Ordering in magnetic films with surface anisotropy

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

$$[T_{c, \text{bulk}} - T_c(N)]/T_{c, \text{bulk}} \approx A/N^\lambda.$$  \hfill (1.1)

For the exponent $\lambda$ the finite-size scaling theory \cite{1,2} yields $\lambda = 1/\nu_b$, where $\nu_b$ is critical index for the bulk correlation length. The above result has been derived with the Ising model, or the field model with 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 $d \leq 3$ in the isotropic limit at low temperatures, the film behaves as a system of dimensionality $d' = d - 1 \leq 2$ and cannot order because of long-wavelength fluctuations. This means that the amplitude $A$ in Eq. (1.1) should diverge in the isotropic limit. Moreover, even the functional form of Eq. (1.1) should change to reflect explicitly 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 $\eta J$ with $\eta \ll 1$, so that $\eta' \equiv 1 - \eta$ measures the anisotropy) it was shown in Refs.

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that Eq. (1.1) is only valid for rather thick films, \( N\kappa \gg 1 \), where \( \kappa \equiv 1/\xi_{c,\perp} = \sqrt{2d/(1-\eta)} \) 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 \( A \sim 1/\kappa \). In the range \( N\kappa \ll 1 \) a \( d' \)-dimensional behavior is realized, which is characterized by \( \lambda = 1 \) and \( A \sim \ln[1/(\kappa,N)] \) 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 a \( d' \)-dimensional monolayer with the exchange interaction \( NJ \), which yields

\[
T_c(d,J,\eta',N) \equiv T_c(d',NJ,\eta'/d',1). \tag{1.2}
\]

Although the results of Refs. \( \cite{3,4} \) 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 \( D \geq 2 \).

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, we will consider here 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 Refs. \( \cite{3,4} \). One can expect that the surface anisotropy stabilizes ordering in films with \( d \leq 3 \) 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 be \( \eta_{s}^{\text{eff}} \sim \eta_{s}/N \). The latter should result in a more pronounced suppression of \( T_c \) in magnetic films. This can be immediately seen in the case of extremely small surface anisotropy, where the analogue of Eq. (1.2) reads

\[
T_c(d,J,\eta_{s},N) \equiv T_c(d',NJ,\eta_{s}/N,1). \tag{1.3}
\]

A specific feature of the model with pure surface anisotropy is the absence of the 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 Eq. (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 Eq. (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., \( \eta_{s}^{\prime} = 1 \)), is \( T_c(1) = (d'/d)J_0/D \). For the simple cubic lattice one has \( W_3 = 1.51639 \), 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 \( T_c^{\text{bulk}} \) 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 3 the bulk Curie temperature is suppressed even stronger. For the continuous-dimension model introduced in Ref. \( \cite{3} \), one has \( W_{3,0} = 1.719324 \) and \( W_{2.5} = 2.527059 \). In two dimensions
and below, \( W_d \) diverges and thus \( T_{c,\text{bulk}} \) 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 \( \eta'_s \). Thus, for \( d \leq 2 \) the surface anisotropy is the only source of ordering. This situation is realized only in the limit \( D \to \infty \), however. 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 plays a major role already for \( d = 3 \). 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 \( T_{c,\text{bulk}} \) occurs for whatever small 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 Sec. 2, the closed system of equations describing the \( D \to \infty \) component spin-vector model in the symmetric phase is written down. In Sec. 3, the analytical calculation of the correction to \( T_c \) in films with a weak surface anisotropy is presented. In Sec. 4, the surface phase transition is considered. The results of numerical calculations are at appropriate places in sections above. In Sec. 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

\[
\mathcal{H} = -\frac{1}{2} \sum_{ij} J_{ij} \left( m_{z_i} m_{z_j} + \eta_{ij} \sum_{\alpha=2}^D m_{\alpha_i} m_{\alpha_j} \right), \quad |m_i| = 1, \tag{2.1}
\]

where dimensionless anisotropy factors satisfy \( \eta_{ij} \leq 1 \). This model was introduced, in the isotropic form, by Stanley, who showed that its partition function in the spatially homogeneous case in the limit \( D \to \infty \) coincides with that of the spherical model. There are, however, a number of essential differences between the exactly solvable limit \( D \to \infty \) of Eq. (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.

