Ordering in magnetic films with surface anisotropy

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Abstract.   The effects of the surface exchange anisotropy on the ordering of ferromagnetic films are studied for the exactly solvable classical spin-vector model with $D \to \infty$ components. For small surface anisotropy $\eta'_s \ll 1$ (defined relative to the exchange interaction), the shift of T_c in a film consisting of $N \gg 1$ layers behaves as $T_c^{\text{bulk}} - T_c(N) \propto (1/N) \ln(1/\eta'_s)$ in three dimensions. The finite-size scaling limit $T_c^{\text{bulk}} - T_c(N) \propto 1/(\eta'^{1/2} N^2)$, which is realized for the model with a bulk anisotropy $\eta' \ll 1$ in the range $N\eta'^{1/2} \gtrsim 1$, never appears for the model with the pure surface anisotropy. Here for $N \exp(-1/\eta'_s) \gtrsim 1$ in three dimensions, film orders at a temperature above T_c^{bulk} (the surface phase transition). In the semi-infinite geometry, the surface phase transition occurs for whatever small values of η'_s (i.e., the special phase transition corresponds to T_c^{bulk}) in dimensions three and lower.

1. Introduction

Reduction of Curie temperatures, T_c, of ferromagnetic films consisting of $N \gg 1$ layers with respect to the bulk value is usually represented in the form

$$[T_c^{\text{bulk}} - T_c(N)]/T_c^{\text{bulk}} \cong A/N^\lambda. \tag{1.1}$$

For the exponent λ the finite-size scaling theory [1, 2] yields $\lambda = 1/\nu_b$, where ν_b is the critical index for the bulk correlation length. The above result has been derived with the Ising model, or the field model with a one-component order parameter, in mind. For weakly anisotropic Heisenberg model and, in general, for models with several spin components, the nearly Goldstone modes can drastically change the character of ordering in magnetic films. In particular, in the dimensionality range $d \leqslant 3$ in the isotropic limit at low temperatures, the film behaves as a system of dimensionality $d' = d - 1 \leqslant 2$ and cannot order because of long-wavelength fluctuations. This means that the amplitude A in equation (1.1) should diverge in the isotropic limit. Moreover, even the functional form of equation (1.1) should change to explicitly reflect the d'-dimensional nature of a nearly isotropic film. For the model with the uniaxial exchange anisotropy (longitudinal spin components coupled by J and transverse components coupled by ηJ with $\eta \leqslant 1$, so that $\eta' \equiv 1 - \eta$ measures the anisotropy) it was shown in [3, 4] that equation (1.1) is only valid for rather thick films, $N\kappa_c \gtrsim 1$, where $\kappa_c \equiv 1/\xi_{c\perp} = \sqrt{2d(1/\eta - 1)}$ is the inverse transverse correlation length at the bulk critical point, which goes to zero in the isotropic limit. Here, in three dimensions for the classical spin-vector model with $D \to \infty$ components one has $\lambda = 2$ and $A \sim 1/\kappa_c$. In the range $N\kappa_c \lesssim 1$ a d'-dimensional behaviour is realized, which is characterized by $\lambda = 1$ and $A \sim \ln[1/(\kappa_c N)]$

in three dimensions, $d = 3$. For extremely small anisotropies, the film orders at such low temperatures that spins along the direction perpendicular to the surface are strongly correlated with each other and they can be considered as single composite spins. Thus, the film is mapped on the d'-dimensional monolayer with the exchange interaction NJ, which yields [4]

$$T_c(d, J, \eta', N) \cong T_c(d', NJ, d\eta'/d', 1). \qquad (1.2)$$

Although the results of [3, 4] have been obtained for the infinite-component classical vector model, the qualitative features of this solution should be shared by the more realistic Heisenberg model, $D = 3$. In particular, formula (1.2) is model independent and valid for all $D \geqslant 2$.

The purpose of this paper is to study ordering in magnetic films with a *surface* anisotropy. The latter arises, typically, due to the violation of the symmetry of a crystal field acting on the magnetic ions at the surface. Although this anisotropy has a single-site form, here we will consider the anisotropy of the exchange interactions between the surfaces spins, instead. This leads to the same qualitative results and allows one to use the formalism developed for the exchange-anisotropy models in [3–6]. One can expect that the surface anisotropy stabilizes ordering in films with $d \leqslant 3$ and $N \gg 1$ weaker than the bulk one. If the surface anisotropy is very small, then $T_c \ll T_c^{\text{bulk}}$, and at such low temperature, its influence should redistribute over N layers, so that its effective value is $\eta'_{\text{eff}} \sim \eta'_s/N$. The latter should result in a more pronounced suppression of T_c in magnetic films. This can be seen immediately in the case of extremely small surface anisotropy, where the analogue of equation (1.2) reads

$$T_c(d, J, \eta'_s, N) \cong T_c(d', NJ, \eta'_s/N, 1). \qquad (1.3)$$

A specific feature of the model with pure surface anisotropy is the absence of a finite length scale, such as the transverse correlation length $\xi_{c,\perp} \equiv 1/\kappa$, at criticality. As a result, the system is always in the range $N\kappa \ll 1$ and there is no crossover to the finite-size scaling regime of equation (1.1). As a result, for a small surface anisotropy, the corresponding analytical solution for the Curie temperature of the film holds in a much wider range of N.

If surface anisotropy exceeds a critical value $\eta_{s,c}(N)$, the Curie temperature of the film exceeds the bulk Curie temperature: $T_c > T_c^{\text{bulk}}$. The possibility of this effect, which is absent in the mean-field approximation (MFA), can be seen from the following simple arguments. The isotropic large-D model orders at $T_c^{\text{bulk}} = J_0/(DW_d)$, where J_0 is the zero Fourier component of the exchange interaction and $W_d \equiv P_d(1)$ (see equation (2.21)) is the Watson integral containing the information on the lattice dimensionality and structure. On the other hand, the Curie temperature of the monolayer with the (surface) anisotropy of the extreme Ising type, $\eta_s = 0$ (i.e., $\eta'_s = 1$), is $T_c(1) = (d'/d)J_0/D$. For the simple cubic lattice one has $W_3 = 1.516\,39$, so that the Curie temperature of the anisotropic monolayer slightly exceeds the isotropic bulk Curie temperature. That is, the lack of interacting neighbours at the surface can be compensated for by a stronger suppression of T_c^{bulk} due to long-wavelength fluctuations making contribution to W_d. It is clear that the bilayer has a substantially higher value of T_c than the monolayer, and that in dimensions lower than three the bulk Curie temperature is suppressed even more. For the continuous-dimension model introduced in [6], one has $W_{3.0} = 1.719\,324$ and $W_{2.5} = 2.527\,059$. In two dimensions and below, W_d diverges and thus T_c^{bulk} goes to zero in the isotropic limit. On the other hand, the theory predicts a finite-temperature surface phase transition for any nonzero values of the surface anisotropy η'_s. Thus, for $d \leqslant 2$ the surface anisotropy is the only source of ordering. However, this situation is only realized in the limit $D \to \infty$. Since in two dimensions the surface is one-dimensional, ordering at the surface should be destroyed by thermal fluctuations of the longitudinal spin components for any finite D. In fact, surface anisotropy already plays a major role for $d \leqslant 3$. We will see below that $\eta_{s,c}(N)$ goes to zero in the limit $N \to \infty$ in this dimensionality range. Thus, in the semi-infinite geometry a surface phase transition above T_c^{bulk} occurs for however small a

value of the surface anisotropy, i.e., the bulk Curie temperature is the temperature of the special phase transition as well!

The main part of this paper is organized as follows. In section 2 the closed system of equations describing the $D \to \infty$ component spin-vector model in the symmetric phase is written down. In section 3 the analytical calculation of the correction to T_c in films with a weak surface anisotropy is presented. In section 4 the surface phase transition is considered. The results of numerical calculations are at appropriate places in sections above. In section 5 the results obtained are summarized, and possibilities of finding similar regimes in more realistic models are discussed.

2. Basic equations and their solution

The Hamiltonian of the anisotropic classical D-component spin-vector model can be written in the form

$$\mathcal{H} = -\frac{1}{2} \sum_{ij} J_{ij} \left(m_{zi} m_{zj} + \eta_{ij} \sum_{\alpha=2}^{D} m_{\alpha i} m_{\alpha j} \right) \qquad |m_i| = 1 \tag{2.1}$$

where dimensionless anisotropy factors satisfy $\eta_{ij} \leqslant 1$. This model was introduced, in the isotropic form, by Stanley, who showed that its partition function in the spatially homogeneous case in the limit $D \to \infty$ [7] coincides with that of the spherical model [8]. There are, however, a number of essential differences between the exactly solvable limit $D \to \infty$ of equation (2.1) and the spherical model. In particular, there is only one correlation function (CF) in the spherical model, and thus this model cannot incorporate anisotropy. In the $D \to \infty$ model, there are longitudinal and transverse CFs which differ below T_c, even in the spatially homogeneous isotropic case [9].

