xi)\cos(qz)\Bigg\{\frac{k_{\rm B}(T - T_{\rm cb})}{J_1} + a^2\left(\frac{\kappa}{\kappa_{\rm L}} - 1\right) \times \left[\xi^{-2} - q^2 + \frac{2q}{\xi}\tan(qz)\right] + \frac{a^4}{12}\left(\frac{4\kappa}{\kappa_{\rm L}} - 1\right) \times \left[\xi^{-4} - \frac{6q^2}{\xi^2} + q^4 + 4\left(\frac{q}{\xi^3} - \frac{q^3}{\xi}\right)\tan(qz)\right]\Bigg\} = 0. \quad (32)$$

This equation is the continuum analog of equation (22), and again we must require that the coefficient of $\tan(qz)$ in the curly bracket must vanish identically, in order that equation (27) holds for arbitrary z. As above (Eq. (23)), one obtains an equation for the wavenumber q describing the modulated structure,

$$q^2 = \xi^{-2} + 6a^{-2}\frac{\kappa/\kappa_{\rm L} - 1}{(4\kappa/\kappa_{\rm L} - 1)} \xrightarrow[\kappa \to \kappa_{\rm L}]{} 8a^{-2}(\kappa - \kappa_{\rm L}) + \xi^{-2}. \quad (33)$$

Comparing equation (33) with equation (23) we note, using $\varphi \equiv qa$, that the latter equation can be reduced for small q and large ξ to equation (33), using $\cos(qa) \approx 1 - (qa)^2/2$, $\cosh(a/\xi) \approx 1 + (a/\xi)^2/2$. However, even for $\xi \to \infty$, equations (23, 33) agree only to leading order in $(\kappa - \kappa_{\mathrm{L}})$, while higher order terms differ. The condition that the differential equation, equation (27), approximates accurately the difference equation, equation (16), is only satisfied if *all* characteristic lengths are very large, both the correlation length ξ and the wavelength of the modulation, $2\pi/q$. Therefore the continuum theory can describe the mean field theory of the ANNNI model (Fig. 1) along the full region of the ferromagnetic critical line, $T_{\mathrm{cb}}(\kappa)$, $0 \leq \kappa \leq \kappa_{\mathrm{L}}$, and at only a small part of the critical line $T_{\mathrm{mb}}(\kappa)$, of the modulated phase near the Lifshitz point (*i.e.*, $\kappa/\kappa_{\mathrm{L}} - 1 \ll 1$).

To find the result for $T_{\mathrm{mb}}(\kappa)$ that would result from equation (32) one uses equation (33) to obtain a quadratic equation for ξ^{-2} which is solved by

$$(a/\xi)^{-2} = -\frac{3(\kappa/\kappa_{\mathrm{L}} - 1)}{4\kappa/\kappa_{\mathrm{L}} - 1} + \sqrt{\frac{3k_{\mathrm{B}}(T - T_{\mathrm{cb}})}{J_1(4\kappa/\kappa_{\mathrm{L}} - 1)}} \cdot \quad (34)$$

At the Lifshitz point ($\kappa = \kappa_{\mathrm{L}}$, $T_{\mathrm{cb}} = T_{\mathrm{L}}$) the first term on the right hand side of equation (34) vanishes, and equation (34) reduces to equation (11) for large ξ. For $\kappa > \kappa_{\mathrm{L}}$ we find from the condition $\xi^{-2} = 0$ the critical line $T_{\mathrm{mb}}(\kappa)$ of the modulated phase,

$$\frac{k_{\mathrm{B}}\left[T_{\mathrm{mb}}(\kappa) - T_{\mathrm{cb}}(\kappa)\right]}{J_1} = \frac{3(\kappa/\kappa_{\mathrm{L}} - 1)^2}{4\kappa/\kappa_{\mathrm{L}} - 1}, \quad (35)$$

which agrees with equation (13) in leading order in $(\kappa/\kappa_{\mathrm{L}} - 1)^2$, while higher order terms $(\kappa/\kappa_{\mathrm{L}} - 1)^3$, etc. already differ. For $\kappa > \kappa_{\mathrm{L}}$ and $T \geq T_{\mathrm{mb}}$, equation (34) yields

$$(a/\xi)^2 \approx \frac{1}{2} k_{\mathrm{B}} \frac{T - T_{\mathrm{mb}}(\kappa)}{(\kappa/\kappa_{\mathrm{L}} - 1)J_1} \quad (36)$$

which agrees with the correlation length $\xi_\perp$ as extracted from the structure factor, equation (14), to leading order in $(\kappa/\kappa_{\mathrm{L}} - 1)$.

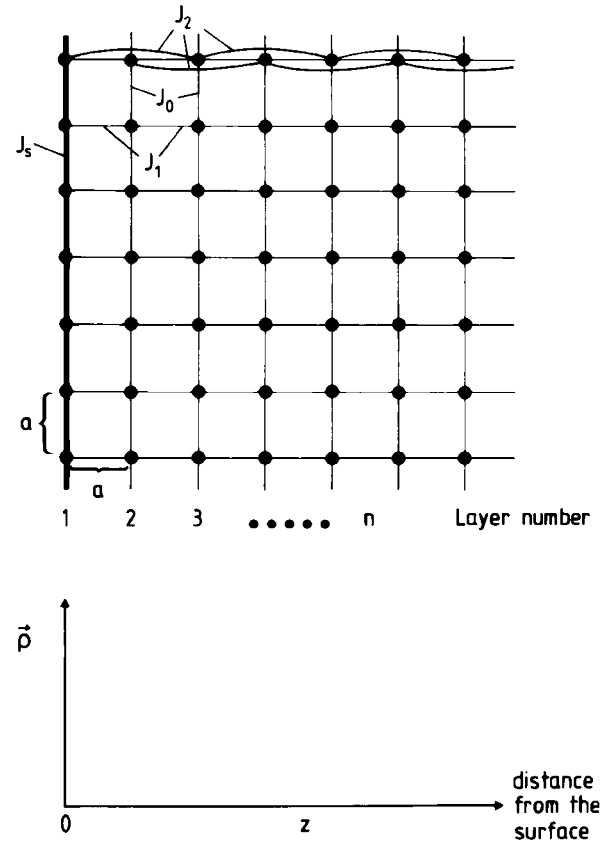

Fig. 2. Cross section perpendicular to the surface plane of a semi-infinite simple cubic Ising magnet (or ANNNI-model, respectively, the surface plane being oriented perpendicular to the direction where the modulation appears). Nearest neighbor exchange constants in the surface plane are denoted as J_{s}, while the exchange constants in all interior planes parallel to the surface is J_0. The nearest neighbor exchange in the z-direction perpendicular to the surface is J_1 next nearest neighbor exchange in the z-direction is J_2 (it is shown explicitly in the top row only). The lattice spacing is denoted by a. In the continuum treatment, the lateral coordinates are denoted as $\boldsymbol{\rho}$.

3 Theoretical framework of surface criticality: a brief review

Since we wish to extend the description of surface criticality of standard ferromagnets [22–24] to Lifshitz points and modulated phases, it is useful to briefly recall the basic elements of the phenomenological description of surface effects on magnets within mean field theory, and thus introduce also the basic definitions and notation.

Considering a semi-infinite nearest neighbor Ising magnet with a free surface at $z = 0$ (layer number $n = 1$, *cf.* Fig. 2), we use the Hamiltonian (the next nearest neighbor exchange $J_2 \equiv 0$ here)

$$H_{NN} = -J_0 \sum_{\langle i,j \rangle_{n>1}} S_i S_j - J_1 \sum_{n,j \in n, j \in n+1} S_i S_J - J_{\mathrm{s}} \sum_{\langle i,j \rangle_{n=1}} S_i S_j - H \sum_i S_i - H_1 \sum_{i \in n=1} S_i. \quad (37)$$

Here the notation $\langle i,\, j \rangle_n$ means that the sum runs once over all nearest neighbor pairs in layer n, and we have allowed only the exchange J_{s} in layer $n = 1$ to differ from the exchange J_0 in all the other layers. In addition, a surface magnetic field H_1 is admitted as usual [22–24].

3.1 The surface layer susceptibility χ_{11} and associated correlation functions

Writing layerwise molecular field equations as is done in equation (15) and linearizing them one obtains an equation analogous to equation (16) but augmented with a boundary condition at the surface [22–24,27] (for simplicity we treat only $H_1 \neq 0$ but use $H = 0$ here)

$$(z_\parallel J_0 - k_{\mathrm{B}}T)M_n + J_1(M_{n-1} + M_{n+1}) = 0, \; n \geq 2, \quad (38)$$

$$(z_\parallel J_{\mathrm{s}} - k_{\mathrm{B}}T)M_1 + J_1 M_2 = -H_1, \qquad n = 1. \quad (39)$$

Writing $M_n = \hat{A}\exp(-na/\xi_\mathrm{b})$ one finds $\sinh(a/2\xi_\mathrm{b}) = \sqrt{k_\mathrm{B}(T-T_\mathrm{cb})/J_1}/2$ with $k_\mathrm{B}T_\mathrm{cb} = z_\parallel J_0 + 2J_1$ [36] and the amplitude $\hat{A}$ is determined from the boundary condition as $\hat{A} = H_1\exp(a/\xi_\mathrm{b})/[k_\mathrm{B}T - z_\parallel J_\mathrm{s} - J_1\exp(-a/\xi_\mathrm{b})]$. It now is useful to define a response function χ_{11} [22–24]

$$\chi_{11} = (\partial M_1/\partial H_1)_{H,T} \qquad (40)$$

which becomes for the mean field ferromagnet $\chi_{11} = \exp(a/\xi_\mathrm{b})/[k_\mathrm{B}T - z_\parallel J_\mathrm{s} - J_1\exp(-a/\xi_\mathrm{b})]$. From this result one discovers that for sufficiently large J_s the surface may order at a temperature T_cs above T_cb, which is simply found from the vanishing of the denominator, $k_\mathrm{B}T_\mathrm{cs}/J_1 = z_\parallel J_\mathrm{s}/J_1 + \exp(-a/\xi_\mathrm{b})$. This "surface transition" T_cs merges at T_cb for $J_\mathrm{s} = J_\mathrm{sc}$, found from $\xi_\mathrm{b} \to \infty$ at $T_\mathrm{cs} = T_\mathrm{cb}$ as

$$J_\mathrm{sc}/J_1 = J_0/J_1 + z_\parallel^{-1}. \qquad (41)$$

The point ($T = T_\mathrm{cb}$, $J_\mathrm{s} = J_\mathrm{sc}$) in the plane of variables (T, J_s) is the surface-bulk multicritical point (Fig. 3) [22–24]: the two-dimensional criticality (divergent correlation length $\xi_\parallel$ for correlations in the surface plane) and the bulk three-dimensional criticality (divergent correlation length ξ_b) coincide. Thus one must distinguish three different cases for the singularity of χ_{11}, defining a length λ by

$$a/\lambda \equiv z_\parallel(J_\mathrm{sc} - J_\mathrm{s})/J_1, \qquad (42)$$

namely for $T \to T_\mathrm{cb}$ we have λ nonnegative and then

$$\chi_{11} \approx J_1^{-1}(a/\lambda)\left(1 - \frac{\lambda - a}{\xi_\mathrm{b}}\right) \approx J_1^{-1}(a/\lambda)\left[1 - (\lambda/a - 1)\frac{\sqrt{T-T_\mathrm{cb}}}{\sqrt{J_1/k_\mathrm{B}}}\right], \quad J_\mathrm{s} < J_\mathrm{sc},$$

$$\chi_{11} \approx J_1^{-1}(a/\xi_\mathrm{b}) \approx J_1^{-1}\sqrt{J_1/k_\mathrm{B}}/\sqrt{T-T_\mathrm{cb}}, \quad J_\mathrm{s} = J_\mathrm{sc},$$

while for $J_\mathrm{s} > J_\mathrm{sc}$ the "extrapolation length" λ is negative and hence χ_{11} diverges with a Curie-Weiss law at T_cs,

$$\chi_{11} = \frac{[k_\mathrm{B}(T-T_\mathrm{cs})]^{-1}\exp(a/\xi_\mathrm{b})}{1 - \dfrac{a}{2\xi_\mathrm{b}}\exp(-a/\xi_\mathrm{b})J_1/(T-T_\mathrm{cb})}, \quad J_\mathrm{s} > J_\mathrm{sc}.$$

Hence defining an exponent γ_{11} for the singular part χ_{11}^sing of χ_{11} as

$$\chi_{11}^\mathrm{sing} \propto t^{-\gamma_{11}} \qquad (43)$$

where $t = (T - T_\mathrm{cb})k_\mathrm{B}/J_1$ for $J_\mathrm{s} \le J_\mathrm{sc}$ but $t = k_\mathrm{B}(T - T_\mathrm{cs})/J_1$ for $J_\mathrm{s} > J_\mathrm{sc}$, we find $\gamma_{11} = -1/2$, $J_\mathrm{s} < J_\mathrm{sc}$, $\gamma_{11} = +1/2$, $J_\mathrm{s} = J_\mathrm{sc}$, $\gamma_{11} = 1 (= \gamma_\mathrm{b})$, $J_\mathrm{s} > J_\mathrm{sc}$. It is useful to recall that χ_{11} can be expressed as a sum of correlation functions over spins in the surface plane [22–24] $k_\mathrm{B}T\chi_{11} = \sum_{j\in n=1}\langle S_iS_j\rangle$, $i \in n = 1$. The scaling relation for the spin correlation function $g_\parallel(\boldsymbol{\rho}) = \langle S_iS_j\rangle$ (where $\boldsymbol{\rho} = \boldsymbol{\rho}_i - \boldsymbol{\rho}_j$ is a vector in the surface plane, *cf.* Fig. 2) then reads, d being the dimensionality ($d = 3$ here), $g_\parallel(\rho) = \rho^{-(d-2+\eta_\parallel)}\tilde{g}_\parallel(\rho/\xi_\parallel)$ where $\xi_\parallel = \xi_\mathrm{b}$ for $J_\mathrm{s} \le J_\mathrm{sc}$ but $\xi_\parallel = a\sqrt{J_\mathrm{s}/k_\mathrm{B}}/\sqrt{T-T_\mathrm{cs}}$ for $J_\mathrm{s} > J_\mathrm{sc}$. One then finds the scaling relation

$$\gamma_{11} = \nu_\mathrm{b}(1 - \eta_\parallel) \qquad (44)$$

where ν_b is the critical exponent of ξ_b (for $J_\mathrm{s} \le J_\mathrm{sc}$) or of $\xi_\parallel$ (for $J_\mathrm{s} > J_\mathrm{sc}$), respectively. Of course, in mean field theory one has $\nu_\mathrm{b} = 1/2$ throughout but different values apply ($\nu_\mathrm{b} \approx 0.63\,(d = 3)$, $\nu_\mathrm{b} = 1 (d = 2)$ [37]) beyond mean field. The mean-field results for the exponent $\eta_\parallel$ can be shown to be [22–24] $\eta_\parallel = 2$, $J_\mathrm{s} < J_\mathrm{sc}$, $\eta_\parallel = 0$, $J_\mathrm{s} \ge J_\mathrm{sc}$.