The system of equations describing the spatially inhomogeneous \( D \to \infty \) model both above and below \( T_c \) was obtained in Ref. [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 (\( \alpha \geq 2 \)) spin components, \( s_{ij} \equiv D(m_{\alpha_i} m_{\alpha_j}) \), and the spatially varying gap parameter, \( G_i \). (The definition of \( G_i \) can be found in Ref. [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 \( d \)th dimension. The equations can be easily generalized for the anisotropy factors taking the values \( \eta_{nn} \) within the \( n \)th layer and \( \eta_{n,n \pm 1} \) for the interaction between the \( n \)th and \( (n \pm 1) \)th layers. For the model with nearest-neighbor (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 \( n = 1, 2, ..., N \):  

\[
2 b_n \eta_{nn} \sigma_{nn'} - \eta_{n,n+1} \sigma_{n+1,n'} - \eta_{n,n-1} \sigma_{n-1,n'} = 2d \delta \delta_{nn'}, \tag{2.2}
\]

where \( b_n \) is given by

\[
b_n = d/(\eta_{nn} G_n) - d' \lambda_q', \tag{2.3}
\]
\( \lambda_q \) for the \( d \)-dimensional hypercubic lattice reads

\[
\lambda_q = \frac{1}{d'} \sum_{i=1}^{d'} \cos(q_i),
\]

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

\[
\theta \equiv \frac{T}{T_{\text{MFA}}(\infty)}, \quad T_{\text{MFA}}(\infty) = \frac{J_0}{D},
\]

where for hypercubic lattices \( J_0 = 2dJ \). The quantities \( \sigma_{0,n'} \) and \( \sigma_{N+1,n'} \) in the nonexistent layers, which enter equations (2.3) at the film boundaries \( n = 1 \) and \( n = N \), are set to

\[
\sigma_{0,n'} = \sigma_{N+1,n'} = 0
\]

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

\[
s_{nn} \equiv \int \frac{d^d q}{(2\pi)^d} \sigma_{nn}(q) = 1,
\]

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

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

\[
\eta_{11} = \eta_{NN} = \eta_s \leq 1, \quad \eta_{nn} = \eta_{n,n \pm 1} = \eta \leq 1 \quad (nn \neq 1, NN),
\]

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

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

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

\[
\tilde{b}_n = d/(\eta G_n) - d' \lambda_q' + (1 - \eta_s/\eta)d' \lambda_q'(\delta_{n,1} + \delta_{nN}).
\]

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

\[
\hat{B}\tilde{\sigma} = \text{diag}(2d\theta/\eta_{nn}), \quad B_{nn} = 2b_n, \quad B_{n,n \pm 1} = -\eta_{n,n \pm 1}/\eta_{nn},
\]

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 wave vector \( q \), is proportional to the unity matrix, the eigenvalues and eigenvectors of \( \hat{B} \) can be defined as

\[
\hat{B}\hat{U}_\rho = [\mu_\rho + 2d'(1 - \lambda_q')]\hat{U}_\rho, \quad \rho = 1, 2, \ldots, N,
\]

the eigenvectors \( \hat{U}_\rho \) being independent of \( q \). It should be noted that matrix \( \hat{B} \) is nonsymmetric, \( B_{n,n \pm 1} = -\eta_{n,n \pm 1}/\eta_{nn} \neq B_{n \pm 1,n} = -\eta_{n,n \pm 1}/\eta_{n,1,n \pm 1} \), if anisotropy factors \( \eta_{nn} \) change from one layer to the other. In this case its left eigenvectors \( \hat{W}_\rho^T \)
differ from its right eigenvectors $U_{\rho}$. The Green function $\sigma_{nn'}$ can be expanded over the set of eigenvectors of the problem as follows

$$\sigma_{nn'}(q) = \frac{2d\theta}{\eta_{n'n'}} \sum_{\rho=1}^{N} \frac{U_{\rho}W_{\rho'n'}}{\mu_{\rho} + 2d'(1 - \lambda_{q})},$$

(2.13)

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

$$s_{nn} = \frac{2d\theta}{\eta_{nn}} \sum_{\rho=1}^{N} \frac{U_{\rho}W_{\rho'n'}}{2d' + \mu_{\rho}} \frac{2d'}{2d' + \mu_{\rho}} = 1,$$