The system of equations describing the spatially inhomogeneous $D \to \infty$ model both above and below T_c was obtained in [5]. At or above T_c in zero field, the magnetization $\langle m_i \rangle$ is zero and the model is described by the closed system of equations for the correlation functions of transverse ($\alpha \geqslant 2$) spin components, $s_{ij} \equiv D \langle m_{\alpha i} m_{\alpha j} \rangle$, and the spatially varying gap parameter, G_i. (The definition of G_i can be found in [5]; here it is nonessential.) In the film geometry, it is convenient to use the Fourier representation in $d' = d - 1$ translationally invariant dimensions parallel to the surface and the site representation in the dth dimension. The equations can easily be generalized for the anisotropy factors taking the values η_{nn} within the nth layer and $\eta_{n,n\pm1}$ for the interaction between the nth and $(n \pm 1)$th layers. For the model with nearest-neighbour (nn) interactions, the equation for the Fourier-transformed CF $\sigma_{nn'}(q)$ then takes the form of a system of second-order finite-difference equations in the set of layers $n = 1, 2, \ldots, N$:

$$2b_n \eta_{nn} \sigma_{nn'} - \eta_{n,n+1} \sigma_{n+1,n'} - \eta_{n,n-1} \sigma_{n-1,n'} = 2d\theta \delta_{nn'} \tag{2.2}$$

where b_n is given by

$$b_n = d/(\eta_{nn} G_n) - d' \lambda'_q. \tag{2.3}$$

λ'_q for the d-dimensional hypercubic lattice reads

$$\lambda'_q = \frac{1}{d'} \sum_{i=1}^{d'} \cos(q_i) \tag{2.4}$$

and the lattice spacing has been set to unity. In equation (2.2), θ is the reduced temperature defined by

$$\theta \equiv \frac{T}{T_c^{\text{MFA}}(\infty)} \qquad T_c^{\text{MFA}}(\infty) = \frac{J_0}{D} \tag{2.5}$$

where for hypercubic lattices $J_0 = 2dJ$. The quantities $\sigma_{0,n'}$ and $\sigma_{N+1,n'}$ in the nonexisting layers, which enter equations (2.2) at the film boundaries $n = 1$ and $n = N$, are set to

$$\sigma_{0,n'} = \sigma_{N+1,n'} = 0 \qquad (2.6)$$

as free boundary conditions. The autocorrelation functions in each of N layers, s_{nn}, satisfy the set of constraint equations

$$s_{nn} \equiv \int \frac{d^{d'}q}{(2\pi)^{d'}} \sigma_{nn}(q) = 1 \qquad (2.7)$$

which are the consequence of the spin rigidity, $|m_i| = 1$. A straightforward algorithm for numerically solving the equations above is to compute, for a given set of G_n, all σ_{nn} from the system of linear equations (2.2) and then insert the results in equation (2.7) to obtain, after integration over the Brillouin zone, a set of nonlinear equations for G_n.

The first step of the routine described above can be conveniently performed with the help of the continued-fraction formalism which is described in detail in [4, 6]. For a particular type of model with surface and bulk anisotropies, which is defined by

$$\eta_{11} = \eta_{NN} = \eta_s \leqslant 1 \qquad \eta_{nn} = \eta_{n,n\pm1} = \eta \leqslant 1 \qquad (nn \neq 11, NN) \quad (2.8)$$

and which will be studied below, it is convenient to rewrite equations (2.2) in the form

$$2\tilde{b}_n \sigma_{nn'} - \sigma_{n+1,n'} - \sigma_{n-1,n'} = (2d\theta/\eta)\delta_{nn'} \qquad (2.9)$$

where $\tilde{b}_n = (\eta_s/\eta)b_n$ for $n = 1, N$ and $\tilde{b}_n = b_n$ otherwise. Explicitly,

$$\tilde{b}_n = d/(\eta G_n) - d'\lambda'_q + (1 - \eta_s/\eta)d'\lambda'_q(\delta_{n,1} + \delta_{nN}). \qquad (2.10)$$

An alternative way to find $\sigma_{nn'}$, which is more appropriate for the analytical treatment, is to represent equations (2.2) in the matrix form

$$\hat{B}\hat{\sigma} = \text{diag}(2d\theta/\eta_{nn}) \qquad B_{nn} = 2b_n \qquad B_{n,n\pm1} = -\eta_{n,n\pm1}/\eta_{nn} \qquad (2.11)$$

so that the solution for $\sigma_{nn'}$ is given by $\sigma_{nn'} = (2d\theta/\eta_{n'n'})B_{nn'}^{-1}$. Since the diagonal part of the matrix $\hat{B}$, which depends on the wavevector q, is proportional to the unity matrix, the eigenvalues and eigenvectors of $\hat{B}$ can be defined as

$$\hat{B}\hat{U}_\rho = [\mu_\rho + 2d'(1 - \lambda'_q)]\hat{U}_\rho \qquad \rho = 1, 2, \ldots, N \qquad (2.12)$$

the eigenvectors $\hat{U}_\rho$ being independent of q. It should be noted that matrix $\hat{B}$ is nonsymmetric, $B_{n,n\pm1} = -\eta_{n,n\pm1}/\eta_{nn} \neq B_{n\pm1,n} = -\eta_{n,n\pm1}/\eta_{n\pm1,n\pm1}$, if anisotropy factors η_{nn} change from one layer to the other. In this case its left eigenvectors $\hat{W}_\rho^T$ differ from its right eigenvectors $\hat{U}_\rho$. The Green function $\sigma_{nn'}$ can be expanded over the set of eigenvectors of the problem as follows

$$\sigma_{nn'}(q) = \frac{2d\theta}{\eta_{n'n'}} \sum_{\rho=1}^{N} \frac{U_{n\rho}W_{\rho n'}^T}{\mu_\rho + 2d'(1 - \lambda'_q)}. \qquad (2.13)$$

Here matrix $\hat{U}$ is composed of the right eigenvectors $\hat{U}_\rho$ as columns and $\hat{W}^T$ is composed of the left eigenvectors $\hat{W}_\rho^T$ as rows. The right and left eigenvectors satisfy the biorthogonality condition $\sum_n W_{n\rho}U_{n\rho'} = \delta_{\rho\rho'}$. In general, matrix $\hat{U}$ in nonunitary: $\hat{U}^{-1} = \hat{W}^T \neq \hat{U}^T$. Integration in equation (2.7) can be performed analytically with the result

$$s_{nn} = \frac{2d\theta}{\eta_{nn}} \sum_{\rho=1}^{N} \frac{U_{n\rho}W_{\rho n}^T}{2d' + \mu_\rho} P_{d'}\left(\frac{2d'}{2d' + \mu_\rho}\right) = 1 \qquad (2.14)$$

where $P_{d'}(X)$ is the lattice Green function for the layer, which is defined similarly to the lattice Green function $P(X) \equiv P_d(X)$ below. Using this method with tabulated values of $P_{d'}(X)$

can save computer time, in comparison to the continued-fraction method. On the other hand, the continued-fraction method is fast enough and already implemented, so that it is used here. The diagonalization formalism above is used for analytically solving the problem in the next two sections.

After the set of G_n for a given temperature has been determined, one can compute the longitudinal CF $\sigma_{nn'}^{zz}(q)$ from equations (2.2) and (2.3), where all anisotropy factors $\eta_{nn'}$ are replaced by one. The Curie temperature of the film θ_c can now be found from the equation

$$[\sigma_{nn}^{zz}(q=0)]^{-1} = 0. \tag{2.15}$$

In a usual situation, the above condition should be used in the middle of the film, $n \sim N/2$, because for large N the critical divergence of the spin CF at the surface is suppressed [6,10,11]. If ordering of the film is driven by the surface, it is more convenient to use equation (2.15) for $n = 1$. This equation has, in general, N roots, as we will see below. One should choose the maximal root for θ_c, all other roots are unphysical. Below θ_c, the spontaneous magnetization appears, and the very form of the equations change.

One can also represent $\sigma_{nn'}^{zz}$ in the form of equation (2.13) with $\eta_{n'n'} \Rightarrow 1$, where eigenvalues λ_ρ^z and eigenvectors components $U_{n\rho}^z$ correspond to the problem with the matrix $\hat{B}^z$. The latter is defined by equation (2.11), where anisotropy factors $\eta_{nn'}$ are replaced by one. Since $\hat{B}^z$ is a real symmetric matrix, $(\hat{B}^z)^T = \hat{B}^z$, matrix $\hat{U}^z$ is unitary: $(\hat{U}^z)^{-1} = (\hat{U}^z)^T$, i.e., $U_{\rho n}^{z,-1} = U_{n\rho}^z$. The eigenvalue problem corresponding to the longitudinal CF can be written in the form of a discrete Schrödinger equation for a particle with mass $m = \frac{1}{2}$:

$$-\psi_{n-1} + 2\psi_n - \psi_{n+1} + V_n\psi_n = E\psi_n \qquad V_n = 2d(1/G_n - 1) \tag{2.16}$$

as in quantum tight-binding models. This form is useful for the interpretation of the results; the eigenvectors and eigenvalues of equation (2.16) are more compact forms of the quantities introduced above:

$$\sigma_{nn'}^{zz}(q) = 2d\theta \sum_{\rho=1}^{N} \frac{\psi_{n\rho}\psi_{n'\rho}}{E_\rho + q^2} \qquad q \ll 1 \tag{2.17}$$

where $E_\rho \equiv \mu_\rho^z$ and $\psi_{n\rho} \equiv U_{n\rho}^z$. The condition for the Curie temperature of the film has the form

$$E_1(\theta_c) = 0 \tag{2.18}$$

where E_1 is the lowest of the eigenvalues E_ρ. The $N - 1$ solutions corresponding to $E_\rho = 0$, $\rho \geqslant 2$, are unphysical. It should be noted that for the transverse correlation function the problem cannot, in general, be interpreted quantum mechanically, since the matrix $\hat{B}$ may be non-Hermitean, as is the case for the model with surface anisotropy. The eigenvalues of the transverse problem, μ_ρ, exceed the longitudinal eigenvalues E_ρ; in the Ising limit $\eta \ll 1$ one has $\mu_\rho \propto 1/\eta$, whereas E_ρ become independent of η.