3.2 Surface thermodynamics and surface excess quantities

Let us consider for the moment a thin film of thickness $2L$ with two equivalent free surfaces of surface area S. Then the free energy F of the system for $L \to \infty$, $S = \infty$ is split into a bulk free energy density per spin $f_\mathrm{b}(T, H)$ and a surface correction $f_\mathrm{s}(T, H, H_1)$ as [22–24]. $F/(SL) = f_\mathrm{b}(T,H) - L^{-1}f_\mathrm{s}(T, H, H_1)$. Just as one derives bulk magnetization per spin M_b and susceptibility χ_b from the derivatives $M_\mathrm{b} = -(\partial f_\mathrm{b}/\partial H)_T$, $\chi_\mathrm{b} = (\partial M_\mathrm{b}/\partial H)_T = -(\partial^2 f_\mathrm{b}/\partial H^2)_T$ one can derive corresponding surface excess quantities

$$M_\mathrm{s} = -(\partial f_\mathrm{s}/\partial H)_{T,H_1},$$
$$\chi_\mathrm{s} = (\partial M_\mathrm{s}/\partial H)_{T,H_1} = -(\partial^2 f_\mathrm{s}/\partial H^2)_{T,H_1}, \qquad (45a)$$

as well as local quantities characterizing the surface layer

$$M_1 = -(\partial f_\mathrm{s}/\partial H_1)_{T,H},$$
$$\chi_{11} = (\partial M_1/\partial H_1)_{T,H} = -(\partial^2 f_\mathrm{s}/\partial H_1^2)_{T,H}, \qquad (45b)$$
$$\chi_1 = (\partial M_1/\partial H)_{T,H_1} = (\partial M_\mathrm{s}/\partial H_1)_{T,H} = -(\partial^2 f_\mathrm{s}/\partial H\partial H_1)_T. \qquad (45c)$$

It is of interest to note that the surface excess quantities can also be written in terms of sums over layers (we refer now to semi-infinite systems again when we put ∞ as upper limit of the sums),

$$M_\mathrm{s} = \sum_{n=1}^{\infty}(M_\mathrm{b} - M_n), \quad \chi_\mathrm{s} = \sum_{n=1}^{\infty}(\chi_\mathrm{b} - \chi_n),$$

noting that M_n, χ_n can be found by generalizing equations (45) by including a field H_n that acts on spins in the nth layer. One then can define further critical exponents β_1, β_s, γ_1, γ_s as follows

$$M_1(H = H_1 = 0) \propto (-t)^{\beta_1}, \; M_\mathrm{s}(H = H_1 = 0) \propto (-t)^{\beta_\mathrm{s}}, \qquad (46a)$$

$$\chi_1(H = H_1 = 0) \propto t^{-\gamma_1}, \; \chi_\mathrm{s}(H = H_1 = 0) \propto t^{-\gamma_\mathrm{s}}. \qquad (46b)$$

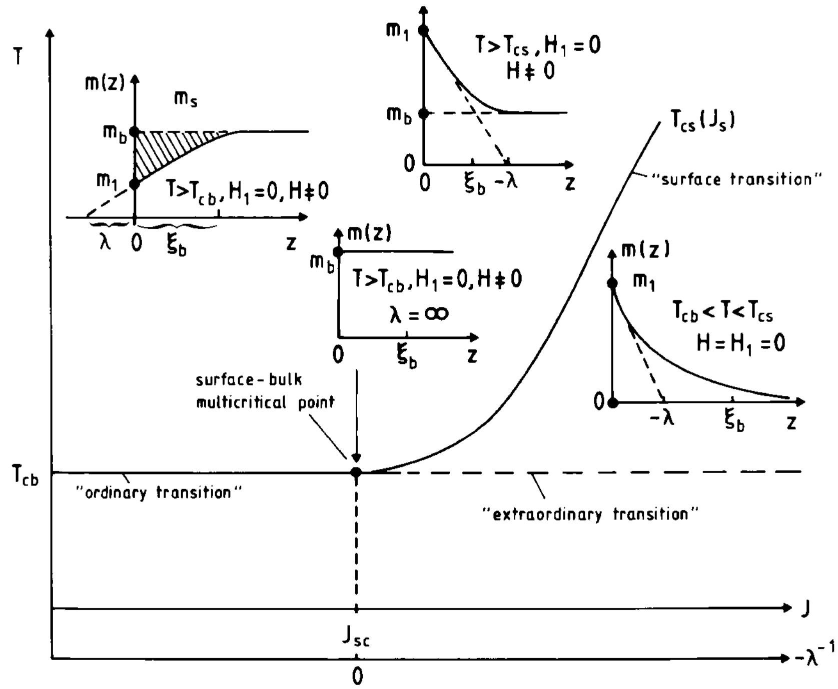

Fig. 3. Schematic phase diagram of the surface of a semi-infinite nearest neighbor Ising ferro-magnet (Eq. (37)) in the plane of variables temperature T and surface exchange J_s (or inverse extrapolation length λ^{-1}, respectively, $\lambda^{-1}=0$ corresponds to $J_s=J_{sc}$, *cf.* Eq. (42)). For $J_s<J_{sc}$ the surface orders at T_{cb} where the bulk does ("ordinary transition"), while for $J_s>J_{sc}$ two dimensional order occurs at the surface region for $T=T_{cs}(J_s)$ the "surface transition". Further singularities caused in the surface quantities at $T=T_{cb}$ when the bulk orders is called the "extraordinary transition". The schematic order parameter profiles $m(z)$ are the continuum analogs of the layer magnetization M_n discussed in equation (38). In the absence of a surface field, $M_1<M_b$ for $\lambda>0$ while $M_1>M_b$ for $\lambda<0$, at the surface-bulk multicritical point ($\lambda=\infty, J_s=J_{sc}$) the order parameter profile for $H_1=0$ is perfectly flat.

In mean field theory, these exponents become for (the "ordinary transition", remember $M_b\propto(-t)^{\beta_b}$, $\chi_b\propto t^{-\gamma_b}$ with $\beta_b=1/2$, $\gamma_b=1$)

$$\beta_1=1,\quad \beta_s=0,\quad \gamma_1=1/2,\quad \gamma_s=3/2 \tag{47}$$

while at the surface-bulk multicritical point (also called the "special transition") $J_s=J_{sc}$ we have $\beta_1=1/2$, $\gamma_1=1$, and neither β_s nor γ_s are defined there since $M_n=M_b$ and $\chi_n=\chi_b$ and hence the surface excess quantities vanish. For the surface transition, these exponents simply have the bulk (two-dimensional) values. At this point, we recall that profiles such as M_b-M_n are controlled by the transverse correlation length $\xi_\perp$, $M_b-M_n\propto\exp[-na/\xi_\perp]$, but since for a ferromagnet as considered in equation (37) we have $\xi_\perp=\xi_b$ it follows that the singular part of M_s simply becomes proportional to the singular part of the product $M_b\xi_b\propto(-t)^{\beta_b-\nu_b}=(-t)^0$, and similarly the singular part of χ_s becomes proportional to the singular part of the product $\chi_b\xi_b\propto t^{-\gamma_b-\nu_b}=t^{-3/2}$, *cf.* equation (47). It turns out that these scaling relations are true beyond mean field theory,

$$\beta_s=\beta_b-\nu_b,\quad \gamma_s=\gamma_b+\nu_b. \tag{48}$$

However, care will be needed when we generalize this approach to the Lifshitz point where two correlation lengths $\xi_\parallel$, $\xi_\perp$ with different exponents $\nu_\parallel=1/2$, $\nu_\perp=1/4$ need to be used and from the above remarks it should be obvious that both $\xi_\parallel$ and $\xi_\perp$ play a role in surface critical phenomena.

As a final point of this section, we define the crossover exponent ϕ_{SB} from the merging of the surface transition at the surface-bulk multicritical point,

$$T_{cs}(J_s)/T_{cb}-1\propto(J_s-J_{sc})^{1/\phi_{SB}}. \tag{49}$$

From equations (40, 41) it is easy to show that $\phi_{SB}=1/2$. This finding justifies the shape of the phase boundaries drawn in Figure 3, where we have also shown qualitatively the geometric interpretation of λ (Eq. (42)).

4 Linear molecular field theory for the semi-infinite ANNNI model: lattice treatment

We now return to the ANNNI model, equation (3), but consider a semi-infinite case with the same surface perturbations as in equation (37); *i.e.*, we add a term involving J_2 to that equation,

$$\mathcal{H}=\mathcal{H}_{NN}-J_2\sum_{n,i\in n,j\in n+2}S_iS_j.$$

$$\chi_1 = \chi_b \frac{R_+N_- - R_-N_+ - (R_- - R_+)[z_\parallel(J_0 - J_s) + J_1 + J_2] + (N_- - N_+)J_2}{R_+N_- - R_-N_+} \quad (60)$$

The generalization of equation (38) then simply is equation (16), for $n \geq 3$, while in both layers $n = 1$ and $n = 2$ we now have separate boundary conditions,

$$(z_\parallel J_s - k_B T)\tilde{M}_1 + J_1\tilde{M}_2 + J_2\tilde{M}_3 = - H_1 + M_b[z_\parallel(J_0 - J_s) + J_1 + J_2] \equiv K_1, \quad (50)$$

$$(z_\parallel J_0 - k_B T)\tilde{M}_2 + J_1(\tilde{M}_1 + \tilde{M}_3) + J_2\tilde{M}_4 = J_2 M_b, \quad (51)$$

which complement the equation describing the behavior in the bulk, equation (16).

4.1 Transition to ferromagnetic order

Considering first the case $\kappa < \kappa_L$ and $T \to T_{cb}(\kappa)$, the solution of equation (16) is

$$\tilde{M}_n = A_+ \exp[-(n-1)a/\xi_+] + A_- \exp(-(n-1)a/\xi_-), \quad (52)$$

where ξ_+, ξ_- are the two solutions of equation (17) and the amplitudes A_+, A_- are found from the two boundary conditions equations (50, 51). The surface layer magnetization M_1 can be written as

$$M_1(T, H, H_1) = M_b + \tilde{M}_1 = M_b + A_+ + A_- \quad (53)$$

and the surface excess magnetization M_s becomes

$$M_s(T, H, H_1) = -\sum_{n=1}^{\infty} \tilde{M}_n = -\frac{A_+}{1 - \exp(\frac{-a}{\xi_+})} - \frac{A_-}{1 - \exp(\frac{-a}{\xi_-})}. \quad (54)$$

Using equation (45) one then can derive also the susceptibilities χ_{11}, χ_1 and χ_s that characterize the surface critical behavior.