(2.14)

where $P_{\rho}(X)$ is the lattice Green function for the layer, which is defined similarly to the lattice Green function $P(X) \equiv P_{\rho}(X)$ below. Using this method with tabulated values of $P_{\rho}(X)$ 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 will be used here. The diagonalization formalism above will be 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 $\sigma^{zz}_{nn'}(q)$ from Eqs. (2.2) and (2.3), where all anisotropy factors $\eta_{n'n'}$ are replaced by 1. The Curie temperature of the film $\theta_c$ can now be found from the equation

$$[\sigma^{zz}_{nn}(q = 0)]^{-1} = 0.$$  

(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 \[0 \quad 1 \quad 0\]. If ordering of the film is driven by the surface, it is more convenient to use Eq. (2.15) for $n = 1$. This equation has, in general, $N$ roots, as we will see below. One should choose the maximal root for $\theta_c$, all other roots are unphysical. Below $\theta_c$, the spontaneous magnetization appears, and the very form of the equations change.

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

$$-\psi_{n-1} + 2\psi_n - \psi_{n+1} + V_n \psi_n = E \psi_n, \quad V_n = 2d(1/G_n - 1),$$

(2.16)

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

$$\sigma^{zz}_{nn'}(q) = 2d\theta \sum_{\rho=1}^{N} \frac{\psi_{\rho n'\rho}}{E_{\rho} + q^2}, \quad q \ll 1,$$

(2.17)

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

$$E_1(\theta_c) = 0,$$

(2.18)
where \( E_1 \) is the lowest of the eigenvalues \( E_\rho \). The \( N - 1 \) solutions corresponding to \( E_\rho = 0, \rho \geq 2 \), are unphysical. It should be noted that for the transverse correlation function the problem cannot, in general, be interpreted quantum mechanically, since the matrix \( B \) may be non-Hermitean, as is the case for the model with surface anisotropy. The eigenvalues of the transverse problem, \( \mu_\rho \), exceed the longitudinal eigenvalues \( E_\rho \); in the Ising limit \( \eta \ll 1 \) one has \( \mu_\rho \propto \frac{1}{\eta} \), whereas \( E_\rho \) become independent of \( \eta \).

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 Eq. (2.7). The physical reason for that is irrelevance of fluctuations of the single eigenvalues of the interaction is given by Eq. (2.4) with \( d' \Rightarrow d \) and \( q \Rightarrow k \). The solution \( G \) of Eq. (2.19) increases with lowering temperature \( \theta \); at \( G = 1 \) the gap in the longitudinal CF closes, longitudinal susceptibility diverges, and the phase transition occurs. This defines the bulk transition temperature \[ \theta_{c} = \frac{1}{P(\eta G) - 1} \] (2.21) that generalizes the well known result for the spherical model \( \theta_c = 1/P(1) \) [6]. The lattice Green function \( P(X) \) satisfies \( P(0) = 1 \) and has a singularity at \( X \rightarrow 1 \), the form of which in different dimensions can be found in Ref. [6]. For \( d \leq 2 \), 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 \( G \rightarrow 1 \). Below \( \theta_c \), the spontaneous magnetization appears, and \( G \) sticks to 1.

In Eq. (2.20) one has \( \lambda_k \equiv 1 - k^2/(2d) \) in the long-wavelength limit. Thus the inverse transverse correlation length \( \kappa \) following from Eq. (2.20) is defined by \[ \kappa^2 = \frac{2d[1/(\eta G) - 1]}{[1/(\eta G) - 1]} \] (2.22) Its critical-point value \( \kappa_c = \sqrt{2d[1/(\eta G) - 1]} \) measures the bulk anisotropy and varies between 0 for the isotropic model and \( \infty \) for the classical Ising model. The inverse longitudinal correlation length \( \kappa_\perp \) is determined by \( \kappa_\perp^2 = \frac{2d[1/(\eta G) - 1]}{[1/(\eta G) - 1]} \) and it diverges at the critical point. In contrast to finite-\( D \) theories, where the longitudinal correlation length \( \xi_\perp \equiv 1/\kappa_\perp \) plays the major role in the scaling, here in the limit \( D \rightarrow \infty \) it becomes only a slave variable, whereas all the physical quantities, except the longitudinal CF, are scaled with the transverse correlation length \( \xi_{\perp,\perp} \equiv 1/\kappa_\perp \).