One should note that the longitudinal CF is, in our formalism, only a 'slave' quantity, it does not affect the basic equations of the model and is not subject to a constraint condition similar to equation (2.7). The physical reason for this is the irrelevance of fluctuations of the *single* longitudinal component in comparison to those of $D - 1$ transverse ones in the limit $D \to \infty$.

In the spatially homogeneous bulk sample one has $G_n = G$ and $\eta_{nn} = \eta_{n,n\pm1} = \eta$, and the transverse CF can easily be found [4,6]. The resulting equation for the gap parameter has the form

$$\theta G P(\eta G) = 1 \tag{2.19}$$

where

$$P(X) \equiv \int \frac{d^d k}{(2\pi)^d} \frac{1}{1 - X\lambda_k} \tag{2.20}$$
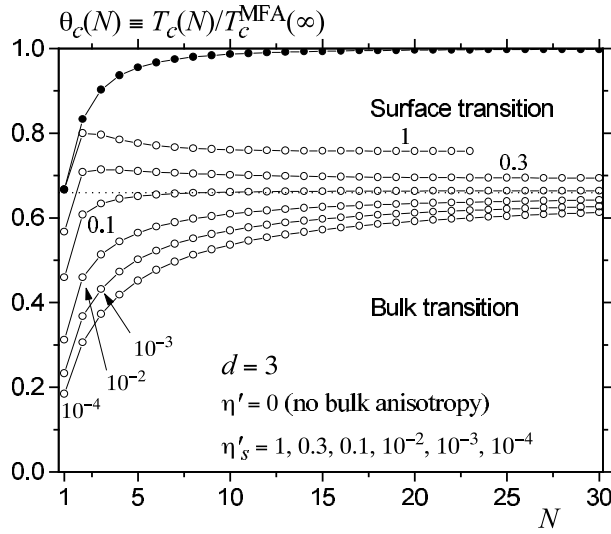
Figure 1. Curie temperatures of the N-layer simple cubic lattice film for different values of surface anisotropy. The horizontal dotted line is the bulk value of T_c. Solid circles are the values of T_c for the model with the bulk anisotropy $\eta' = 1$ (classical Ising model).

is the lattice Green function. The quantity $\lambda_k \equiv J_k/J_0$ for the nearest-neighbour interaction is given by equation (2.4) with $d' \Rightarrow d$ and $q \Rightarrow k$. The solution G of equation (2.19) increases with lowering temperature θ; at $G = 1$ the gap in the longitudinal CF closes, longitudinal susceptibility diverges, and the phase transition occurs. This defines the bulk transition temperature [12]

$$\theta_c^{\text{bulk}} = 1/P(\eta) \tag{2.21}$$

that generalizes the well known result for the spherical model $\theta_c = 1/P(1)$ [8]. The lattice Green function $P(X)$ satisfies $P(0) = 1$ and has a singularity at $X \to 1$, the form of which in different dimensions can be found in [6]. For $d \leqslant 2$, the Watson integral $W \equiv P(1)$ goes to infinity; thus, formula (2.21) yields nonzero values of the Curie temperature only for the anisotropic model, $\eta < 1$. It should be noted that in the anisotropic case the critical indices of the model coincide with the mean-field ones due to the suppression of the singularity of $P(\eta G)$ for $G \to 1$. Below θ_c, the spontaneous magnetization appears, and G sticks to one.

In equation (2.20) one has $\lambda_k \cong 1 - k^2/(2d)$ in the long-wavelength limit. Thus, the inverse transverse correlation length κ following from equation (2.20) is defined by

$$\kappa^2 \equiv 2d[1/(\eta G) - 1]. \tag{2.22}$$

Its critical-point value $\kappa_c \equiv \sqrt{2d[1/\eta - 1]}$ measures the bulk anisotropy and varies between 0 for the isotropic model and ∞ for the classical Ising model. The inverse longitudinal correlation length κ_z is determined by $\kappa_z^2 \equiv 2d[1/G - 1]$ and it diverges at the critical point. In contrast to finite-D theories, where the longitudinal correlation length $\xi_{cz} \equiv 1/\kappa_z$ plays the major role in the scaling, here in the limit $D \to \infty$ it becomes only a slave variable, whereas all the physical quantities, except the longitudinal CF, are scaled with the transverse correlation length $\xi_{c,\perp} \equiv 1/\kappa$ [4, 6].

Numerical solution of the problem with the method described in this section above yields the results for $\theta_c(N)$ of the three-dimensional film with a simple cubic structure, which are shown in figure 1. One can see that for small transverse anisotropies, $\theta_c(N)$ approaches its bulk

limit much slower than the solution for the model with bulk anisotropy $\eta = 0$ (classical Ising model), which is shown by solid circles. Since in the latter case transverse spin components are switched off, the result coincides with that of the mean-field approximation [13]

$$\theta_c(N) = 1 - \frac{1}{d}\left(1 - \cos\frac{\pi}{N+1}\right) \cong 1 - \frac{1}{2d}\left(\frac{\pi}{N}\right)^2 \qquad (N \gg 1). \qquad (2.23)$$

As can be seen from figure 1, the suppression of the Curie temperature in films with a weak surface anisotropy may be quite pronounced, especially in comparison with the mean-field result shown by solid circles. Large T_c shifts in films have been observed in many experiments (see, e.g., [14]). For larger values of η'_s, the film orders above T_c^{bulk}. This is an indication that ordering at the surface occurs first and thus determines the Curie temperature of the film. The decrease of $\theta_c(N)$ with N in this region can be easily explained. For $N \to \infty$ both surfaces order independently at some $\theta_c(\infty)$. For finite N, the surfaces interact with each other across the film and thus help each other to order. The interaction between surfaces, and thus the corresponding increase of θ_c, should decay exponentially with the film thicknes N, the characteristic length being the bulk correlation length. One can see that for $\eta'_s = 1$ surfaces order at a temperature substantially higher than θ_c^{bulk}, where the bulk correlation length is rather short. With lowering η'_s, the bulk correlation length at θ_c increases, and the effect of the interaction of surfaces becomes more and more pronounced. The mechanism described above is considered in more detail in section 4.

The Curie temperatures of films consisting of one and two layers can be calculated analytically since there is no inhomogeneity of the gap parameter G_n. For the monolayer the result can be obtained by a straightforward renormalization of equation (2.21) and has the form $\theta_c^{-1} = [d/(d-1)]P_{d'}(\eta)$ (there is no difference between the models with bulk and surface anisotropies). For the bilayer, the surface-anisotropy model orders, evidently, at lower temperatures than the bulk-anisotropy one. For the latter, the expression for θ_c can be found in [4]. For the surface-anisotropy model, the result has the form

$$\theta_c^{-1} = \frac{1}{2}\left[\frac{d}{d'}P_{d'}(\eta_s) + P_{d'}\left(\frac{d'}{d}\eta_s\right)\right]. \qquad (2.24)$$

For $\eta_s = 0$ one has $P = 1$, and this formula yields $\theta_c = 2(d-1)/(2d-1)$, which becomes $\frac{4}{5}$ for $d = 3$ (see figure 1). For comparison, for the model with the bulk anisotropy $\eta = 1$, the mean-field formula (2.23) yields $\theta_c = (2d-1)/(2d)$ for $N = 2$. This becomes $\frac{5}{6}$ for $d = 3$ (see figure 1). An interesting feature of the solution for the surface-anisotropy model is that the Curie temperature of the bilayer becomes independent of the lattice structure in the Ising limit $\eta_s = 0$. The result obtained above depends on the lattice dimensionality d only and, e.g., it is the same for the simple cubic model ($d = 3$) and the three-dimensional continuous-dimension model ($d = 3.0$) [6]. In the Ising limit, the lattice structure comes into play for trilayers and thicker films, where the inhomogeneity of the gap parameter G_n becomes essential.

The thickness dependence of Curie-temperature shifts in films with small surface anisotropies are shown in figure 2 in the log scale. For $N \gg 1$ they can be represented by the formula

$$\theta_c^{-1}(N) \cong \theta_{c,\text{bulk}}^{-1} + \frac{3}{\pi N}\ln\frac{1}{c_3\kappa_s} \qquad \kappa_s \equiv \sqrt{2d'(1/\eta_s - 1)} \qquad (2.25)$$

with $\theta_{c,\text{bulk}}^{-1} \equiv P_3(1) = 1.516\,39$ and the fitting parameter $c_3 \approx 1.36$. This result, which is derived analytically in the next section, is simpler than that for the model with the bulk anisotropy [3,4]. The latter has the form ($\kappa_c N \ll 1$)

$$\theta_c^{-1}(N) \cong \theta_{c,\text{bulk}}^{-1} + \frac{3}{\pi N}\ln\frac{1}{a_3\kappa_c N} \qquad \kappa_c \equiv \sqrt{2d(1/\eta - 1)} \qquad (2.26)$$
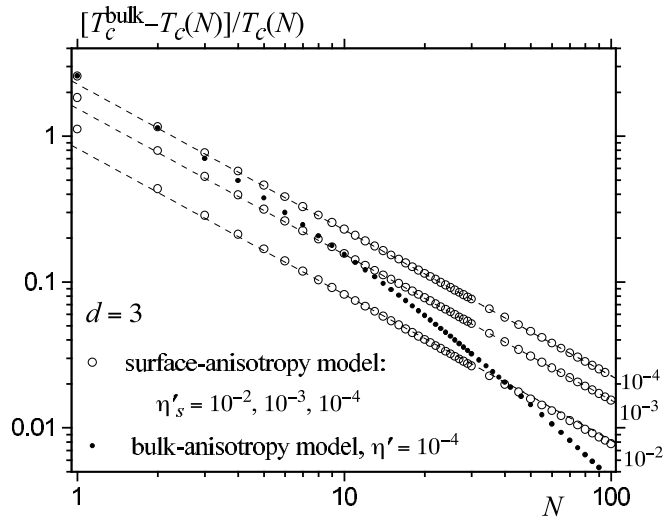
Figure 2. Curie-temperature shifts in simple cubic lattice films for small values of surface anisotropy. Dashed lines represent equation (2.25) with $c_3 = 1.36$.
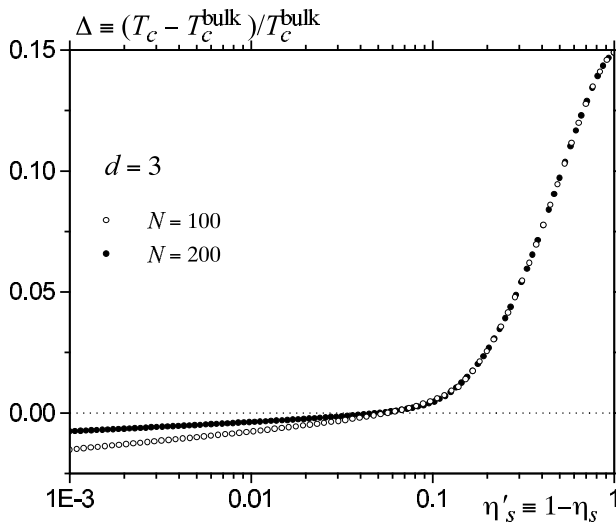