Thus the task is to obtain the amplitudes A_+, A_- from the boundary conditions, equations (50, 51), which yield a set of two linear equations $A_+N_+ + A_-N_- = K_1$, $A_+R_+ + A_-R_- = J_2 M_b$ where we have introduced the following abbreviations

$$N_+ = z_\parallel J_s - k_B T + J_1 \exp(-a/\xi_+) + J_2 \exp(-2a/\xi_+), \quad (55)$$

$$N_- = z_\parallel J_s - k_B T + J_1 \exp(-a/\xi_-) + J_2 \exp(-2a/\xi_-), \quad (56)$$

$$R_+ = [z_\parallel J_0 - k_B T + 2J_1 \cosh(a/\xi_+) + J_2 \exp(-2a/\xi_+)] \times \exp(-a/\xi_+), \quad (57)$$

$$R_- = [z_\parallel J_0 - k_B T + 2J_1 \cosh(a/\xi_-) + J_2 \exp(-2a/\xi_-)] \times \exp(-a/\xi_-). \quad (58)$$

This yields the desired susceptibilities as

$$\chi_{11} = (R_- - R_+)/(R_+N_- - R_-N_+), \quad (59)$$

see equation (60) *above*

and

$$\chi_s = \chi_b \left\{ \frac{R_-[z_\parallel(J_0 - J_s) + J_1 + J_2] - N_-J_2}{(R_+N_- - R_-N_+)[1 - \exp(-a/\xi_+)]} + \frac{-R_+[z_\parallel(J_0 - J_s) + J_1 + J_2] + N_+J_2}{(R_+N_- - R_-N_+)[1 - \exp(-a/\xi_-)]} \right\}. \quad (61)$$

We first assume that the common factor $(R_+N_- - R_-N_+)$ in the denominator of these expressions stays nonzero (and positive) when we lower the temperature towards $T_{cb}(\kappa)$: then χ_{11} does not diverge at all, there occurs no surface transition, rather we have the critical singularities of χ_{11}, χ_1 and χ_s associated with the "ordinary" transition, *i.e.* [22–25], *cf.* equations (45–47),

$$\chi_1 = \hat{\chi}_1(\kappa)[T/T_{cb}(\kappa) - 1]^{1/2},$$
$$\chi_s = \hat{\chi}_s(\kappa)[T/T_{cb}(\kappa) - 1]^{-3/2}. \quad (62)$$

In order to derive explicit expressions for the critical amplitudes $\hat{\chi}_1(\kappa)$, $\hat{\chi}_s(\kappa)$, and to show that equations (60, 61) indeed reduce to equation (62) in the limit $T \to T_{cb}(\kappa)$ we recall from equations (19, 20) that $\xi_+ \to \infty$ in this limit, while ξ_- remains finite. Hence we can expand the expressions N_+, R_+ as follows, using equation (7) for $T_{cb}(\kappa)$, $N_+ = N_+^c - (a/\xi_+)(J_1 + 2J_2)$, $N_+^c = z_\parallel(J_s - J_0) - J_1 - J_2$, $R_+ = R_+^c - (a/\xi_+)J_2$, $R_+^c = -J_2$, N_+^c, R_+^c denoting the values of these expressions at $T = T_{cb}(\kappa)$. From equation (60) we then find

$$\chi_1 = \chi_b \frac{a}{\xi_+} \frac{R_-^c(J_1 + 2J_2) - J_2N_-^c + J_2[J_2 + z_\parallel(J_s - J_0)]}{R_+^cN_-^c - R_-^cN_+^c}, \quad (63)$$

which already shows that we reproduce the correct exponent, since $\chi_b \propto t^{-1}$, $\xi_+ \propto t^{-1/2}$ and hence $\chi_1 \propto t^{-1/2}$ as well. In order to discuss the critical amplitude, we consider in more detail the denominator of equation (63).

In the limit where $J_2 \to 0$ (nearest neighbor case), one can also show from equation (17) that $a/\xi_- \to \infty$ and then we have simply $R_c^+N_c^- - R_c^-N_c^+ = J_1[z_\parallel(J_0 - J_s) + J_1]$ and noting that $R_c^- \to J_1$ for $J_2 \to 0$, one finds in the nearest neighbor case the well-known result [22,24]

$$\chi_1 = \chi_b \frac{a}{\xi_+} / \left[1 + z_\parallel \frac{(J_0 - J_s)}{J_1}\right], \quad (64)$$

which shows that in this limit equation (62) holds provided $J_s < J_{sc}$, as given by equation (41). Here we are

$$z_{\|}(J_{\rm sc}-J_0)/J_1 = \frac{1-3\kappa+2\kappa^2-\exp\left(-\frac{a}{\xi_-}\right)[2(1-\kappa)^2-\kappa]+\exp\left(-\frac{2a}{\xi_-}\right)(1-\kappa-\kappa^2)-\exp\left(-\frac{3a}{\xi_-}\right)\kappa(1-\kappa)}{(1-\kappa)\left(1-2\exp\left(-\frac{a}{-\xi}\right)\right)+\exp\left(-\frac{2a}{\xi_-}\right)-\kappa\exp\left(-\frac{3a}{\xi_-}\right)}\cdot \quad (68)$$

interested in the behavior near the Lifshitz point where ξ_- also diverges (*cf.* Eq. (19)) and then the exponentials in equations (56, 58) also can be expanded. This yields

$$\chi_1 = \chi_{\rm b}\frac{(a^2/\xi_-\xi_+)(J_1^2+5J_1J_2+5J_2^2)}{J_2[J_2-z_{\|}(J_0-J_{\rm s})]}\cdot \quad (65)$$

From equation (19) we see that near the Lifshitz point both ξ_- and ξ_+^{-1} each contribute a term proportional to $(1-\kappa/\kappa_{\rm L})^{-1/2}$ and hence the singular κ-dependence cancels, and thus

$$\hat{\chi}_1(\kappa) = \frac{2\sqrt{k_{\rm B}T_{\rm cb}/J_1}}{1+4z_{\|}(J_0-J_{\rm s})/J_1}\cdot \quad (66)$$

Next we consider the divergence of $\chi_{\rm s}$. From equation (61) we conclude that for $T\to T_{\rm cb}(\kappa)$ we have

$$\chi_{\rm s} \approx \chi_{\rm b}(\xi_+/a)\frac{R_-^{\rm c}[z_{\|}(J_0-J_{\rm s})+J_1+J_2]-N_-^{\rm c}J_2}{R_+^{\rm c}N_-^{\rm c}-R_-^{\rm c}N_+^{\rm c}} = \chi_{\rm b}(\xi_+/a). \quad (67)$$

Thus the power law expected in equation (62) for $\chi_{\rm s}$ is indeed verified, and the critical amplitude of $\chi_{\rm s}$ simply becomes the product of the critical amplitudes of $\chi_{\rm b}$ and ξ_+.

4.2 The surface transition

Next we turn to the surface transition, which occurs if $J_{\rm s}$ exceeds a critical value $J_{\rm sc}$, which is simply found putting $R_+^{\rm c}N_-^{\rm c}-R_-^{\rm c}N_+^{\rm c}=0$, *i.e.*

see equation (68) *above.*

Noting from equation (19) that for $T = T_{\rm cb}(\kappa)$, $\exp(-a/\xi_-) = (\sqrt{\kappa_{\rm L}/\kappa}-\sqrt{(\kappa_{\rm L}/\kappa-1)})^2$, a tedious but straightforward algebra yields

$$z_{\|}(J_{\rm sc}-J_0)/J_1 = \frac{\frac{1}{2}-\frac{5}{2}\kappa+2\kappa^2+(1-3\kappa)\sqrt{\kappa_{\rm L}-\kappa}}{\frac{1}{2}-2\kappa+\sqrt{\kappa_{\rm L}-\kappa}}\cdot \quad (69)$$

For the nearest neighbor-case ($\kappa = 0$) this reduces to equation (41), as it should, while at the Lifshitz point $\kappa=\kappa_{\rm L}=1/4$ we find

$$z_{\|}(J_{\rm sc}^{\rm L}-J_0)/J_1 = 1/4. \quad (70)$$

For $J_{\rm s} > J_{\rm sc}$ the first divergence of χ_1 and χ_{11} occurs not at $T = T_{\rm cb}(\kappa)$ but already at $T = T_{\rm cs}(\kappa) > T_{\rm cb}(\kappa)$. This surface critical temperature is located from the condition

$$R_+N_- - R_-N_+ = 0, \quad J_{\rm s} > J_{\rm sc}, \quad (71)$$

where now the full expressions for N_+, N_-, R_+, R_- (Eqs. (55–58)) rather than their critical parts must be used. From equations (59–61) we recognize that χ_{11}, χ_1 and $\chi_{\rm s}$ have exactly the same type of divergence, namely

$$\chi_{11} \propto \chi_1 \propto \chi_{\rm s} \propto (T-T_{\rm cs}(\kappa))^{-1}, \quad (72)$$

which follows because $R_+N_- - R_-N_+$ can be expanded at $T = T_{\rm cs}(\kappa)$ for $T_{\rm cs}(\kappa) > T_{\rm cb}(\kappa)$ in a Taylor series in $T - T_{\rm cs}(\kappa)$ because ξ_+ for $T > T_{\rm cb}$ is analytic in T (*cf.* Eq. (17)).

An interesting question is to clarify how $T_{\rm cs}(\kappa)$ is enhanced beyond $T_{\rm cb}(\kappa)$ when $J_{\rm s}$ exceeds $J_{\rm sc}$ only slightly. In this case it is permissible to expand N_+, R_+ to first order, using also $k_{\rm B}T \approx k_{\rm B}T_{\rm cb}(\kappa) = z_{\|}J_0 + 2J_1 + 2J_2$. Using equation (69), we can rewrite this condition, equation (71), for the surface transition as

$$\frac{a}{\xi_+} = [z_{\|}(J_{\rm s}-J_{\rm sc})/J_1]\{(1-\kappa)[1-2\exp(-a/\xi_-)] + \exp(-2a/\xi_-) - \kappa\exp(-3a/\xi_-)\}/D, \quad (73)$$

with a denominator D

$$D = \kappa z_{\|}\frac{J_{\rm s}-J_0}{J_1}+1-4\kappa+2\kappa^2 - (2-7\kappa+4\kappa^2)\exp(-a/\xi_-) + (1-2\kappa-\kappa^2)\exp(-2a/\xi_-) - (\kappa-2\kappa^2)\exp(-3a/\xi_-). \quad (74)$$

From equation (73) it follows, remembering equation (20), that for $J_{\rm s} > J_{\rm sc}$ the right hand side of this equation is of order $[T - T_{\rm cb}(\kappa)]^{1/2}$ while expanding $\exp(-a/\xi_-)$ around its finite value at $T = T_{\rm cb}(\kappa)$ yields higher order corrections of order $[T - T_{\rm cb}(\kappa)]^1$ only, which can be neglected here. In this asymptotic limit, we also may replace $J_{\rm s}$ in the denominator D by $J_{\rm sc}$, of course. We then find

$$\frac{a}{\xi_+} = [z_{\|}(J_{\rm s}-J_{\rm sc})/J_1]\frac{(1+2\sqrt{\kappa_{\rm L}-\kappa})^2}{4\kappa^2-8\kappa+2+(4-8\kappa)\sqrt{\kappa_{\rm L}-\kappa}}\cdot \quad (75)$$

At this point, it is interesting to compare this with the corresponding approximation for $\kappa = 0$ namely ($T_{\rm cb} = z_{\|}J_0 + 2J_1$ for $\kappa = 0$!)

$$a/\xi_{\rm b} = z_{\|}J_{\rm s}/J_1+1-k_{\rm B}T_{\rm cs}/J_1 \approx z_{\|}J_{\rm s}/J_1+1-k_{\rm B}T_{\rm cb}/J_1 = z_{\|}(J_{\rm s}-J_0)/J_1 - 1 = z_{\|}(J_{\rm s}-J_{\rm sc})/J_1 \quad (76)$$

where in the last step equation (41) was used. Using $\kappa = 0$, $\kappa_L = 1/4$ in equation (75), equation (76) is recovered as it should be. Recalling now equation (20), we finally obtain

$$k_B[T_{cs}(\kappa)-T_{cb}(\kappa)]/J_1 = (1-\kappa/\kappa_L)[z_\parallel(J_s-J_{sc})/J_1]^2 \times \frac{(1+2\sqrt{\kappa_L-\kappa})^4}{[4\kappa^2-8\kappa+2+(4-8\kappa)\sqrt{\kappa_L-\kappa}]^2}\cdot \quad (77)$$

One sees that the denominator in equation (77) for $\kappa \to \kappa_L$ simply becomes 1/16, and thus the amplitude $A(\kappa)$ in the relation

$$k_B[T_{cs}(\kappa)-T_{cb}(\kappa)]/J_1 = A(\kappa)[z_\parallel(J_s-J_{sc})/J_1]^{1/\phi_{SB}} \quad (78)$$

simply vanishes linearly for $\kappa \to \kappa_L$, $A(\kappa) = 16(1-\kappa/\kappa_L)$, and the "crossover exponent" at the surface-bulk multicritical point is $\phi_{SB} = 1/2$ throughout the ferromagnetic phase, for $0 \le \kappa < \kappa_L$.