Figure 3. Curie temperature of ferromagnetic films with simple cubic structure versus surface anisotropy.

with $a_3 \approx 0.35$, and N under the logarithm makes the thickness dependence of θ_c shift substantially faster than $1/N$ (see figure 2). For $\kappa_c N \gtrsim 1$ the bulk-anisotropy model shows a crossover to the finite-size scaling regime described by equation (1.1) with $\lambda = 2$. No such crossover occurs for the model with surface anisotropy.

In figure 3 the Curie temperatures of 100- and 200-layer ferromagnetic films with simple cubic structure are shown as function of the surface anisotropy. The film Curie temperature becomes greater than the bulk one for $\eta'_s \gtrsim 0.05$. In this range it becomes independent of the film thickness, which is in accord with the surface character of the phase transition. Below the critical value of the surface anisotropy, the film Curie temperature falls below θ_c^{bulk}. One

can clearly see both the log dependence of the θ_c shift on the surface anisotropy and the $1/N$ dependence on the film thickness, as is given by equation (2.25). More careful analysis shows (see section 4) that the critical value of the surface anisotropy, which is defined from the condition $T_c(N, \eta'_{s,c}) = T_c^{\text{bulk}}$ tends to zero with the increase of the film thickness for $d \leqslant 3$. In three dimensions this dependence is logarithmic: $\eta'_{s,c}(N) \sim 1/\ln N$. This means that equation (2.25) is valid for sufficiently small anisotropy, $\eta'_s \ll \eta'_{s,c}(N)$, or, in other words, in the thickness range $N \exp(-1/\eta'_s) \lesssim 1$. For however small a value of η'_s, it will break down for very large N. Deviation of the numerically calculated points for $\eta'_s = 10^{-2}$ in figure 2 downwards from the straight line corresponding to equation (2.26) is a manifestation of this incipient breakdown.

3. Isotropic and weakly anisotropic films

To get an idea about ordering in films with small surface anisotropies in $d \leqslant 3$ dimensions, it is convenient to start with isotropic films. These films cannot order for any finite thickness, N, because they are systems of dimension $d' \leqslant 2$ and thus long-wavelength thermal fluctuations preclude ordering. On the other hand, it is physically clear that immediately below the bulk value of the Curie temperature the susceptibility of a thick film should become extremely high. This means that the lowest eigenvalue μ_1 in equation (2.13) becomes extremely close to zero. The contribution of this eigenvalue dominates in the the constraint relation (2.14), and this makes possible analytical calculation of μ_1. Since for the isotropic model there is no difference between longitudinal and transverse CFs, here we use more compact notations E_ρ and $\psi_{n\rho}$ (see equation (2.17)). First, equation (2.14) can be summed over all layers with the use of the orthogonality of wavefunctions $\sum_n \psi_{n\rho} \psi_{n\rho'} = \delta_{\rho\rho'}$, which yields

$$\sum_{\rho=1}^{N} \frac{2d'}{2d' + E_\rho} P_{d'} \left(\frac{2d'}{2d' + E_\rho} \right) = \frac{d'N}{d\theta}. \tag{3.1}$$

Next, one can subtract these equations for θ_c^{bulk} and θ from each other and separate the leading term with very small $E_1(\theta)$. This yields

$$P_{d'} \left(\frac{2d'}{2d' + E_1(\theta)} \right) - \Sigma_N \simeq \frac{d'N}{d} \left(\frac{1}{\theta} - \frac{1}{\theta_c^{\text{bulk}}} \right). \tag{3.2}$$

Since E_ρ with $\rho \leqslant 2$ are not expected to change so strongly as E_1 at the temperature interval $\theta_c^{\text{bulk}} - \theta$, the quantity Σ_N can be expected to be subdominant in comparison to other parts of equation (3.2).

For the simple cubic lattice, P_2 is the Green function of the square lattice which is given by $P_2(X) \cong (1/\pi) \ln[8/(1 - X)]$ for $X \cong 1$. Adopting this in equation (3.2) and exponentiating yields

$$E_1(\theta) \cong C_N(\theta) \exp \left[-\frac{2\pi N}{3} \left(\frac{1}{\theta} - \frac{1}{\theta_c^{\text{bulk}}} \right) \right] \tag{3.3}$$

where

$$C_N(\theta) = E_1(\theta_c^{\text{bulk}}) \prod_{\rho=2}^{N} \frac{E_\rho(\theta_c^{\text{bulk}})}{E_\rho(\theta)}. \tag{3.4}$$

Keeping high-lying eigenvalues with $\rho \sim N$ in the above formula is not justified, because $P_2(X)$ does not have its asymptotic form above in this case. On the other hand, the latter change negligibly for θ close to θ_c^{bulk} and thus the corresponding numerators and denominators in equation (3.4) cancel each other. The low-lying eigenvalues also cannot change significantly
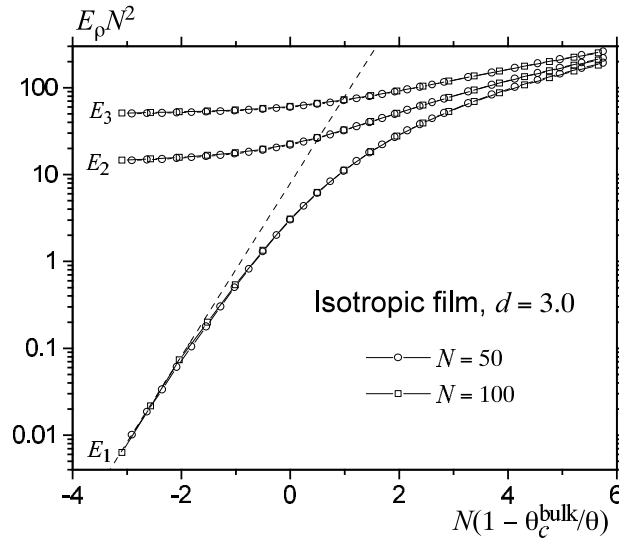
Figure 4. Temperature dependence of three lowest eigenvalues E_ρ for the isotropic film in $d = 3.0$ dimensions. Dashed lines represent equation (3.3) with $\pi \Rightarrow 2$ and $c_N = 8/N^2$.

in this temperature interval, thus the product in equation (3.4) should be of order unity. This leads to the order-of-magnitude estimation

$$C_N \sim E_1(\theta_c^{\text{bulk}}) \sim C/N^2 \tag{3.5}$$

which is sufficient for our purposes, since C_N will enter under the logarithm in the expression for the shift of the Curie temperature of the film. The second step in equation (3.5) can be justified as follows. For thick films at the bulk criticality, G_n is close to one in the main part of the film, excluding the regions near the surfaces. Thus, for estimation of the eigenvalues one can set $G_n = 1$ in the whole film, which amounts to the approximation $E_1(\theta_c^{\text{bulk}}) \sim E_1^{\text{MFA}}(\theta_c^{\text{bulk}})$. Solution of the Schrödinger equation (2.16) with the potential $V_n = 0$ yields eigenvalues

$$E_\rho^{\text{MFA}}(\theta_c^{\text{bulk}}) = 2(1 - \cos q_\rho) \qquad q_\rho \equiv \pi\rho/(N + 1) \tag{3.6}$$

(so that $E_1^{\text{MFA}}(\theta_c^{\text{bulk}}) \sim 1/N^2$ for $N \gg 1$) and eigenfunctions

$$\psi_{n\rho} = C_{N\rho} \sin(nq_\rho) \qquad C_{N\rho} \sim 1/\sqrt{N} \tag{3.7}$$

which describe a particle hopping in a rigid box.

The picture described above is confirmed by numerical calculations, the results of which are shown in figure 4. The latter were performed for the continuous-dimension model in $d = 3.0$. The dashed line in figure 4 represents equation (3.3), where the transition from the sc lattice to the $d = 3.0$ lattice is performed by the replacement $\pi \Rightarrow 2$, according to the general rule which can be found in [4, 6]. The constant C in equation (3.5) fits to 8 in $d = 3.0$ dimensions.

One can ask what the variation of the gap parameter G_n in the isotropic film below the bulk criticality looks like. The answer in the limit $\theta \ll 1$ follows from the observation that all spins become strongly correlated and thus all $\sigma_{nn'}$ become nearly the same for $q = 0$. Then, from equation (2.2), it immediately follows that $b_1 = b_N \cong \frac{1}{2}$ and $b_n \cong 1$ inside the film. This yields

$$G_n \cong \begin{cases} 2d/(2d - 1) & n = 1, N \\ 1 & n \neq 1, N \end{cases} \tag{3.8}$$
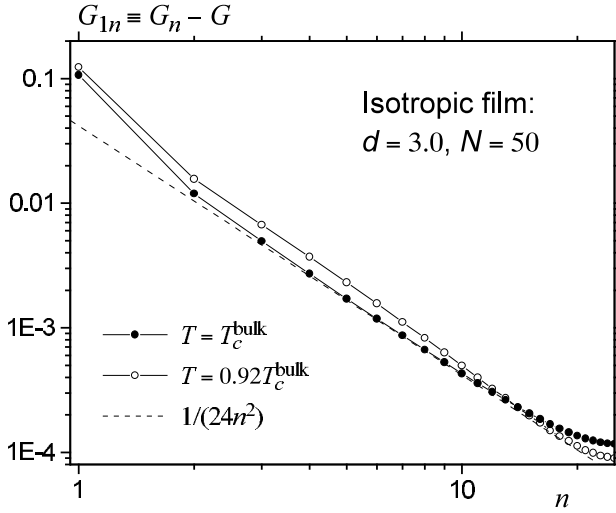
Figure 5. Gap parameter (energy–density) profile in the isotropic ferromagnetic film in $d = 3.0$ dimensions at and below the bulk criticality.

for $\theta \ll 1$. The corresponding zero-temperature eigenvalues can be calculated analytically and read

$$E_\rho(0) = 2(1 - \cos \bar{q}_\rho) \qquad \bar{q}_\rho = \pi(\rho - 1)/N. \tag{3.9}$$

These eigenvalues are all shifted downwards with respect to those of equation (3.6), and the lowest eigenvalue is exactly zero, in accord with equation (3.3). The eigenfunction of this eigenvalue is constant throughout the film: $\psi_{n,1} = 1/\sqrt{N}$. This is due to attraction of the particle to the potential wells at the boundaries of the box: $V_1 = V_N = -1$. Note that using equation (3.9) and equation (3.6) in equation (3.4) yields $C_N = O(1)$ at $\theta \ll 1$, in contrast to estimation (3.5) just below the bulk criticality.

Calculation of the variation of the gap parameter G_n in the film at $\theta < \theta_c^{\text{bulk}}$ is an analytically intractable nonlinear problem, and the result of equation (3.3) does not help much. Linearization at $\theta \ll 1$ shows that deviations of G_n from the zero-temperature result of equation (3.8) are linear in temperature. A compact analytical solution can only be obtained for the trilayer.

The deviation of the gap parameter from the bulk value, which is defined by $G_{1n} \equiv G_n - G$, is shown in figure 5 for the isotropic film in $d = 3.0$ dimensions, at and slightly below the bulk criticality (in both cases $G = 1$). This deviation is proportional to the nonuniform part of the energy density [6]. At the bulk criticality, G_n has the universal form

$$G_n \cong 1 + \frac{\frac{1}{4} - \mu^2}{2dn^2} \qquad \mu = \frac{d - 3}{2} \qquad 1 \ll n \lesssim N/4 \tag{3.10}$$

for $2 < d < 4$, as for the semi-infinite model [6, 10, 11]. This yields the large-distance form

$$V_n \cong -(\tfrac{1}{4} - \mu^2)/n^2 \qquad 1 \ll n \lesssim N/4 \tag{3.11}$$

for potential V_n in equation (2.16). Note that in [10, 11], the quantity $V(z) \cong -(G_n - 1) \cong 2dV_n$ was used. At $T = 0.92T_c^{\text{bulk}}$, the profile of G_{1n} looks rather indefinite: in the middle of the film the tendency to the zero-temperature solution of equation (3.8) is already seen, whereas closer to the boundaries G_{1n} still increases with lowering temperature. In the whole range of n, the relative deviation of G_{1n} from the bulk-criticality result is of order one. On the

other hand, at such temperature the argument of the exponential in equation (3.3) is already -10, thus E_1 is very small and futher lowering of the temperature leads to the instability of the numerical algorithm. Fortunately, the problem of finding the temperature variation of the gap-parameter profile in the film below the bulk Curie temperature becomes nonessential in the physically relevant three-dimensional case, because here the suppression of T_c of the film is not so strong (see below).

As we have see above, in isotropic films in $d \leqslant 3$ dimensions E_1 is very small in a wide range of temperatures but turns to zero only at $T = 0$. If there is a small anisotropy in the system, the basic equations for the transverse CF $\sigma_{nn'}$, equations (2.2) and (2.7), are slightly modified, and the variation of the gap parameter G_n in the film slightly changes. These changes can be found perturbatively, although it is not easy to do analytically. When G_n is inserted into the equation for the longitudinal CF $\sigma_{nn'}^{zz}$, perturbations of G_n perturb, in turn, E_1. Since $E_1(\theta)$ goes almost horizontally, a small anisotropy is sufficient to cause E_1 to cross the zero level at a transition temperature that is not small.

The first step, finding the perturbed variation of the gap parameter G_n, can be performed qualitatively in the following way. If surface and bulk anisotropies, $\eta_s' \equiv 1 - \eta_s$ and $\eta' \equiv 1 - \eta$, are small, one sets $q = 0$ in the last term of equation (2.10), since this term creates a gap in the transverse CF σ_{nn} and it should be essential at small wavevectors. After that, defining $G_n^{(0)}$ as the solution of the isotropic problem, one immediately finds that G_n adjusts so that $\tilde{b}_n$ retains its isotropic value, i.e.,

$$d/(\eta G_n) + (1 - \eta_s/\eta)d'(\delta_{n,1} + \delta_{nN}) = d/G_n^{(0)}. \tag{3.12}$$

This defines the correction to G_n due to anisotropy, which are positive. Now, proceeding to the longitudinal CF, one can write for the eigenvalue problem of equation (2.16) $V_n = V_n^{(0)} + V_n^{(1)}$, where

$$V_n^{(1)} = -2d(1 - \eta)/G_n^{(0)} - 2d'(\eta - \eta_s)(\delta_{n,1} + \delta_{nN}). \tag{3.13}$$

Numerical calculations show, however, that the surface part of this perturbation is somewhat oversimplified. It is not strictly localized in the boundary layer but redistributed over some region, decaying in three dimensions slightly faster than $1/n^3$, presumably as $1/(n^3 \ln n)$. This feature is nonessential for the determination of the T_c shift below; the difference of the result with respect to those obtained with the use of the simplified form of equation (3.13) will be absorbed into analytically unknown numerical factors.

The first-order corrections to E_ρ due to the diagonal perturbation $V_n^{(1)}$ have the form

$$E_\rho^{(1)} = \sum_{n=1}^{N} V_n^{(1)} \psi_{n\rho}^2 \tag{3.14}$$

as in the usual quantum-mechanical perturbation theory. In the temperature range of interest, slightly below the bulk criticality, the variation of the gap parameter G_n does not strongly differ from that at bulk criticality. Thus, estimation of $\psi_{n\rho}^2$ in equation (3.14) can be done at $T = T_c^{\mathrm{bulk}}$. Here, not too close to the surfaces and the middle of the film, one should consider the Schrödinger equation (2.16) with the potential V_n given by equation (3.11). The standing-wave solution of this equation for $n \gtrsim 1$ in the semi-infinite geometry can be expressed through the Bessel functions and labelled with the wavevector taking continuous values from the interval $(0, \infty)$ [6, 10, 11]. In the film this wavevector becomes quantized, and the normalized expression for $\psi_{n\rho}$ in the region $n \lesssim N/2$ reads

$$\psi_{n\rho} \sim (nq_\rho/N)^{1/2} J_\mu(nq_\rho) \qquad q_\rho \sim \pi\rho/N. \tag{3.15}$$

Thus for using $J_\mu(z) \sim z^\mu$, $z \ll 1$, one obtains

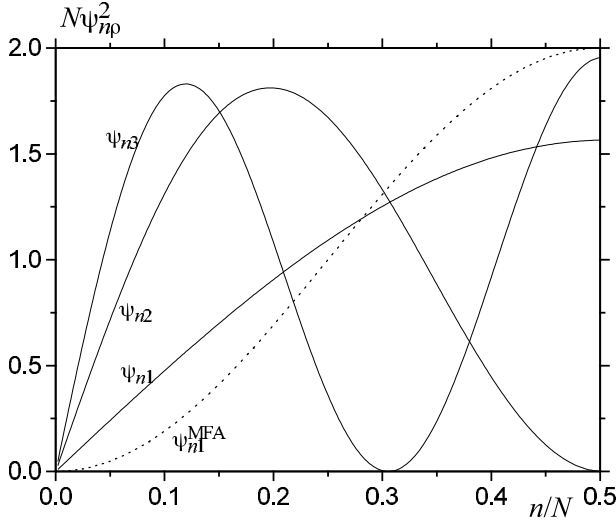$$\psi_{n,1}^2 \sim n^{1+2\mu}/N^{2(1+\mu)} \qquad \psi_{1,1}^2 \sim 1/N^{2(1+\mu)}. \tag{3.16}$$

Figure 6. Numerically calculated squares of normalized eigenvectors $\psi_{n\rho}$ for the isotropic film ($N = 500$) in $d = 3.0$ dimensions at bulk criticality. Linear behaviour at small n is in accord with equation (3.15). The mean-field result of equation (3.7) is shown by the dotted curve.