4.3 Surface effects at the Lifshitz point and in the modulated phase

For $\kappa \ge \kappa_L$ we use equation (21) to replace equation (52) by

$$\tilde{M}_n = A\exp[-(n-1)a/\xi]\cos[(n-1)\phi + \Psi] \quad (79)$$

where ξ, ϕ are still given by equations (23, 24), where the amplitude A and phase Ψ have to be chosen such that the boundary conditions equations (50, 51) are fulfilled. This yields again a set of two linear equations for the amplitudes $A_c \equiv A\cos\Psi$, $A_s \equiv -A\sin\Psi$, $A_cN_c + A_sN_s = K_1$, $A_cR_c+A_sR_s = J_2M_b$, where we have introduced again abbreviations as follows,

$$N_c = (z_\parallel J_s - k_BT) + J_1\exp(-a/\xi)\cos\phi + J_2\exp(-2a/\xi)\cos 2\phi, \quad (80)$$

$$N_s = J_1\exp(-a/\xi)\sin\phi + J_2\exp(-2a/\xi)\sin 2\phi, \quad (81)$$

$$R_c = (z_\parallel J_0 - k_BT)\cos\phi\, e^{-a/\xi} + J_1 + J_1e^{-2a/\xi}\cos 2\phi + J_2e^{-3a/\xi}\cos 3\phi, \quad (82)$$

$$R_s = (z_\parallel J_0 - k_BT)\sin\phi\, e^{-a/\xi} + J_1e^{-2a/\xi}\sin 2\phi + J_2e^{-3a/\xi}\sin 3\phi. \quad (83)$$

Using again equations (42–44, 53, 54) we find the desired susceptibilities

$$\chi_{11} = -(\partial\tilde{M}_1/\partial K_1)_T = -R_s/(R_sN_c - R_cN_s), \quad (84)$$

$$\chi_1 = \chi_b\frac{R_sN_c-R_cN_s+R_s[z_\parallel(J_0-J_s)+J_1+J_2]-N_sJ_2}{R_sN_c-R_cN_s}, \quad (85)$$

and

$$\chi_s = (\partial M_s/\partial H)_{H_1=0} = -\frac{\partial}{\partial H}\left(\sum_{n=1}^{\infty}\tilde{M}_n\right) = -\frac{\partial}{\partial H}\frac{A_c(1-e^{-a/\xi}\cos\phi)+A_se^{-a/\xi}\sin\phi}{1+e^{-2a/\xi}-2e^{-a/\xi}\cos\phi}\cdot \quad (86)$$

Since equations (12–14) imply that for $\kappa > \kappa_L$ the bulk susceptibility does stay finite when T_{mb} is approached, *cf.* also equation (6)

$$\chi_b = \hat{\Gamma}/(1 - T_{mb}/T + q^2\hat{\xi}_\perp^2) \propto (\kappa/\kappa_L - 1)^{-1} \quad (87)$$
$$T=T_{mb},\, \kappa\to\kappa_L.$$

It is obvious that also none of the susceptibilities χ_{11}, χ_1 and χ_s diverges as T_{mb} is approached (provided the denominator $R_sN_c - R_cN_s$ is nonzero; the vanishing of this denominator again locates the surface transition, as will be discussed below). This fact is of course expected, since H is not a field conjugate to the order parameter of the modulated phase, it is conjugate to the ferromagnetic order parameter, and response functions to non-ordering fields indeed must stay finite at the transition. However, singularities do occur as $\kappa \to \kappa_L$ at $T = T_{mb}(\kappa)$. *E.g.*, from equation (23) we can use $\cos\phi = \kappa_L/\kappa$, $\sin\phi = \sqrt{1-\kappa_L^2/\kappa^2} \approx \sqrt{2}\sqrt{1-\kappa_L/\kappa}$ to show that the singularity of χ_s then becomes

$$\chi_s\big|_{T=T_{mb}(\kappa)} \approx -\left(\frac{\partial A_s}{\partial H}\right)_{H_1=0}\frac{1}{\sqrt{2}\sqrt{1-\kappa_L/\kappa}} = \frac{R_c[z_\parallel(J_0-J_s)+J_1+J_2]+J_2N_c}{R_sN_c-R_cN_s}\frac{\chi_b}{\sqrt{2}\sqrt{1-\kappa_L/\kappa}} \propto (\kappa/\kappa_L-1)^{-2}. \quad (88)$$

Here we have used the result that $R_sN_c - R_cN_s$ vanishes as $(\kappa/\kappa_L - 1)^{1/2}$, see below. In order to evaluate in more detail the singularities of χ_{11}, χ_1 and χ_s as $\kappa \to \kappa_L$ or as the surface transition is approached, we first note the limiting values $N_c(T = T_{mb}) = N_c^m$, $N_s(T = T_{mb}) = N_s^m$, $R_c(T = T_{mb}) = R_c^m$ and $R_s(T = T_{mb}) = R_s^m$, as the transition to the modulated phase is approached,

$$N_c^m = z_\parallel(J_s - J_0) - J_1\left(\frac{1}{2}\frac{\kappa_L}{\kappa} + \kappa\right),$$

$$N_s^m = \frac{1}{2}J_1\sqrt{1-\frac{\kappa_L^2}{\kappa^2}},$$

$$R_c^m = J_1/4, \qquad R_s^m = -\kappa J_1\sqrt{1-\frac{\kappa_L^2}{\kappa^2}}.$$

Since

$$R_s^mN_c^m - R_c^mN_s^m = \kappa J_1\sqrt{1-\frac{\kappa_L^2}{\kappa^2}}\left\{\kappa J_1 - z_\parallel(J_s - J_0)\right\}, \quad (89)$$

the analog to equation (69) for the critical enhancement J_{sc} needed to have a surface transition for $\kappa > \kappa_L$ is

$$z_\parallel(J_{sc} - J_0)/J_1 = \kappa. \quad (90)$$

From equation (78) we find then along the critical line of the modulated phase

$$\chi_{11} = [\kappa J_1 + z_{\|}(J_0 - J_{\rm s})]^{-1} \qquad (91)$$

We now evaluate χ_{11}, χ_1 and $\chi_{\rm s}$ approaching the Lifshitz point at fixed $\kappa = \kappa_{\rm L}$ as a function of temperature, noting that then, to leading order, $\phi = a/\xi$ as $\xi \to \infty$. We then find for T near $T_{\rm L} \approx (z_{\|}J_0 + 3J_1/2)/k_{\rm B}$ that $N_{\rm c} \approx z_{\|}(J_{\rm s} - J_0) - 3J_1/4 - (1/2)J_1 a/\xi$, $N_{\rm s} \approx (1/2)J_1 a/\xi$, $R_{\rm c} \approx (1/4)J_1(1 + a/\xi)$, $R_{\rm s} \approx -(1/4)J_1 a/\xi(1 + a/\xi)$. From equations (78, 79, 84–86) we find hence

$$\chi_{11} = [z_{\|}(J_0 - J_{\rm s}) + J_1/4 + (1/2)J_1 a/\xi]^{-1}, \qquad (92)$$

$$\chi_1 = \frac{1}{2}\chi_{\rm b} J_1 (a/\xi)^2 \times \frac{1}{[z_{\|}(J_0 - J_{\rm s}) + J_1/4 + (1/2)J_1 a/\xi](1 + a/\xi)}, \qquad (93)$$

and noting $1 + \exp(-2a/\xi) - 2\exp(-a/\xi)\cos\phi \approx 2(a/\xi)^2$, $1 - \exp(a/\xi)\cos\phi \approx a/\xi$, $\exp(-a/\xi)\sin\phi \approx a/\xi$ we see that $\chi_{\rm s} \propto \chi_{\rm b}\xi$ since the derivatives $\partial A_{\rm c}/\partial H$, $\partial A_{\rm s}/\partial H$ both are proportional to $\chi_{\rm b}$ with constants of proportionality that stay finite at $T_{\rm L}$. Defining now surface exponents $\gamma_{11}^{\rm L}$, $\gamma_1^{\rm L}$, $\gamma_{\rm s}^{\rm L}$ at the Lifshitz point as follows

$$\chi_{11}^{\rm sing} \propto (T/T_{\rm L} - 1)^{-\gamma_{11}^{\rm L}}, \qquad \chi_1 \propto (T/T_{\rm L} - 1)^{-\gamma_1^{\rm L}}, \qquad \chi_{\rm s} \propto (T/T_{\rm L} - 1)^{-\gamma_{\rm s}^{\rm L}}, \qquad (94)$$

and remembering that now we have to identify ξ as $\xi_\perp$ (Eq. (11)) with $\xi \propto (T/T_{\rm L} - 1)^{-1/4}$, we immediately derive the exponents

$$\gamma_{11}^{\rm L} = -1/4, \quad \gamma_1^{\rm L} = 1/2, \quad \gamma_{\rm s}^{\rm L} = 5/4. \qquad (95)$$

These results satisfy the scaling relation ($\nu_{\rm b}^{\rm L} = \nu_\perp^{\rm L} = 1/4$ here)

$$\gamma_{\rm s}^{\rm L} = \gamma_{\rm b}^{\rm L} + \nu_{\rm b}^{\rm L} = 1 + 1/4 = 5/4 \qquad (96)$$

which is the extension of equation (48) to a Lifshitz point. It turns out that other scaling relations [22–24] carry over to the present case as well, such as for instance

$$2\gamma_1^{\rm L} - \gamma_{11}^{\rm L} = 1 + 1/4 = \gamma_{\rm s}^{\rm L} = 5/4. \qquad (97)$$

In fact, using the scaling property of the surface excess free energy $f_{\rm s}(T, H, H_1)$ following [22–24], with $t = T/T_{\rm L} - 1$,

$$f_{\rm s}(T, H, H_1) = t^{2-\alpha_{\rm s}^{\rm L}} \tilde{f}_{\rm s}(t^{-\Delta_{\rm b}^{\rm L}} H, t^{-\Delta_1^{\rm L}} H_1), \qquad (98)$$

one can express most critical exponents of interest in terms of a surface exponent $\alpha_{\rm s}^{\rm L}$ for the specific heat, with $\alpha_{\rm s}^{\rm L} = \alpha_{\rm b}^{\rm L} + \nu_{\rm b}^{\rm L} = 0 + 1/4 = 1/4$ at a Lifshitz point within mean field theory, the "gap exponent" in the bulk, $\Delta_{\rm b}^{\rm L}$ ($= 3/2$ here, as for an ordinary mean field ferromagnet: the bulk equation of state within mean field at a Lifshitz point is identical to that of an ordinary ferromagnet), while $\Delta_1^{\rm L}$ is the relevant new exponent that is the outcome of the present calculation and could not have been guessed from bulk properties. Noting equations (42–44), one immediately concludes [22–24]

$$-\gamma_{11}^{\rm L} = 2 - \alpha_{\rm s}^{\rm L} - 2\Delta_1^{\rm L}, \quad \textit{i.e.}\ \Delta_1^{\rm L} = 3/4, \qquad (99)$$

and the relations $-\gamma_1^{\rm L} = 2 - \alpha_{\rm s}^{\rm L} - \Delta_1^{\rm L} - \Delta_{\rm b}^{\rm L}$ and $-\gamma_{\rm s}^{\rm L} = 2 - \alpha_{\rm s}^{\rm L} - 2\Delta_{\rm b}^{\rm L}$ then obviously are fulfilled with the exponent values that have been found above. It is also of interest to consider the exponents of surface layer order parameter ($\beta_1^{\rm L}$) and surface excess order parameter ($\beta_{\rm s}^{\rm L}$), *cf.* equation (46)

$$\beta_1^{\rm L} = 2 - \alpha_{\rm s}^{\rm L} - \Delta_1^{\rm L} = 1, \quad \beta_{\rm s}^{\rm L} = \beta_{\rm b}^{\rm L} - \nu_{\rm b}^{\rm L} = 1/4. \qquad (100)$$

Of course, other scaling relations such as [22–24] $\gamma_{11}^{\rm L} + \beta_1^{\rm L} = \Delta_1^{\rm L}$ hold as well. However, extension of scaling laws involving correlations (*e.g.* Eq. (44)) is more subtle, due to the anisotropic character of the Lifshitz point. We suggest that $\nu_{\|}^{\rm L} = 1/2$ should be taken in equation (44), yielding $\eta_{\|}^{\rm L} = 3/2$.

Finally we consider the surface transition again, assuming that $J_{\rm s}$ exceeds $J_{\rm sc}$ (Eq. (90)) only slightly. Then the quantities $N_{\rm c}$, $N_{\rm s}$, $R_{\rm c}$, $R_{\rm s}$ can be expanded (since ξ is large one can simplify the relation $\cos\varphi = (\kappa_{\rm L}/\kappa)/\cosh(a/\xi) \approx (\kappa_{\rm L}/\kappa)[1 - (a/\xi)^2/2]$ and use similar simplifications for $\cos 2\varphi$, $\sin\varphi$, etc.).

$$N_{\rm c} \approx z_{\|}(J_{\rm s} - J_0) - \frac{1}{2}J_1\frac{\kappa_{\rm L}}{\kappa} - \kappa J_1\left(1 + \frac{2a}{\xi}\right) + \frac{1}{2}J_1\left(\frac{a}{\xi}\right)^2\left(\frac{\kappa}{\kappa_{\rm L}} - \frac{\kappa_{\rm L}}{\kappa}\right),$$

$$N_{\rm s} \approx \frac{1}{2}J_1\sqrt{1 - \kappa_{\rm L}^2/\kappa^2}\left[1 + \frac{1}{2}\left(\frac{a}{\xi}\right)^2\frac{(2\kappa_{\rm L}^2/\kappa^2 - 1)}{(1 - \kappa_{\rm L}^2/\kappa^2)}\right],$$

$$R_{\rm c} \approx \frac{1}{4}J_1(1 + a/\xi),$$

$$R_{\rm s} \approx -\kappa J_1\sqrt{1 - \kappa_{\rm L}^2/\kappa^2}\left[1 + \frac{a}{\xi} + \frac{1}{2}\frac{(a/\xi)^2}{(1 - \kappa_{\rm L}^2/\kappa^2)}\right],$$

where thus terms of order $(a/\xi)^2$ and lower have been kept.