For comparison, the MFA solution of equation (3.7) yields $\psi_{11}^2 \sim 1/N^3$. Strong increase of the probability of finding the particle near the boundaries for $N \gg 1$ in our case, which is illustrated in figure 6, is due to the long-range attractive potential V_n. Note that at low temperatures, where G_n approaches its limiting form given by equation (3.8), this effect becomes even stronger: $\psi_{n,1}^2 \cong 1/N$. But there are no bound states near the surface in the isotropic model at any temperatures.

Now, from equation (3.14) one obtains for the surface- and bulk-anisotropy models

$$E_1^{(1,\text{surface})} \sim -\kappa_s^2/N^{2(1+\mu)} \qquad E_1^{(1,\text{bulk})} \cong -\kappa_c^2 \tag{3.17}$$

where in the bulk case $G_n^{(0)} \cong 1$ in the main part of the film and the normalization of eigenvectors $\psi_{n\rho}$ has been used. The Curie temperature of the film can be found from equation (2.18) in the form $E_1^{(0)} + E_1^{(1)} = 0$, where $E_1^{(0)}$ is given for $d = 3$ by equations (3.3) and (3.4). Explicitly, one has

$$\left\{ \begin{matrix} \kappa_s^2 \\ (\kappa_c N)^2 \end{matrix} \right\} \sim \exp\left[-\frac{2\pi N}{3} \left(\frac{1}{\theta_c} - \frac{1}{\theta_c^{\text{bulk}}} \right) \right] \tag{3.18}$$

for the surface- and bulk-anisotropy models, respectively. This results in equations (2.25) and (2.26), where the numbers c_3 and a_3 cannot be found analytically and should be fitted to the numerical solution. Remember that this analytical scheme for determination of θ_c works if the argument of the exponential above is large. The method evidently breaks down for the bulk-anisotropy model, if $\kappa_c N \gtrsim 1$. Here the result for θ_c crosses over to the finite-size scaling solution of equation (1.1) with $\lambda = 2$ and $A \sim 1/\kappa_c$ [3,4]. For the model with surface anisotropy, equation (3.18) also breaks down at sufficiently large N due to the surface phase transition, which will be considered in more detail in the next section.

For very small anisotropy, the film orders at the temperature $\theta_c \ll \theta_c^{\text{bulk}} \sim 1$, where $\psi_{n,1}^2 \cong 1/N$ and in equation (3.3) $C_N = O(1)$ (see the comment after equation (3.8)). This yields

$$\theta_c^{-1}(N) \cong \frac{3}{\pi N} \ln \frac{\sqrt{N}}{\kappa_s} \qquad \theta_c^{-1}(N) \cong \frac{3}{\pi N} \ln \frac{1}{\kappa_c} \tag{3.19}$$

for the surface- and bulk-anisotropy models, respectively, in accord with equations (1.3) and (1.2). It should be stressed that the applicability conditions for the formulae above are difficult to fulfil for thick films, $N \gg 1$. For the latter, the shift of the Curie temperature is typically small and equations (2.25) and (2.26) are relevant.

Let us consider now ferromagnetic films in dimensions lower than three. For the continuous-dimension model [6] the lattice Green function of layers, $P_{d'}$, is given by

$$P_{d'}(X) = \frac{d'}{\Lambda^{d'}} \int_0^\Lambda \frac{q^{d'-1} dq}{1 - X\lambda_q'} \qquad \lambda_q' \cong 1 - q^2/(2d'). \tag{3.20}$$

For X close to one this yields

$$P_{d'}(X) \cong \begin{cases} C_{d'}/\kappa_{d'}^{2-d'} & d' < 2 \\ W_{d'} + C_{d'}\kappa_{d'}^{d'-2} & d' > 2 \end{cases} \qquad \kappa_{d'} \equiv \sqrt{2d'(1/X - 1)} \ll 1 \tag{3.21}$$

where the Watson integral $W_{d'}$ and the coefficient $C_{d'}$ are given by

$$W_{d'} = \frac{(d')^2}{(d')^2 - 4} \qquad C_{d'} = \frac{d'}{\Lambda^{d'}} \frac{\pi d'}{\sin[(2 - d')\pi/2]}. \tag{3.22}$$

In three dimensions, the exact result is $P_{3.0'} = [1/(2X)] \ln[(1 + X)/(1 - X)]$. One should not mix up $P_{3.0'}$ (two continuous dimensions) with $P_{2.0}$ (one discrete dimension and one continuous dimension), etc.

For $d < 3$ the first term of equation (3.2) is of order $1/E_1^{(3-d)/2}$ and it dominates over Σ_N. The latter is determined by other low-lying eigenvalues which are of order $E_\rho \sim (\rho/N)^2$. Thus, $\Sigma_N \sim N^{3-d} C_{d'}$. This correction term is retained in the formulae in order to provide correct limiting transition $d \to 3$. Using equation (3.21) and equating E_1 to the anisotropic correction $E_1^{(1)}$ with the opposite sign, one obtains

$$\theta_c^{-1} \cong \theta_{c,\text{bulk}}^{-1} + \frac{dC_{d'}}{d'N} \left(\frac{1}{(-E_1^{(1)})^{(3-d)/2}} - \frac{\Sigma_N}{C_{d'}} \right). \tag{3.23}$$

Inserting here expressions for $E_1^{(1)}$ from equation (3.17) and using the value of μ from equation (3.10), one arrives at the final results

$$\theta_c^{-1} \cong \theta_{c,\text{bulk}}^{-1} + \frac{d'}{\Lambda^{d'}} \frac{\pi d}{\sin[(3 - d)\pi/2]} \frac{1 - (c_d \kappa_s)^{3-d} N^{(3-d)^2/2}}{(\bar{c}_d \kappa_s)^{3-d} N^{d-2+(3-d)^2/2}} \tag{3.24}$$

for the surface-anisotropy model and

$$\theta_c^{-1} \cong \theta_{c,\text{bulk}}^{-1} + \frac{d'}{\Lambda^{d'}} \frac{\pi d}{\sin[(3 - d)\pi/2]} \frac{1 - (a_d \kappa_c N)^{3-d}}{\kappa_c^{3-d} N} \tag{3.25}$$

for the bulk-anisotropy model. Here c_d, $\bar{c}_d$, and a_d are numbers that should be fitted to the numerical solution. One can check that for $d \to 3$ the formulae above go over to equations (2.25) and (2.26) (the additional factors $2/\pi$ in the latter are due to the difference between $d = 3.0$ and $d = 3$ models). Moreover, both equations (3.24) and (3.25) cross over to the single result $\theta_c^{-1} - \theta_{c,\text{bulk}}^{-1} \sim 1/N^{d-2}$ [4, 15] in dimensions above three, which is well defined in the isotropic limit.

4. Surface phase transition in films

The surface of a semi-infinite magnetic system orders at a temperature above the bulk Curie temperature if there is a bound surface state of the Schrödinger equation (2.16), which lies below the continuum of the delocalized (bulk) states, i.e., $E_1 < V_\infty$. In this case, with lowering temperature E_1 reaches the zero value before all other (bulk) eigenvalues, and it dominates the
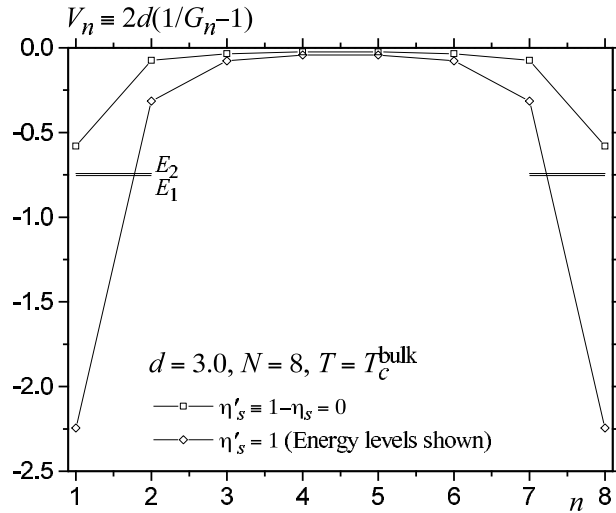
Figure 7. Numerically calculated effective potentials V_n for the isotropic film ($\eta'_s = 0$) and that with the extreme surface anisotropy, $\eta'_s = 1$, for $N = 8$ in $d = 3.0$ dimensions at the bulk criticality.

longitudinal susceptibility $\chi_{zn} = \sigma^{zz}_{nn}(q = 0)/\theta$ (see equation (2.17)) in the boundary region, where the eigenfunction ψ_{n1} is localized. An example of the surface bound states is shown in figure 7 for the $N = 8$ film in $d = 3.0$ dimensions at the bulk criticality. For the isotropic model, the potential wells near the surfaces are not strong enough to create a bound state. In contrast, for the extremely strong surface anisotropy the wells are deeper and there are bound states in each of the wells, which show a small tunnel splitting. Both models possess bulk states with $E_\rho > 0$, which are not shown. The surface-anisotropy dependence of several lowest energy levels for thick films at the bulk criticality is shown in figure 8. One can see that the energy levels $E_\rho > 0$ nearly scale with $1/N^2$, which is characteristic for the bulk. Negative energies correspond to the states localized near the surfaces, here $E_{1,2}$ are nearly degenerate and practically independent of N.

A natural question is how strong the surface anisotropy should be to create a potential well which can accomodate a bound state. The well known result in quantum mechanics (see, e.g., [16]) is that in one dimension a however small potential well creates a bound state with the energy quadratic in the volume of the well: $E \cong -\frac{1}{4}[\int_{-\infty}^{\infty} V(x)\,dx]^2$ for $\hbar = 1$ and $m = \frac{1}{2}$. If, however, the potential well is situated near a potential hump or near a rigid wall, localization of the particle costs additional potential or kinetic energy, respectively, and it requires that the well strength exceeds some critical value. In this case the result is

$$E \cong -A(P - P_c)^\zeta + \text{const} \tag{4.1}$$

where P is appropriately determined strength of the well and for *short-range* potential wells $\zeta = 2$. In the particular case of a rectangular well of depth V_0 and width a, which is sided by a rigid wall, one has $P = a\tilde{q}$, $\tilde{q} \equiv \sqrt{V_0}$, $P_c = \pi/2$, and $A = \pi^2/(2a)^2$. If the potential $V(x)$ has a long tail, the situation becomes more complicated, and the exponent ζ deviates from two, as we shall see below.

Calculation of the critical strength P_c in equation (4.1) for our problem (2.16) requires, in general, knowing the potential V_n in the whole range of n including the surface region, $n \sim 1$. Whereas at the bulk criticality the asymptotic form of V_n is given by equation (3.11), the values of V_n for $n \sim 1$ can only be determined numerically [6]. Nevertheless, it can be shown that the
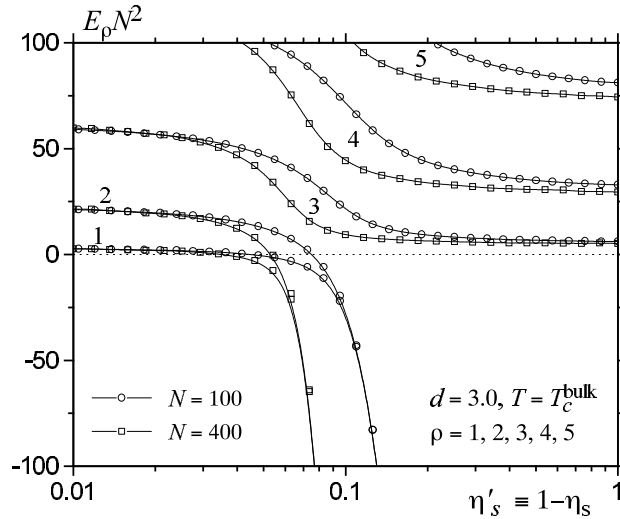
Figure 8. Surface-anisotropy dependence of the lowest energy levels of the potential V_n for $N = 100$ and $N = 400$ films at the bulk criticality.

isotropic semi-infinite model at the bulk criticality in $d \leqslant 3$ dimensions is in the critical state, $P = P_c$. A however small surface anisotropy η'_s makes the well deeper in the region $n \sim 1$ and it thus creates a surface bound state. As was argued above, this leads to the surface phase transition. This strong result follows from the form of the spin CF, which in the asymptotic region $n, n' \gg 1$ for $q \ll 1$ reads [6, 10, 11]

$$\sigma_{nn'}(q) = 2d\theta \begin{cases} \sqrt{nn'}I_\mu(qn)K_\mu(qn') & n \leqslant n' \\ \sqrt{nn'}I_\mu(qn')K_\mu(qn) & n' \leqslant n \end{cases} \tag{4.2}$$

with μ defined by equation (3.10). Far from the boundary, $qn, qn' \gg 1$, this CF reduces to its bulk value, $\sigma_{nn'}(q) = (d\theta/q)\exp(-q|n - n'|)$. In the region $n, n' \sim 1$ equation (4.2) is modified by nonsingular factors of order unity [6]. The spin CF above is proportional to the Green function which can be used to calculate perturbations of the solution of the problem (2.16), with $E = q^2$, due to small perturbations of the potential V_n. Such a perturbation theory, fails, however, in the bulk, since the bulk Green function above also diverges for $q \to 0$. A however small perturbation of V_n changes the wavefunctions with $E \to 0$ in a nonperturbative way, which leads to formation of bound states for attractive perturbations [16]. To analyse the semi-infinite problem, one can use

$$I_\mu(z) \cong \frac{1}{\Gamma(1 + \mu)} \left(\frac{z}{2}\right)^\mu [1 + O(z^2)] \qquad z \ll 1$$
$$K_\mu(z) = \frac{\pi}{2\sin(\pi\mu)}[I_{-\mu}(z) - I_\mu(z)] \tag{4.3}$$

for the modified Bessel and Macdonald functions. One can see that for $\mu \leqslant 0$ (i.e., $d \leqslant 3$) the Green function above diverges in the limit $q \to 0$ (for $d = 3$ logarithmically), whereas for $\mu > 0$ (i.e., $d > 3$) it remains finite in this limit. Thus, in $d > 3$ dimensions there should be a critical value of the surface anisotropy, $\eta_{s,c}$, above which there is a surface phase transition, whereas for $d \leqslant 3$ one has $\eta_{s,c} = 0$.

Different behaviour for $d > 3$ and $d < 3$ observed above is entirely due to the different forms of V_n for $n \sim 1$, whereas in the asymptotic region $n \gg 1$ the potential V_n given by equation (3.11) is the same below and above three dimensions. If one goes away from $d = 3$ in

both directions, the attractive tail of V_n weakens, but for $d < 3$ the depth of the well increases in the surface region, $n \sim 1$, (see figure 1(b) of [6]), so that the well always remains in the critical state. In the limit $d \to 2$ the attractive tail of V_n disappears, and the variation of the gap parameter G_n approaches equation (3.8), which corresponds to $V_1 = V_N = -1$, $V_n = 0$ ($n \neq 1, N$). It can be checked directly that a however small further decrease of the boundary value of this potential leads, for the semi-infinite problem, $N = \infty$, to the formation of a bound state. Determination of V_n for $n \sim 1$ is an analytically intractable nonlinear problem. Nevertheless, Bray and Moore [10, 11] could obtain the spin CF of equation (4.2), which has *different* forms for $d > 3$ and $d < 3$ and contains the relevant information, without explicitly analysing the region $n \sim 1$!

Now let us analyse how the energy of the surface bound state depends on the strength of the potential well if the latter slightly exceeds its critical value. For simplification, we will consider, instead of equation (2.16), a continuous Schrödinger equation $-\psi'' + V(x)\psi = E\psi$ with the potential $V(x)$ modelled as

$$V(x) = \begin{cases} \infty & x < 0 \\ -V_0 & 0 \leqslant x \leqslant a \\ -(\frac{1}{4} - \mu^2)/x^2 & x > a \end{cases} \tag{4.4}$$

(cf equation (3.11)). If we choose $a = \pi/2$, then for $d = 2$ the long tail of $V(x)$ disappears and $V_0 = 1$ becomes the critical depth of the potential well, as for the original discrete problem. In general, this method says nothing about the critical value of the surface anisotropy, but allows the determination of the exponent ζ in equation (4.1). The bound solution of the problem above, if it exists, has the form

$$\psi(x) = \begin{cases} C_1 \sin(\tilde{q}x) & 0 \leqslant x \leqslant a & (\tilde{q} \equiv \sqrt{E + V_0}) \\ C_2 \sqrt{\tilde{\kappa}x} K_\mu(\tilde{\kappa}x) & x > a & (\tilde{\kappa} \equiv \sqrt{-E}). \end{cases} \tag{4.5}$$

Here, for very small $|E|$, one can neglect E in $\tilde{q}$ and use the small-argument form of $K_\mu(z)$, which follows from equation (4.3). Then the boundary conditions at $x = a$ result in the equation determining $\tilde{\kappa}$:

$$\tilde{q}a \cot \tilde{q}a = \frac{1}{2} - |\mu| - \frac{2|\mu|(\tilde{\kappa}ar_\mu)^{2|\mu|}}{1 - (\tilde{\kappa}ar_\mu)^{2|\mu|}} \qquad r_\mu \equiv \frac{1}{2}\left[\frac{\Gamma(1-\mu)}{\Gamma(1+\mu)}\right]^{1/(2|\mu|)}. \tag{4.6}$$

Setting $\tilde{\kappa} = 0$ determines the critical value of the well strength P_c, say, its depth V_0. For P slightly above P_c, equation (4.6) can be represented in the form

$$B(P - P_c) \cong \frac{|\mu|(\tilde{\kappa}ar_\mu)^{2|\mu|}}{1 - (\tilde{\kappa}ar_\mu)^{2|\mu|}} \tag{4.7}$$

which yields

$$E = -\tilde{\kappa}^2 \cong -\frac{1}{(ar_\mu)^2}\left[\frac{B(P - P_c)}{|\mu| + B(P - P_c)}\right]^{1/|\mu|} \qquad \mu \equiv \frac{d-3}{2} \tag{4.8}$$

for the energy of the bound state. One can see that the 'classical' one-dimensional behaviour with the quadratic dependence of $|E|$ on $P - P_c$ is only realized for $d = 2$ and $d = 4$ where $|\mu| = \frac{1}{2}$ and the long tail of $V(x)$ in equation (4.4) disappears. For $d = 3$ equation (4.8) regularizes to the expression

$$E \cong -\left(\frac{2}{ae^\gamma}\right)^2 \exp\left[-\frac{1}{B(P - P_c)}\right] \qquad \gamma = 0.5772 \tag{4.9}$$

which resembles the well known result for the energy of the bound state in two dimensions [16]. Indeed, in two dimensions the radial part $\psi(r)$ of the wavefunction $\Psi(r, \phi) =$

$r^{-1/2}\psi(r)\exp(\pm im\phi)$, $m = 0, 1, 2, \ldots$ for the problem *without* potential energy satisfies the one-dimensional Schrödinger equation with the effective potential energy written in equation (4.4) for $x > a$, with $\mu \Rightarrow m$ (see, e.g., [17]). Now, returning to the original problem with the surface anisotropy, one can notice that the depth of the potential wells near the surfaces change linearly with η'_s, thus, one can replace $P - P_c$ by $\eta'_s - \eta'_{s,c}$ in equations (4.8) and (4.9), where $\eta'_{s,c} = 0$ for $d \leqslant 3$.