Now the condition for the surface transition, $R_{\rm s}N_{\rm c} - R_{\rm c}N_{\rm s} = 0$, becomes simply

$$\kappa z_{\|}/(J_{\rm s} - J_{\rm sc})/J_1 = 2\kappa^2(a/\xi) + (a/\xi)^2(1/4 - 2\kappa^2). \qquad (101)$$

At the Lifshitz point, where $\xi/a = (J_1/4k_{\rm B})^{1/4}(T - T_{\rm L})^{-1/4}$, equation (101) reduces to

$$k_{\rm B}(T_{\rm cs} - T_{\rm L})/J_1 = 4[z_{\|}(J_{\rm s} - J_{\rm sc})/J_1]^4, \ \ J_{\rm s} \geq J_{\rm sc}. \qquad (102)$$

Thus if we again define a crossover exponent $\phi_{\rm SB}^{\rm L}$ for the surface-bulk multicritical Lifshitz point, we obtain

$$\phi_{\rm SB}^{\rm L} = 1/4. \qquad (103)$$

On the other hand, in the regime of the modulated phase ($\kappa > \kappa_L$) we find an equation analogous to equation (77), namely $\left(\text{note Eq. (14)}, (a/\xi)^2 = k_B[T - T_{mb}(\kappa)]/\left[J_1\left(\frac{\kappa}{\kappa_L} - \frac{\kappa_L}{\kappa}\right)\right]\right)$

$$k_B(T_{cs} - T_{mb}(\kappa))/J_1 = \frac{1}{\kappa}(1 - \kappa_L^2/\kappa^2)[z_\parallel(J_s - J_{sc})/J_1]^2,\quad J_s \geq J_{sc}, \tag{104}$$

and hence $\phi_{SB} = 1/2$ also for the modulated phase. As in equations (77, 78), the amplitude $A(\kappa)$ vanishes linearly in $\kappa_L - \kappa$ as $\kappa \to \kappa_L$ from above.

5 Ginzburg-Landau theory for the semi-infinite ANNNI model

5.1 Derivation of boundary conditions

We now wish to study surface effects on the ANNNI model in the framework of the continuum theory, equation (27). We now use the expansion, equation (25), in the discrete boundary conditions, equations (50, 51), to derive the following boundary conditions ($M_n = M_b + m(z)$ where $z = 0$ means $n = 1$)

$$(z_\parallel J_s - k_BT + J_1 + J_2)m(0) + (J_1 + 2J_2)a\left(\frac{\partial m}{\partial z}\right)_{z=0} + (J_1 + 4J_2)\frac{a^2}{2}\left(\frac{\partial^2 m}{\partial z^2}\right)_{z=0} + (J_1 + 8J_2)\frac{a^3}{6}\left(\frac{\partial^3 m}{\partial z^3}\right)_{z=0} = -H_1 + M_b[z_\parallel(J_0 - J_s) + J_1 + J_2] = K_1, \tag{105}$$

and

$$(z_\parallel J_0 - k_BT + 2J_1 + J_2)m(0) + (z_\parallel J_0 - k_BT + 2J_1 + 3J_2)\, a\left(\frac{\partial m}{\partial z}\right)_{z=0} + (z_\parallel J_0 - k_BT + 4J_1 + 9J_2)\frac{a^2}{2}\left(\frac{\partial^2 m}{\partial z^2}\right)_{z=0} + (z_\parallel J_0 - k_BT + 8J_1 + 27J_2)\,\frac{a^3}{6}\left(\frac{\partial^3 m}{\partial z^3}\right)_{z=0} = J_2M_b. \tag{106}$$

We now use $k_BT_{cb} = z_\parallel J_0 + 2J_1 + 2J_2$ for $\kappa < \kappa_L$ and use also $k_B(T - T_{cb}) = J_1(a/\xi_+)^2(1 - \kappa/\kappa_L)$ and define an extrapolation length λ now such that for $J_2 = 0$ equation (42) is reproduced, namely

$$\lambda = \frac{(1-\kappa)a}{1 + z_\parallel(J_0 - J_s)/J_1}\,\cdot \tag{107}$$

Note, however, that for $J_s = 0$ near the Lifshitz point ($\kappa = \kappa_L = 1/4$)λ is less than a.

We now can rewrite equations (105, 106) in the form

$$m(0) - \left[\frac{\lambda + \left(\frac{a}{\xi_+}\right)^2\left(1 - \frac{\kappa}{\kappa_L}\right)}{(1 + z_\parallel(J_0 - J_s)/J_1)a}\right]\left(\frac{\partial m}{\partial z}\right)_{z=0} + \frac{1-3\kappa}{1-\kappa}\frac{a\lambda}{2}\left(\frac{\partial^2 m}{\partial z^2}\right)_{z=0} + \frac{5-17\kappa}{(1-\kappa)}\frac{a^2\lambda}{6}\left(\frac{\partial^3 m}{\partial z^3}\right)_{z=0} = \frac{-\kappa M_b - K_1/J_1}{1 + z_\parallel(J_0 - J_s)/J_1} \equiv K_1', \tag{108}$$

$$m(0)\left[1 - \frac{1}{\kappa}\left(\frac{a}{\xi_+}\right)^2\left(1 - \frac{\kappa}{\kappa_L}\right)\right] - \left[1 + \frac{1}{\kappa}\left(\frac{a}{\xi_+}\right)^2\left(1 - \frac{\kappa}{\kappa_L}\right)\right]a\left(\frac{\partial m}{\partial z}\right)_{z=0} + \left(\frac{2}{\kappa} - 7\right)\frac{a^2}{2}\left(\frac{\partial^2 m}{\partial z^2}\right)_{z=0} + \left(\frac{6}{\kappa} - 25\right)\frac{a^3}{6}\left(\frac{\partial^3 m}{\partial z^3}\right)_{z=0} = -M_b. \tag{109}$$

In these boundary conditions, we have kept terms that allow us to include all terms up to third order in ξ_+^{-1}, ξ_-^{-1}. As will be argued below, only terms of order ξ_-^{-3} actually are needed (since ξ_- stays finite at T_{cb}), while lower order terms will suffice in the vanishing inverse correlation length ξ_+^{-1}.

5.2 Calculation of the surface susceptibilities χ_{11}, χ_1 and χ_s

We now write the solution of equation (27) with the boundary conditions equations (108, 109) in analogy with equation (52) as

$$m(z) = A_+\exp(-z/\xi_+) + A_-\exp(-z/\xi_-), \tag{110}$$

where now ξ_+, ξ_- are given by equation (28) or equations (30, 31), respectively. We note that in analogy with equations (53, 54) we now have

$$M_1(T,H,H_1) = M_b + m(0) = M_b + A_+ + A_-, \tag{111}$$

$$M_s(T,H,H_1) = -\frac{1}{a}\int_0^\infty m(z)\mathrm{d}z = -(\xi_+/a)A_+ - (\xi_-/a)A_-. \tag{112}$$

Of course, expanding the exponentials in equation (54) we immediately recover equation (112), while terms in the next order of the expansion of $1 - \exp(-a/\xi_\pm) \approx a/\xi_\pm - (-a/\xi_\pm)^2/2 \pm$ ... are already missed. Therefore the continuum theory can describe the leading singularities of χ_{11}, χ_1 and χ_s only, as is well known from the nearest neighbor case [22–24], *cf.* also Section 2.3. Inserting equation (110) in the boundary conditions, equations (108, 109), one obtains $A_+N_+ + A_-N_- = K_1'$,

$A_+R_+ + A_-R_- = -M_\mathrm{b}$, where the abbreviations N_+, N_-, R_+, R_- now take the form

$$N_+ = 1 + \frac{\lambda}{\xi_+} + \frac{1-3\kappa}{2(1-\kappa)}\frac{a\lambda}{\xi_+^2} + \frac{1-7\kappa}{6(1-\kappa)}\frac{a^2\lambda}{\xi_+^3}, \tag{113}$$

$$N_- = 1+\frac{\lambda}{\xi_-}+\frac{1-3\kappa}{2(1-\kappa)}\frac{a\lambda}{\xi_-^2}+\frac{1-4\kappa}{1-\kappa}\frac{a^2\lambda}{\xi_+^2\xi_-}-\frac{5-17\kappa}{6(1-\kappa)}\frac{a^2\lambda}{\xi_-^3}, \tag{114}$$

$$R_+ = 1 + \frac{a}{\xi_+} + \frac{1}{2}\left(\frac{a}{\xi_+}\right)^2 + \frac{1}{6}\left(\frac{a}{\xi_+}\right)^3, \tag{115}$$

$$R_- = 1 + \frac{a}{\xi_-} + \left(\frac{1}{\kappa} - \frac{7}{2}\right)\left(\frac{a}{\xi_-}\right)^2 - \left(\frac{1}{\kappa} - 4\right)\left(\frac{a}{\xi_+}\right)^2 + \frac{a^3}{\xi_+^2\xi_-}\left(\frac{1}{\kappa} - 4\right) - \left(\frac{1}{\kappa} - \frac{25}{6}\right)\left(\frac{a}{\xi_-}\right)^3. \tag{116}$$

Noting that

$$\frac{\partial K_1'}{\partial H} = -\chi_\mathrm{b}, \ \frac{\partial K_1'}{\partial H_1} = \frac{J_1^{-1}}{1 + z_\parallel(J_0 - J_\mathrm{s})/J_1},$$

and using the abbreviation $\Delta = R_+N_- - R_-N_+$ we find the desired susceptibilities χ_1, χ_{11} from equation (111) as

$$\chi_1 = \chi_\mathrm{b}\frac{(\Delta + N_+ - N_- - R_+ + R_-)}{\Delta}, \tag{117}$$

$$J_1\chi_{11} = \frac{\lambda}{a}\frac{(R_+ - R_-)}{(1-\kappa)\Delta} \cdot \tag{118}$$

The denominator Δ becomes

$$\begin{aligned}\Delta = &\left(\frac{a}{\xi_-}-\frac{a}{\xi_+}\right)\left(\frac{\lambda}{a}-1\right) \\ &+ \left(\frac{a^2}{\xi_-^2}-\frac{a^2}{\xi_+^2}\right)\left[\frac{1-3\kappa}{2(1-\kappa)}\frac{\lambda}{a} - \left(\frac{1}{\kappa}-\frac{7}{2}\right)\right] \\ &+ \frac{a^3}{\xi_-^3}\left[\frac{1}{\kappa} - \frac{25}{6} - \frac{\lambda}{a}\frac{5-17\kappa}{6(1-\kappa)}\right] \\ &+ \frac{a^2\lambda}{\xi_-^2\xi_+}\left[\frac{1-3\kappa}{2(1-\kappa)} - \left(\frac{1}{\kappa} - \frac{7}{2}\right)\right] \\ &+ O\left(\frac{a^3}{\xi_+^2\xi_-}, \frac{a^3}{\xi_+^3}\right)\end{aligned} \tag{119}$$

while the term appearing in the leading order in the numerator of equation (117) becomes, keeping only the term of order ξ_+^{-1},

$$\Delta+R_- -R_+ +N_+ -N_- \approx \left(\frac{a^2\lambda}{\xi_-^2\xi_+}\right)\left[\frac{1-3\kappa}{2(1-\kappa)} - \frac{1}{\kappa} + \frac{7}{2}\right],$$

and thus χ_1 becomes

$$\chi_1 = \chi_\mathrm{b}\frac{a\lambda}{\xi_+\xi_-}\frac{(1-3\kappa)/2(1-\kappa) - 1/\kappa + 7/2}{(\lambda/a - 1)} \xrightarrow[\kappa\to\kappa_\mathrm{L}]{} \chi_\mathrm{b}\frac{a^2}{\xi_+\xi_-}\frac{1}{1 + 4z_\parallel(J_0 - J_\mathrm{s})/J_1} \cdot \tag{120}$$

Thus we see that it is indeed a term appearing in the third order of the inverse correlation lengths which dominates the behavior of χ_1. Using now the fact that $\chi_\mathrm{b} = \hat{\Gamma}(T/T_\mathrm{cb} - 1)^{-1}$ with $\hat{\Gamma} = 1$ while

$$a/\xi_+ \approx (T/T_\mathrm{cb} - 1)^{1/2}\left(z_\parallel\frac{J_0}{J_1} + \frac{3}{2}\right)^{1/2}(1 - \kappa/\kappa_\mathrm{L})^{-1/2},$$

one finds that near $\kappa = \kappa_\mathrm{L} = 1/4$

$$\chi_1 \approx 2\left(z_\parallel\frac{J_0}{J_1} + \frac{3}{2}\right)^{1/2}\frac{(T/T_\mathrm{cb} - 1)^{-1/2}}{1 + 4z_\parallel(J_0 - J_\mathrm{s})/J_1} \tag{121}$$

i.e. the critical amplitude of the surface layer susceptibility χ_1 does not show a singular behavior as $\kappa \to \kappa_\mathrm{L}$, in leading order. Equation (121) is in full agreement with the corresponding result of the difference equation treatment, equation (66), as it should be.