The temperature of the surface phase transition, θ_c, can now be determined using the results above. At θ_c, which is slightly above θ_c^{bulk}, the energy of the bound state equals zero, but the bulk level of the potential, V_∞, slightly exceeds zero. The value of θ_c can be found equating $|E|$, which is given by equation (4.8), to V_∞:

$$|E| = V_\infty \sim 1 - G \sim \kappa^2 \sim (\theta_c - \theta_c^{\text{bulk}})^{2\nu_b} \tag{4.10}$$

where $\nu_b = 1/(d - 2)$ is the critical index for the bulk correlation length for the $D = \infty$ model. This yields

$$\theta_c - \theta_c^{\text{bulk}} \simeq \left[\frac{B(\eta'_s - \eta'_{s,c})}{|\mu| + B(\eta'_s - \eta'_{s,c})} \right]^{1/\dot\Phi} \qquad \dot\Phi = \frac{|d - 3|}{d - 2}. \tag{4.11}$$

The critical index $\dot\Phi$ was calculated in [18] for the model with arbitrary number of spin components n in the second order in $\varepsilon = 4 - d$. In the limit $n \to \infty$ the result of [18] becomes $\dot\Phi = \frac{1}{2} - \varepsilon/4 - \varepsilon^2/8 + O(\varepsilon^3)$, which is in accord with equation (4.11). Note, however, that the ε expansion fails below three dimensions for the model with an infinite number of spin components, which is considered here.

In films, surface bound states cannot be rigorously separated from the bulk ones. If these bound states are very shallow, which is the case near the special transition ($\theta_c^{\text{surface}} = \theta_c^{\text{bulk}}$), the localization length of the bound states is very large and it exceeds the thickness of the film. Because of this finite-size effect, the critical value of the parameter which controls the surface phase transition (here the surface anisotropy) cannot be determined unambiguously. A natural choice is to define $\eta_{s,c}(N)$ from the condition $\theta_c(N, \eta'_{s,c}) = \theta_c^{\text{bulk}}$. The value of $\eta_{s,c}(N)$ can be found as the point of the intersection of the lowest eigenvalue $E_1(N, \eta'_s)$ with the zero level at the bulk criticality (see figure 8). For the model with symmetric surfaces, however, the second eigenvalue, E_2, also goes down, crosses the zero level at a somewhat larger value of η'_s and then very quickly becomes almost degenerate with E_1. The latter situation corresponds to the two bound states well localized on both surfaces, with a small tunnel splitting. Thus, crossing of $E_2(N, \eta'_s)$ with the zero level, as well as the degeneracy of E_1 with E_2, could also be used as a criterion for the formation of bound states and thus for the special transition. Another, probably better possibility is to consider the film with a surface anisotropy on only one of the two surfaces. Here there is no complication arising from the tunnelling between the bound states across the film; only the lowest eigenvalue E_1 goes over to the bound state, whereas E_2 always remains positive.

In films there is no singularity in the dependence of E_1 on the surface anisotropy, this dependence is linear near $E_1 = 0$. On the other hand, the singularity of $E_1(\eta'_s)$ studied above for the semi-infinite problem above mirrors in the dependence $\eta'_{s,c}(N)$. This dependence can be obtained if one uses a potential of the type of equation (4.4) for a film, sets $\tilde\kappa = 0$ and imposes the symmetry condition on the wavefunction in the middle of the film, $x = L/2$. This yields equation (4.7) with $P \Rightarrow P_c(L)$, $P_c \Rightarrow P_c(\infty)$ and $\tilde\kappa \Rightarrow 2/L$. In terms of the original variables, dropping numerical factors, one can write

$$\eta'_{s,c}(N) - \eta'_{s,c}(\infty) \sim \frac{2|\mu|N^{-2|\mu|}}{1 - N^{-2|\mu|}} \Rightarrow \frac{1}{\ln N} \qquad (d = 3). \tag{4.12}$$

This result, as well as the conjecture $\eta'_{s,c}(\infty) = 0$ for $d \leqslant 3$ made at the beginning of this section, are confirmed by numerical calculations, the results of which are shown in figure 9.
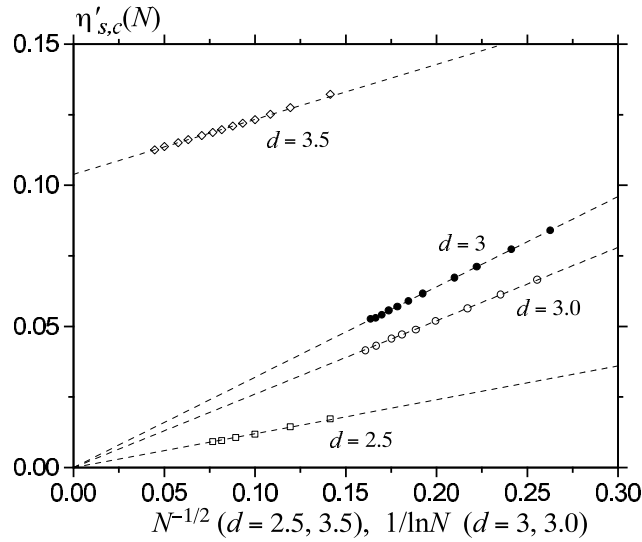
Figure 9. Critical surface anisotropy versus film thickness ($50 \leqslant N \leqslant 500$ for $d = 3$, 3.0, 3.5 and $50 \leqslant N \leqslant 170$ for $d = 2.5$) in different dimensions. The data correspond to the film with surface anisotropy on one of the two surfaces. The straight dashed lines are fits to the numerical data.

Positive values of $\eta'_{s,c}(N)$, even for $d \leqslant 3$, reflect the general tendency of the film to order at a temperature below the bulk Curie temperature. The latter is the case considered in the preceding section, and now it is clear that the applicability criterion for equations (2.25) and (3.24) is $\eta'_s \ll \eta'_{s,c}(N)$. For $d \leqslant 3$, equations (2.25) and (3.24) break down for however small surface anisotropy η'_s, if the film thickness N is large enough. One can see that in three dimensions $\eta'_{s,c}(N)$ decreases logarithmically slowly, thus equation (2.25) works in a wide range $N \lesssim \exp(1/\eta'_s)$ for small surface anisotropies. The applicability range of equation (3.24) shrinks quickly with the descease of the spatial dimension d.

5. Discussion

In this paper it has been shown that the finite-size scaling formula for the T_c shift in magnetic films, equation (1.1), which seems to be the only theoretical tool for interpretation of experiments (see, e.g., [14]), in fact, only describes one of several regimes. For the model with bulk anisotropy, the situation depends on the ratio of the film thickness N and the transverse correlation length $\xi_{c\perp}$, which is usually ignored as a noncritical variable. For $N\kappa_c \gtrsim 1$, where $\kappa_c \equiv 1/\xi_{c\perp}$ at criticality, a different regime described by equation (2.26) [3, 4] is realized instead of equation (1.1). For the model with surface anisotropy, which is present in many experimentally investigated films, equation (1.1) never appears. Instead, the T_c shift follows equation (2.25) in three dimensions for small enough surface anisotropy. If surface anisotropy exceeds the critical value, $\eta'_s > \eta'_{s,c}(N)$, equation (2.25) breaks down and the film orders via the surface phase transition above the bulk Curie temperature (see figure 1). A remarkable result is that $\eta'_{s,c}(N)$ goes to zero in the semi-infinite limit, $N \to \infty$, for $d \leqslant 3$ (see figure 9). That is, a however small surface anisotropy leads to the surface phase transition in the bulk-isotropic semi-infinite model. This is in contrast to the isotropic model with enhanced surface exchange, which does not show any surface phase transition for $d \leqslant 3$. In three dimensions, $\eta'_{s,c}(N) \sim 1/\ln N$, thus equation (2.25) is valid in a wide range of the film thicknesses:

$N \lesssim \exp(1/\eta'_s)$ for $\eta'_s \ll 1$.

One can question whether all these effects, which have been demonstrated above for the $D = \infty$ model, survive for the realistic classical Heisenberg model, $D = 3$. I expect that, in general, these effects should survive, because they are due to the nearly Goldstone modes in a weakly anisotropic magnetic system, and these Goldstone modes are inherent in all models with $D \geqslant 2$. On the other hand, the nonlinear coupling of fluctuations, which arises for a finite number of spin components D, suppresses fluctuations to some extent. This can already be seen from the fact that in the bulk $\theta_c \equiv T_c/T_c^{\mathrm{MFA}}$ monotonically decreases with D and reaches its minimum in the spherical limit $D = \infty$ (strongest fluctuations). For the semi-infinite problem, the surface susceptibility χ_{11} at the ordinary phase transition diverges for $d \leqslant 3$ (i.e., $\gamma_{11}^{\mathrm{ord}} > 0$ for $d < 3$), if $D = \infty$. For finite D, the second-order ε expansion (see, e.g., [18] and references therein, or, for a review, [19]) suggests that $\gamma_{11}^{\mathrm{ord}}$ remains positive at $d = 3$ (no divergence of the surface susceptibility) and probably changes sign at some critical dimension lower than three. Thus, fluctuations are somewhat suppressed, and the situation is a bit closer to the mean-field one ($d = 4$), in comparison to the limit $D = \infty$. This is an indication that in three dimensions a *finite* value of the surface anisotropy may be needed for the surface phase transition, in contrast to the zero value obtained in section 4. Computing this critical value of the surface anisotropy with the help of MC simulations or other methods, as well as searching for the regimes for the T_c shift in the films established above (or rather for their analogues for the Heisenberg model), seems to be an interesting problem.

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