While the numerator of equation (117) had to be calculated to 3rd order in the inverse correlation lengths to pick up the critical singularities, for the calculation of the critical part of χ_{11} it suffices to keep terms up to second order in ξ_+^{-2}, ξ_-^{-2} and $\xi_+^{-1}\xi_-^{-1}$. One obtains

$$J_1\chi_{11} = \frac{\left[1 + \left(\frac{1}{\kappa} - \frac{7}{2}\right)\left(\frac{a}{\xi_-} + \frac{a}{\xi_+}\right)\right]\frac{\lambda/a}{1-\kappa}}{1 - \frac{\lambda}{a} + \left(\frac{a}{\xi_-} + \frac{a}{\xi_+}\right)\left[\left(\frac{1}{\kappa} - \frac{7}{2}\right) - \frac{\lambda}{2a}\frac{1-3\kappa}{1-\kappa}\right]} \cdot \tag{122}$$

Equation (122) is applicable only in between the disorder line $T_\mathrm{d}(\kappa)$ and the critical line $T_\mathrm{cb}(\kappa)$, (*cf.* Fig. 1), *i.e.* in a very narrow region of the phase diagram. At the disorder line, we have for κ near κ_L, (*cf.* Eq. (29)) $a/\xi_+ = a/\xi_- = \sqrt{2}(1 - \kappa/\kappa_\mathrm{L})^{1/2}$, $a/\xi_- + a/\xi_+ = 2\sqrt{2}(1 - \kappa/\kappa_\mathrm{L})^{1/2}$ while at the critical line we have (*cf.* Eqs. (30, 31)),

$$\frac{a}{\xi_-} + \frac{a}{\xi_+} = 2\sqrt{1 - \frac{\kappa}{\kappa_\mathrm{L}}} + \frac{1}{\sqrt{1 - \kappa/\kappa_\mathrm{L}}}\left[k_\mathrm{B}\frac{(T - T_\mathrm{cb}(\kappa))}{J_1}\right]^{1/2}.$$

Thus we recognize the singularity of χ_{11} at $T_\mathrm{cb}(\kappa)$, provided $J_\mathrm{s} < J_\mathrm{sc}$ so no surface transition occurs,

$$\chi_{11} = \chi_{11}^\mathrm{crit.} - \hat{\Gamma}_{11}(\kappa)\left\{k_\mathrm{B}\frac{[T - T_\mathrm{cb}(\kappa)]}{J_1}\right\}^{1/2}, \tag{123}$$

with

$$\chi_{11}^\mathrm{crit.} = \frac{4\lambda}{3aJ_1}\frac{1 + \sqrt{1 - \kappa/\kappa_\mathrm{L}}}{1 - \frac{\lambda}{a} + \left(1 - \frac{\lambda}{3a}\right)\sqrt{1 - \kappa/\kappa_\mathrm{L}}}, \tag{124}$$

$$\hat{\Gamma}_{11}(\kappa) = \frac{J_1^{-1}(2\lambda/3a)^2(1 - \kappa/\kappa_\mathrm{L})^{-1/2}}{\left[1 - \frac{\lambda}{a} + \sqrt{1 - \kappa/\kappa_\mathrm{L}}(1 - \lambda/3a)\right]^2} \cdot \tag{125}$$

Remember that near the Lifshitz point for $J_\mathrm{s} < J_\mathrm{sc}$ the length λ is less than a, hence the denominator of $\chi_{11}^\mathrm{crit.}$ is positive, as it should be. For $\kappa \to \kappa_L$ the critical value $\chi_{11}^{\text{crit.}}$ stays finite, while the amplitude $\hat{\Gamma}_{11}(\kappa)$ diverges, as equation (125) clearly demonstrates.

From equation (112) we finally conclude that the dominant term of the singularity of χ_s is

$$\chi_s = -\frac{\xi_+}{a}\frac{\partial A_+}{\partial H} = -(\xi_+/a)\chi_b \frac{(R_- - N_-)}{\Delta}$$

and noting that, to leading order, $R_- - N_- \approx (a/\xi_-)(1-\lambda/a)$ we recover equation (67), as expected. The result [22–24] that the amplitude of χ_s for $J_s < J_{sc}$ is independent of J_s thus holds throughout the region $\kappa < \kappa_L$ as well.

5.3 The surface transition for $\kappa < \kappa_L$ revisited

From equation (124) we can locate the critical enhancement J_{sc} for the occurrence of a surface transition from the condition $\chi_{11}^{\text{crit.}} \to \infty$, *i.e.*

$$\frac{\lambda_c}{a} = \frac{1+\sqrt{1-\kappa/\kappa_L}}{1+\sqrt{1-\kappa/\kappa_L}/3}, \tag{126}$$

which can be rewritten with the help of equation (107) as

$$\frac{z_\parallel(J_{sc}-J_0)}{J_1} = \frac{1}{4}\frac{1+3\sqrt{1-\kappa/\kappa_L}}{1+\sqrt{1-\kappa/\kappa_L}} \approx \frac{1}{4}+\frac{1}{2}\sqrt{1-\kappa/\kappa_L}. \tag{127}$$

The same result follows from equation (69) to leading order in $\sqrt{1-\kappa/\kappa_L}$ near $\kappa_L = 1/4$, while higher order terms in $\sqrt{1-\kappa/\kappa_L}$ in equation (69) would differ from equation (127), since the differential equation misses the correct magnitude of the (finite) length ξ_- if one moves further away from the Lifshitz point. The correct dependence of $J_{sc}(\kappa)$ over the full range of κ cannot be reproduced by the continuum theory.

For $J_s > J_{sc}$ the first singularity of χ_{11} occurs at a temperature $T_{cs}(\kappa) > T_{cb}(\kappa)$, the surface transition temperature, which we find from the vanishing of the denominator in equation (122), to leading order of J_s near J_{sc},

$$k_B\frac{T_{cs}-T_{cb}(\kappa)}{J_1} = \left(1-\frac{\kappa}{\kappa_L}\right)\left[\frac{4z_\parallel(J_s-J_{sc})}{J_1}\right]^2 \cdot \tag{128}$$

As a result, we see that $T_{cs} - T_{cb}(\kappa) \propto (J_s - J_{sc})^{1/\phi}$, with $\phi = 1/2$ along the ferromagnetic transition line, as expected. A nontrivial feature of equation (128) is the vanishing of the amplitude of this surface transition line as $\kappa \to \kappa_L$.

5.4 Behavior for $\kappa \geq \kappa_L$

While equations (105, 106) hold for all values of κ, equations (108, 109) cannot be used here since we have to use $T_{mb}(\kappa)$ and ξ according to equation (36) rather than $T_{cb}(\kappa), \xi_+$ which are of physical significance for $\kappa < \kappa_L$ only. Noting from Section 5.2, however, that the third order term $(\xi_-^2\xi_+)^{-1}$ in the numerator of equation (117) did not arise from any of the third derivatives in equations (105, 106), we henceforth omit them altogether, and keep only second-order derivatives in the boundary condition. Thus we find from equation (106), keeping only leading terms in $(1-\kappa/\kappa_L)$ by using $\kappa_L/\kappa \approx 1-(\kappa/\kappa_L - 1)$,

$$m(0)\left[1-\frac{2}{\kappa}\left(\frac{a}{\xi}\right)^2\left(\frac{\kappa}{\kappa_L}-1\right)\right] - a\left.\frac{\partial m}{\partial z}\right|_{z=0} + \left(\frac{2}{\kappa}-7\right)\frac{a^2}{2}\left(\frac{\partial^2 m}{\partial z^2}\right)_{z=0} = -M_b, \tag{129}$$

which is the analog of equation (109), and subtracting equations (105, 106) we find

$$m(0) - \lambda\left(\frac{\partial m}{\partial z}\right)_{z=0} + \frac{1-3\kappa}{1-\kappa}\frac{a\lambda}{2}\left(\frac{\partial^2 m}{\partial z^2}\right)_{z=0} = K_1', \tag{130}$$

which is identical with equation (108) if in the latter equation only terms of second order in ξ^{-1} and second derivatives are kept. As expected, to leading order – when one neglects the term of order ξ^{-2} in equation (129) and the analogous term in equation (109), equations (129, 130) apply both for $\kappa \leq \kappa_L$ and $\kappa \geq \kappa_L$, as expected.

We now have to solve equations (129, 130) by the continuum analog of equation (79), *i.e.*

$$m(z) = A\cos(qz+\Psi)\exp(-z/\xi), \tag{131}$$

and thus again using $A_c = A\cos\Psi, A_s = -A\sin\Psi$ we find $A_cN_c + A_sN_s = K_1'$, $A_cR_c + A_sR_s = -M_b$, with (using also Eq. (33))

$$N_c = 1-\frac{\lambda}{a}\frac{1-3\kappa}{1-\kappa}\left(\frac{\kappa}{\kappa_L}-1\right)+\frac{\lambda}{\xi} \tag{132}$$

$$N_s = -\lambda q - \frac{1-3\kappa}{1-\kappa}\frac{q\lambda a}{\xi}, \tag{133}$$

$$R_c = 1-\left(\frac{2}{\kappa}-7\right)\left(\frac{\kappa}{\kappa_L}-1\right)+\frac{a}{\xi}-\frac{2}{\kappa}\left(\frac{a}{\xi}\right)^2\left(\frac{\kappa}{\kappa_L}-1\right), \tag{134}$$

$$R_s = -qa - \left(\frac{2}{\kappa}-7\right)\frac{qa^2}{\xi}\cdot \tag{135}$$

In analogy to equations (84–86) we write the susceptibilities ($\Delta \equiv R_sN_c - R_cN_s$)

$$J_1\chi_{11} = \frac{[(\lambda/a)/(1-\kappa)]\,R_s}{\Delta}, \tag{136}$$

$$\chi_1 = \frac{\chi_b(\Delta + N_s - R_s)}{\Delta} \tag{137}$$

$$J_1\chi_{11} \approx \frac{\left[\dfrac{\lambda/a}{1-\kappa}\right]\left[1+\left(\dfrac{2}{\kappa}-7\right)\dfrac{a}{\xi}\right]}{\left\{1-\dfrac{\lambda}{a}\left[1-2\left(\dfrac{\kappa}{\kappa_{\mathrm{L}}}-1\right)\dfrac{1-5\kappa+5\kappa^2}{\kappa(1-\kappa)}\right]+\dfrac{a}{\xi}\left(\dfrac{2}{\kappa}-7\right)-\dfrac{\lambda}{\xi}\dfrac{1-3\kappa}{1-\kappa}\right\}}. \tag{140}$$

$$\chi_1 = \chi_{\mathrm{b}}\left(\frac{2\lambda}{a}\right)\frac{\left(\dfrac{\kappa}{\kappa_{\mathrm{L}}}-1\right)\dfrac{1-5\kappa+5\kappa^2}{\kappa(1-\kappa)}+\left(\dfrac{a^2}{\xi^2}\right)\dfrac{\kappa}{1-\kappa}}{\left\{1-\dfrac{\lambda}{a}\left[1-2\left(\dfrac{\kappa}{\kappa_{\mathrm{L}}}-1\right)\dfrac{1-5\kappa+5\kappa^2}{\kappa(1-\kappa)}\right]+\dfrac{a}{\xi}\left(\dfrac{2}{\kappa}-7\right)\dfrac{\lambda}{\xi}\dfrac{1-3\kappa}{1-\kappa}\right\}}. \tag{142}$$

and

$$\begin{aligned}\chi_{\mathrm{s}} &= -\frac{\partial}{\partial H}\frac{1}{a}\int_0^\infty m(z)\mathrm{d}z\\ &= \left(\frac{a^2}{\xi^2}+a^2q^2\right)^{-1}\frac{\partial}{\partial H}\left(aqA_{\mathrm{s}}-\frac{a}{\xi}A_{\mathrm{c}}\right)\\ &= \left(\frac{a^2}{\xi^2}+a^2q^2\right)^{-1}\chi_{\mathrm{b}}\left[aq(R_{\mathrm{c}}-N_{\mathrm{c}})+\frac{a}{\xi}(R_{\mathrm{s}}-N_{\mathrm{s}})\right]/\Delta\end{aligned} \tag{138}$$

From equations (132–135) one finds

$$\begin{aligned}\Delta = -qa\Bigg\{&1-\frac{\lambda}{a}\left[1-2\left(\frac{\kappa}{\kappa_{\mathrm{L}}}-1\right)\frac{1-5\kappa+5\kappa^2}{\kappa(1-\kappa)}\right]\\ &-\frac{\lambda}{\xi}\frac{1-3\kappa}{1-\kappa}+\frac{a}{\xi}\left(\frac{2}{\kappa}-7\right)+\frac{2\lambda a}{\xi^2}\frac{\kappa}{1-\kappa}\Bigg\},\end{aligned} \tag{139}$$

and hence

see equation (140) *above.*

At the Lifshitz point, $\kappa=\kappa_{\mathrm{L}}=1/4$, this reduces to

$$\begin{aligned}J_1\chi_{11} &= \frac{(4\lambda/3a)(1+a/\xi)}{1+a/\xi-(\lambda/a)(1+a/3\xi)}\\ &\approx \left[1-\frac{\lambda}{a}\left(1-\frac{2a}{3\xi}\right)\right]^{-1},\end{aligned} \tag{141}$$

which agrees with equation (92), as it should. From equation (140) we see that for $\kappa > \kappa_{\mathrm{L}}$ χ_{11} has a singularity of the same form as on the ferromagnetic side, $\kappa < \kappa_{\mathrm{L}}$, namely as given by equation (123), only $T_{\mathrm{cb}}(\kappa)$ is replaced by $T_{\mathrm{mb}}(\kappa)$. For χ_1, however, we find from equation (137)

see equation (142) *above*

For $\kappa > \kappa_{\mathrm{L}}$ the bulk susceptibility χ_{b} stays finite – it is only $\chi(\mathbf{k})$ that diverges for $k_\perp = q$ as $T \to T_{\mathrm{mb}}$ while $\chi_{\mathrm{b}} = \chi(\mathbf{k}=0)$ does not diverge. Thus the response of M_1 to a bulk field H is no more singular than the response to a surface field H_1, as expected, since H is not the "ordering field" of the modulated phase. At the Lifshitz point, however, we obtain

$$\begin{aligned}\chi_1 &= \frac{\chi_{\mathrm{b}}(2a\lambda/3\xi^2)}{\left(1-\dfrac{\lambda}{a}+\dfrac{a}{\xi}-\dfrac{\lambda}{3\xi}\right)}\\ &= \frac{\dfrac{1}{2}\chi_{\mathrm{b}}J_1\left(\dfrac{a^2}{\xi^2}\right)}{\dfrac{J_1}{4}+z_\|(J_0-J_{\mathrm{s}})+3\left(\dfrac{a}{\xi}\right)\dfrac{J_1}{4}+z_\|(J_0-J_{\mathrm{s}})\dfrac{a}{\xi}},\end{aligned} \tag{143}$$

which agrees with equation (93) to leading order, as it should.

Finally we consider the surface transition again, which can be located by requiring that the denominator of equations (140, 141) vanishes already for temperatures $T > T_{\mathrm{mb}}(\kappa)$ where ξ is still finite, *i.e.*

$$\begin{aligned}1-\frac{\lambda}{a}&\left[1-2\left(\frac{\kappa}{\kappa_{\mathrm{L}}}-1\right)\frac{1-5\kappa+5\kappa^2}{\kappa(1-\kappa)}\right]\\ &+\frac{a}{\xi}\left(\frac{2}{\kappa}-7\right)-\frac{\lambda}{\xi}\frac{1-3\kappa}{1-\kappa}=0.\end{aligned} \tag{144}$$

It is convenient to introduce the critical value λ_{c} corresponding to the critical surface exchange J_{sc} enhancement where the surface transition $T_{\mathrm{sc}}(\kappa)$ merges with $T_{\mathrm{mb}}(\kappa)$ and hence $\xi=\infty$. This critical value is

$$\frac{\lambda_{\mathrm{c}}}{a} = \left[1-2\left(\frac{\kappa}{\kappa_{\mathrm{L}}}-1\right)\frac{1-5\kappa+5\kappa^2}{\kappa(1-\kappa)}\right]^{-1}, \tag{145}$$

and hence the bulk correlation length $\xi_{\mathrm{s}} = \xi(T_{\mathrm{cs}}(\kappa))$ at the temperature $T = T_{\mathrm{cs}}(\kappa)$ of the surface transition can be written as

$$\frac{a}{\xi_{\mathrm{s}}} = \frac{\lambda/\lambda_{\mathrm{c}}-1}{\dfrac{2}{\kappa}-7-\dfrac{\lambda}{a}\dfrac{1-3\kappa}{1-\kappa}} \approx \frac{\lambda/\lambda_{\mathrm{c}}-1}{\dfrac{2}{\kappa}-7-\dfrac{\lambda_{\mathrm{c}}}{a}\dfrac{1-3\kappa}{1-\kappa}}, \tag{146}$$

where in the last step we have restricted attention to the leading order in $\lambda/\lambda_{\mathrm{c}}-1$. Since $\xi(T)$ is given as (Eq. (36))

$(a/\xi)^2 \approx k_B[T - T_{mb}(\kappa)]/[2J_1(\kappa/\kappa_L - 1)]$, equation (146) immediately yields the behavior of $T_{cs}(\kappa)$ in the vicinity of $T_{mb}(\kappa)$ namely

$$\frac{k_B[T_{cs}(\kappa) - T_{mb}(\kappa)]}{J_1} = \frac{2\left(\frac{\kappa}{\kappa_L} - 1\right)\left(\frac{\lambda}{\lambda_c} - 1\right)^2}{\left[\frac{2}{\kappa} - 7 - \frac{\lambda_c}{a}\frac{1-3\kappa}{1-\kappa}\right]^2} \cdot \quad (147)$$

The leading behavior near $\kappa_L = 1/4$ is

$$\frac{k_B[T_{cs}(\kappa) - T_{mb}(\kappa)]}{J_1} \approx \frac{9}{2}\left(\frac{\kappa}{\kappa_L} - 1\right)\left(\frac{\lambda}{\lambda_c} - 1\right)^2 \approx 8\left(\frac{\kappa}{\kappa_L} - 1\right)\frac{(J_s - J_{sc})^2 z_\parallel^2}{J_1^2} \quad (148)$$

which should be compared to the analogous result from the lattice calculation, namely equation (104). Note, however, that equations (128, 148) should only be used in the immediate vicinity of $\kappa = \kappa_L$, while equations (69, 77, 104) hold over the full range of κ, see Figure 4.

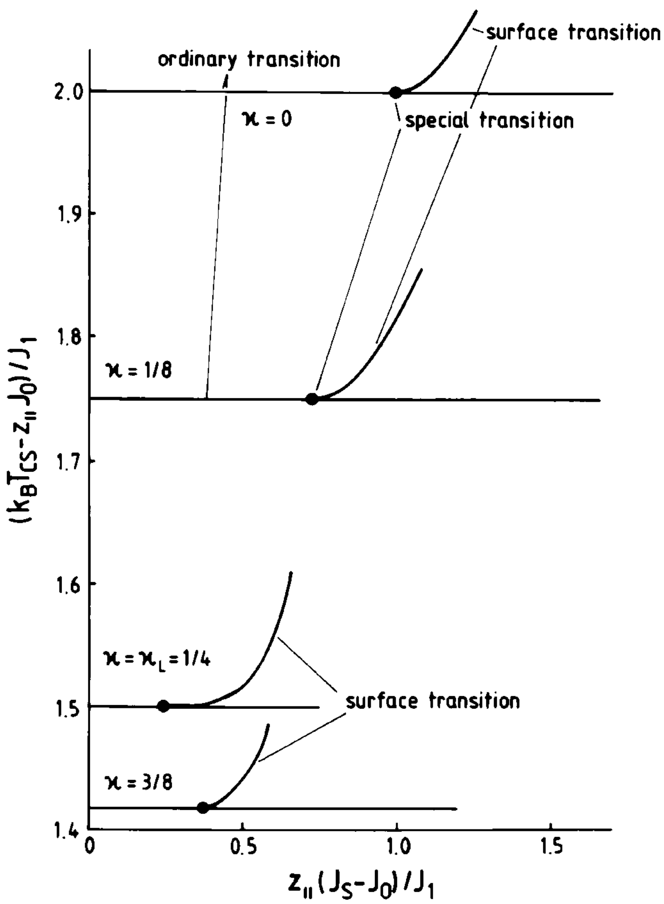

Fig. 4. Some examples of surface phase diagrams of the ANNNI model, plotting the surface phase transition $k_B T_{cs}(\kappa)/J_1$ and the bulk transition $(k_B T_{cb}(\kappa)/J_1$ for $\kappa \le \kappa_L$ and $k_B T_{mb}(\kappa)/J_1$ for $\kappa > \kappa_L$ respectively), *vs.* $z_\parallel(J_s - J_o)/J_1$. Note that by the subtraction of $z_\parallel J_o/J_1$ from all transition temperatures there is no further dependence on the ratio J_o/J_1 or on $z_\parallel$. The surface exchange at the special transition ($J_s = J_{sc}$) first decreases as κ increases up to its minimum value at the Lifshitz point ($\kappa = \kappa_L = 1/4$) and then increases again. Only the leading power law of $T_{cs} - T_{cb} \propto (J_s - J_{sc})^{1/\phi_{SB}}$ is shown in all cases (note $\phi_{SB} = 1/2$ for $\kappa \ne \kappa_L$ but $\phi_{SB} = \phi_{SB}^L = 1/4$ for $\kappa = \kappa_L$), using equations (77, 104), respectively. Note that the amplitude of the quadratic variation $[T_{cs}(\kappa) - T_{mb}(\kappa)]/J_1 \propto [(J_s - J_{sc})z_\parallel/J_1]^2$ is 40/27 for $\kappa = 3/8$ already – the linear vanishing of this amplitude as $\kappa \to \kappa_L$ (Eq. (148)) is relevant in the immediate vicinity of κ_L only.

6 Free energy of the semi-infinite ANNNI model

For analytic treatments beyond the mean field approximation the continuum version of the (nonlinear) free energy functional of mean field theory is a useful starting point. Therefore we derive this functional explicitly, including the bare surface free energy terms, *cf.* [22–24], in the present section.

Again we start from the lattice version, writing the free energy, per lattice plane as $F = E - TS$ considering both internal energy E and entropy S as functionals of the set of layer magnetizations $\{M_i\}, i = 1, 2, \ldots, N_z \to \infty$. The entropy is

$$\frac{S}{k_B} = -\sum_{i=1}^{N_z}\left[\frac{1+M_i}{2}\ln\left(\frac{1+M_i}{2}\right) + \frac{1-M_i}{2}\ln\left(\frac{1-M_i}{2}\right)\right] \approx N_z \ln 2 - \sum_{i=1}^{N_z}\left(\frac{1}{2}M_i^2 + \frac{1}{12}M_i^4\right), \quad (149)$$

where in the following the additive constant $N_z \ln 2$ will be omitted. The energy is written by replacing the spins S_i in the ith plane by their averages M_i in the Hamiltonian, which yields (note that in Eq. (3) each bond is counted once)

$$E = -\frac{z_\parallel J_s}{2}M_1^2 - M_1(H_1 + H) - \frac{1}{2}J_1 M_1 M_2 - \frac{1}{2}J_2 M_1 M_3 - \frac{z_\parallel J_0}{2}M_2^2 - M_2 H - \frac{1}{2}J_1 M_2(M_1 + M_3) - \frac{1}{2}J_2 M_2 M_4 - \sum_{i=3}^{N_z}\left[\frac{z_\parallel J_0}{2}M_i^2 + M_i H + \frac{1}{2}J_1 M_i(M_{i-1} + M_{i+1}) + \frac{1}{2}J_2 M_i(M_{i-2} + M_{i+2})\right]. \quad (150)$$

Omitting the term $M_i^4/12$ in equation (149) the equilibrium condition

$$\left(\frac{\partial F}{\partial M_i}\right)_{T,\{M_{j\neq i}\},H,H_1} = 0 \tag{151}$$

yields exactly the set of equations (16, 50, 51), as it should.

We now again wish to transform differences into differentials, using equation (25), and interpret $\sum_{i=1}^{N_z}\ldots$ as $\int_0^\infty \frac{\mathrm{d}z}{a}\ldots$ in the limit $N_z\to\infty$. However, care is necessary in making this substitution since in the entropy the lower limit of the summation indeed is $i=1$ (Eq. (149)) while in E it is $i=3$ (Eq. (150)). In order to treat both E and S on an equal footing, we formally define also magnetizations M_0, M_{-1} in the non-existing planes adjacent to the other side of the free surface, and subtract the terms generated in this way such that equation (150) is recovered. Thus

$$\begin{aligned} F =& \sum_{i=1}^{N_z}\left[\frac{1}{2}(k_\mathrm{B}T - z_\parallel J_0)M_i^2 + \frac{1}{12}k_\mathrm{B}TM_i^4 - M_iH \right.\\ &\quad - \frac{1}{2}J_1M_i(M_{i-1}+M_{i+1})\\ &\quad \left.-\frac{1}{2}J_2M_i(M_{i-2}+M_{i+2})\right]\\ &- \frac{1}{2}M_1^2 z_\parallel(J_\mathrm{s}-J_0) - M_1H_1 + \frac{1}{2}J_1M_1M_0\\ &+\frac{1}{2}J_2M_1M_{-1} + \frac{1}{2}J_2M_2M_0. \end{aligned} \tag{152}$$

Writing out the first two terms in the sum of equation (152) explicitly it is easy to check that equation (152) reduces to equations (149, 150).

Using now equation (25) we find

$$\begin{aligned} F =& \frac{1}{a}\int_0^\infty \mathrm{d}z\left\{\frac{1}{2}m^2(z)\left[k_\mathrm{B}T - (z_\parallel J_0 + 2J_1 + 2J_2)\right]\right.\\ &\quad + \frac{1}{12}k_\mathrm{B}Tm^4(z) - m(z)H\\ &\quad - \frac{a^2}{2}(J_1+4J_2)m(z)\frac{\partial^2 m}{\partial z^2}\\ &\quad \left.-\frac{a^4}{24}(J_1+16J_2)m(z)\frac{\partial^4 m}{\partial z^4}\right\}\\ &+\frac{1}{2}m^2(0)\left[z_\parallel(J_0-J_\mathrm{s}) + J_1 + 2J_2\right]\\ &- m(0)H_1 - \frac{1}{2}(J_1+2J_2)am(0)\left.\frac{\partial m}{\partial z}\right|_{z=0}\\ &- \frac{1}{2}J_2a^2\left[\left(\frac{\partial m}{\partial z}\right)_{z=0}\right]^2 + \frac{1}{2}(J_1+6J_2)a^2m(0)\left.\frac{\partial^2 m}{\partial z^2}\right|_{z=0}. \end{aligned} \tag{153}$$

Integrating by parts we can reduce this result to the standard form containing in the free energy $(\partial m/\partial z)^2$ and $(\partial^2 m/\partial^2 z)^2$ terms,

$$\begin{aligned} F =& \frac{1}{a}\int_0^\infty \mathrm{d}z\left\{\frac{1}{2}m^2(z)[k_\mathrm{B}T - (z_\parallel J_0 + 2J_1 + 2J_2)]\right.\\ &\quad + \frac{1}{12}k_\mathrm{B}Tm^4(z) - m(z)H\\ &\quad + \frac{a^2}{2}(J_1+4J_2)\left(\frac{\partial m}{\partial z}\right)^2\\ &\quad \left.-\frac{a^4}{24}(J_1+16J_2)\left(\frac{\partial^2 m}{\partial z^2}\right)^2\right\}\\ &+\frac{1}{2}m^2(0)[z_\parallel(J_0-J_\mathrm{s}) + J_1 + 2J_2]\\ &- m(0)H_1 + J_2am(0)\left.\frac{\partial m}{\partial z}\right|_{z=0} - \frac{1}{2}J_2a^2\left[\left(\frac{\partial m}{\partial z}\right)_{z=0}\right]^2\\ &+\frac{1}{2}(J_1+6J_2)a^2m(0)\left.\frac{\partial^2 m}{\partial z^2}\right|_{z=0}. \end{aligned} \tag{154}$$

In this expression, we have neglected in the boundary condition all derivatives of higher than second order. Equation (154) is the central result of this section. We see that it has the general form

$$F = \frac{1}{a}\int_0^\infty \mathrm{d}z f\left(z, \frac{\partial m}{\partial z}\right) + F_\mathrm{s}^{(\mathrm{bare})} \tag{155}$$

where the bare surface free energy depends on the surface layer magnetization $m(z=0)$ and its low-order derivatives, as expected. In the nearest neighbor case ($J_2=0$), both the term involving $(\partial^2 m/\partial z^2)^2$ in the bulk and $\partial^2 m/\partial z^2|_{z=0}$ at the surface can be neglected, and then $F_\mathrm{s}^{(\mathrm{bare})}$ reduces to the well-known standard result [22–24]

$$F_\mathrm{s}^{(\mathrm{bare})} = -m(0)H_1 + \frac{1}{2}m^2(0)[z_\parallel(J_0-J_\mathrm{s}) + J_1],\quad J_2=0 \tag{156}$$

as expected. If one is not interested in the specific properties of the lattice model, one generalizes equation (156) as

$$F_\mathrm{s}^{(\mathrm{bare})} = -m(0)H_1 + \frac{c}{2}m^2(0), \tag{157}$$

where c is some coefficient. For the ANNNI model, the bare surface free energy $F_\mathrm{s}^{(\mathrm{bare})}$ now contains three additional terms, as equation (154) shows. While in the variational minimization of equation (155) the simple structure of equation (156) yields a single boundary condition for $\partial m/\partial z|_{z=0}$, the more complicated structure of equation (154) is responsible for the two boundary conditions for $\partial m/\partial z|_{z=0}$ and $\partial^2 m/\partial z^2|_{z=0}$, to which equations (105, 106) can be reduced if the irrelevant terms of order $(\partial^3 m/\partial z^3)_{z=0}$ are omitted.

7 Conclusions

In this paper, a first study of surface effects on the critical behavior of the ANNNI model has been presented, as a generic model for systems with a uniaxial Lifshitz point separating ferromagnetic and modulated types of ordering. This study has been restricted to the mean field limit of the disordered phase throughout. In addition, we have assumed that the direction normal to the surface coincides with the axis along which competing ferro- and antiferromagnetic interactions and hence a possible modulation of long range order can occur. With a suitable enhancement of the (nearest neighbor) interaction J_s in the surface plane relative to the interaction J_0 in planes parallel to the surface in the interior of the system, a ferromagnetic "surface transition" (two dimensional long range order of ferromagnetic character in the surface plane) can occur, at a transition temperature T_{cs} that is higher than the transition temperature of the bulk, irrespective whether the transition is to a ferromagnetic long range order (at $T_{cb}(\kappa)$ with $\kappa = -J_2/J_1$, the ratio of exchange interactions between next nearest (J_2) and nearest (J_1) neighbor interactions in the axial direction, less than $\kappa_L = 1/4$, the value at the Lifshitz point) or to modulated long range order ($\kappa > \kappa_L$). If we were to consider competing interactions also in the surface plane, a two-dimensional modulated phase in the surface plane could also occur – but this case is out of consideration here and is left to future work.

While for $\kappa > \kappa_L$ and temperatures in between $T_{cb}(\kappa)$ and the disorder line $T_d(\kappa)$, which merges with $T_{cb}(\kappa)$ for $\kappa = \kappa_L$, the order parameter profile of the ferromagnet differs from its bulk value by two exponentials, $\tilde{M}(z) = A_+ \exp(-z/\xi_+) + A_- \exp(-z/\xi_-)$ for $\kappa > \kappa_L$ this deviation has a modulated character, $\tilde{M}(z) = A \exp(-z/\xi) \cos(qz + \Psi)$. While for $T \to T_{cb}(\kappa)$ the leading correlation length ξ_+ shows a mean-field type divergence, $\xi_+ \propto (T/T_{cb} - 1)^{-1/2}$, and for $T \to T_{mb}(\kappa > \kappa_L)$ the length ξ diverges similarly, $\xi_- \propto (T/T_{mb} - 1)^{-1/2}$, the second lengths, ξ_- and $\Lambda = 2\pi/q$ stay finite at the respective transition, but show a divergence as κ approaches the value κ_L at the Lifshitz point, $\xi_- \propto (1 - \kappa/\kappa_L)^{-1/2}$, or $\Lambda \propto (1 - \kappa_L/\kappa)^{-1/2}$, respectively. As is well known, for $\kappa = \kappa_L = 1/4$ the correlation length ξ has a weaker divergence as $T \to T_L$, $\xi \propto (T/T_L - 1)^{-1/4}$, and thus for κ close to κ_L the correlation lengths ξ_+ or ξ have a singular dependence on $\kappa/\kappa_L - 1$, in order to have compatibility with the different divergence of ξ at $\kappa = \kappa_L$ itself, *i.e.* $\xi_+ \propto (1 - \kappa/\kappa_L)^{1/2}(T/T_{cb}(\kappa) - 1)^{-1/2}$ or $\xi \propto (\kappa/\kappa_L - 1)^{1/2} (T/T_{mb}(\kappa) - 1)^{-1/2}$, respectively.

Similar singularities can now be identified in many surface-related properties as well. *E.g.*, for $J_s > J_{sc}(\kappa)$ we find a "surface transition" at a transition temperature $T_{cs}(\kappa)$ which behaves as:

for $\kappa < \kappa_L$

$$T_{cs}(\kappa) - T_{cb}(\kappa) \propto \left(1 - \frac{\kappa}{\kappa_L}\right) \left[\frac{J_s}{J_{sc}(\kappa)} - 1\right]^2;$$

for $\kappa = \kappa_L$

$$T_{cs}(\kappa_L) - T_L(\kappa_L) \propto [J_s/J_{sc}(\kappa_L) - 1]^4;$$

and for $\kappa > \kappa_L$

$$T_{cs}(\kappa) - T_{mb}(\kappa) \propto (\kappa/\kappa_L - 1)[J_s/J_{sc}(\kappa) - 1]^2.$$

Note that $J_{sc}(\kappa)$ decreases from $\kappa = 0$ to a minimum value at $\kappa = \kappa_L$ and from there it increases again $(z_{\|}(J_{sc} - J_0)/J_1 = \kappa)$. The singularities of susceptibilities χ_s, χ_1, χ_{11} in all cases are of simple Curie-Weiss types as T approaches $T_{cs}(\kappa)$ from above.

We emphasize that for characterizing the parameters A_+, A_-\{or A, Ψ\} of the surface excess order parameter profile one needs *two* boundary conditions, and a single boundary condition as is used in the standard ferromagnetic problem would not be sufficient. There two boundary conditions emerge naturally from the lattice version of the mean field theory, since the equations of the local order parameter both in the surface plane (M_1) and in the adjacent interior plane (M_2) differ from the corresponding equation in the bulk. Transforming differences into differentials, one obtains a differential equation for the order parameter profile $m(z)$, which must include terms up to the order $\partial^4 m(z)/\partial z^4$ since the coefficient of the term $\partial^2 m/\partial z^2$ changes sign at the Lifshitz point. This differential equation at the bulk is supplemented by *two* boundary conditions at the surface, including terms in $m(z=0)$, $\partial m/\partial z|_{z=0}$ and $\partial^2 m/\partial z^2|_{z=0}$, respectively. Correspondingly the free energy functional involves a bare surface free energy $F_s^{(\text{bare})}$ that has not just the form $F_s^{(\text{bare})} = 1/2\ \text{cm}^2(z=0) - m(z=0)H_1$ as for the simple ferromagnetic case [22–24], but includes terms of the form $(m\partial m/\partial z)_{z=0}(\partial m/\partial z)^2_{z=0}$ and $m(\partial^2 m/\partial z^2)_{z=0}$, respectively. Coefficients of all these terms have been derived explicitly in terms of the microscopic interaction parameters. In this respect, our treatment differs basically from the treatment of surface effects on the lamellar phase of block copolymers, where one also has a local order parameter deviation of the form $m(z) = A \exp(-z/\xi) \cos(qz + \Psi)$ but one uses the same form of $F_s^{(\text{bare})}$ as for the ferromagnet, and obtains as a second boundary condition the condition $\int_0^\infty m(z)\mathrm{d}z = 0$, due to the conservation of the total concentration of A-monomers and B-monomers separately. In the present case, however, the integral of the deviation, $m_s = \frac{1}{a}\int_0^\infty m(z)\mathrm{d}z$, the surface excess magnetization and associated surface excess susceptibility, do have a nontrivial critical behavior. One finds that χ_s for $\kappa < \kappa_L$ shows a divergence as for the nearest neighbor ferromagnet, $\chi_s \propto \chi_b \xi^+ \propto (T/T_{cb}(\kappa) - 1)^{-3/2}$, and there is a singularity of the "critical amplitude" as $\kappa \to \kappa_L$, due to the behavior of ξ^+ noted above (χ_b shows the standard Curie-Weiss behavior for $\kappa = \kappa_L$ as well). In view of this result, it is no surprise that at the Lifshitz point $\kappa = \kappa_L$ itself the analogous behavior $\chi_s \propto \chi_b \xi \propto (T/T_L - 1)^{-5/4}$ must be interpreted in terms of a distinct surface susceptibility exponent $\gamma_s^L = 5/4$, while in the regime of the modulated phase χ_s stays finite, it shows a cusp-like behavior $\{\chi_s = \chi_s^{\text{crit.}} - \hat{\chi}_s[T/T_{mb}(\kappa) - 1]^{1/2}\}$ of the same type as the surface layer susceptibilities $\chi_{11}(\kappa)$ and $\chi_1(\kappa)$ do. While $\chi_{11}(\kappa)$ has a cusp-like singularity of this type also for $\kappa < \kappa_L$ and hence $\chi_{11}^{\text{crit.}}$ is finite for all κ, both $\chi_1^{\text{crit.}}$ and $\chi_s^{\text{crit.}}$ diverge as κ approaches κ_L from above.

For $\kappa \le \kappa_L$, we find that χ_1 diverges as $(T/T_{cb}(\kappa)-1)^{1/2}$, and hence we conclude $\gamma_1^L = 1/2$ while for $\kappa = \kappa_L$ $\chi_{11} = \chi_{11}^{crit.} - \hat{\chi}_{11}[T/T_L - 1]^{1/4}$, *i.e.* $\gamma_{11}^L = -1/4$. Further critical exponents describing the surface critical behavior at the Lifshitz point follow from scaling laws. The difference in behavior of χ_1 and χ_s for $\kappa < \kappa_L$ and $\kappa > \kappa_L$ is expected, of course, since a uniform field H is conjugate to the order parameter in the bulk for $\kappa \le \kappa_L$ but not for $\kappa > \kappa_L$.

It should be emphasized that the continuum model describes the critical behavior accurately only if also the subleading lengths, ξ_- or Λ, are very large, while the discrete model can describe the critical behavior of the ANNNI model in mean field approximation for all κ. On the other hand, one does not expect that mean field theory is an accurate description of the actual critical behavior of the system at all. The continuum theory might be useful as a starting point for a more accurate treatment employing the renormalization group theory. Clearly the present treatment can be taken as a first step only. Even within mean field theory, a treatment of both the case of other surface orientations, more general interactions (J_1 and J_2 could differ from their bulk values if they couple spins in the surface plane) and the case $T < T_{cb}$ would be of interest.

Also, simulation studies of suitable models as well as experiments on corresponding systems would be very desirable. It is hoped that the present study will stimulate work along these directions.

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Note added in proof

A brief treatment of surface critical behavior near the Lifshitz point was also attempted by G. Gumbs, Phys. Rev. B **33**, 6500 (1986). However, the boundary conditions that he postulated do not seem to agree with those that we have derived. We think his conclusion about the absence of a surface transition is in error. We are grateful to S. Dietrich for drawing our attention to this reference.

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