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 Fig. [6]. One can see that for small transverse anisotropies, \( \theta_c(N) \) approaches its bulk limit much slowerly than the solution for the model with bulk anisotropy \( \eta = 0 \) (classical Ising model), which is shown by solid circles. Since in the
Fig. 1: Curie temperatures of the $N$-layer simple-cubic-lattice film for different values of surface anisotropy. 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).

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 Eq. (2.21) and has the form $\theta_c^{-1} = d/(d-1)|P_f(\eta)|$ (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 $\theta_c$ can be found in Ref. [1]. For the surface-anisotropy model, the
result has the form

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

For \( \eta_s = 0 \) one has \( P = 1 \), and this formula yields \( \theta_c = 2(d-1)/(2d-1) \), which becomes 4/5 for \( d = 3 \) (see Fig. 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 5/6 for \( d = 3 \) (see Fig. 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 (\( d = 3.0 \)). 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 Fig. 2 in the log scale. For \( N \gg 1 \) they can be represented by the formula

\[ \theta_c^{-1}(N) \equiv \theta_c^{-1}_{\text{bulk}} + \frac{3}{\pi N} \ln \frac{1}{c_3 \kappa_s}, \quad \kappa_s \equiv \sqrt{2d'(1/\eta_s - 1)}, \] (2.25)

with \( \theta_c^{-1}_{\text{bulk}} \equiv P_3(1) = 1.51639 \) and the fitting parameter \( c_3 \approx 1.36 \). This result, which will be derived analytically in the next section, is simpler than that for the model with the bulk anisotropy [3, 4]. The latter has the form (\( \kappa_c N \ll 1 \))

\[ \theta_c^{-1}(N) \equiv \theta_c^{-1}_{\text{bulk}} + \frac{3}{\pi N} \ln \frac{1}{a_3 \kappa_c N}, \quad \kappa_c \equiv \sqrt{2d(1/\eta - 1)}, \] (2.26)

with \( a_3 \approx 0.35 \), and \( N \) under the logarithm makes the thickness dependence of \( \theta_c \) shift substantially faster than \( 1/N \) (see Fig. 3). For \( \kappa_c N \gg 1 \) the bulk-anisotropy model shows a crossover to the finite-size-scaling regime described by Eq. (1.1) with \( \lambda = 2 \). No such a crossover occurs for the model with surface anisotropy.

In Fig. 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 $\theta_c^{\text{bulk}}$. One can clearly see both the log dependence of the $\theta_c$ shift on the surface anisotropy and the $1/N$ dependence on the film thickness, as is given by Eq. (2.25). More careful analysis shows (see Sec. 4.) that the critical value of the surface anisotropy, which is defined from the condition $T_c(N, \eta'_s) = T_c^{\text{bulk}}$ tends to zero with the increase of the film thickness for $d \leq 3$. In three dimensions this dependence is logarithmic: $\eta'_{s,c}(N) \sim 1/\ln N$. This means that Eq. (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 whatever small value of $\eta'_s$, it will break down for very large $N$. Deviation of the numerically calculated points for $\eta'_s = 10^{-2}$ in Fig. 2 downwards from the straight line corresponding to Eq. (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 $d \leq 3$ dimensions, it is convenient to start with isotropic films. These films cannot order for any finite thickness $N$ because they are systems of dimension $d' \leq 2$ 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 $\mu_1$ in Eq. (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 $\mu_1$. Since for the isotropic model there is no difference between longitudinal and transverse CFs, we will use here more compact notations $E_\rho$ and $\psi_{n\rho}$ [see Eq. (2.17)]. First, Eq. (2.14) can be summed over all layers with the
use of the orthogonality of wave functions $\sum_n \psi_{n\rho} \psi_{n\rho'} = \delta_{\rho\rho'}$, which yields
\begin{equation}
\sum_{\rho=1}^N \frac{2d'}{2d' + E_\rho} P_{d'} \left( \frac{2d'}{2d' + E_\rho} \right) = \frac{d' N}{d \theta}.
\end{equation}

Next, one can subtract these equations for $\theta_{\text{c bulk}}$ and $\theta$ from each other and separate the leading term with very small $E_1(\theta)$. This yields
\begin{equation}
P_{d'} \left( \frac{2d'}{2d' + E_1(\theta)} \right) - \Sigma_N \cong \frac{d' N}{d} \left( \frac{1}{\theta} - \frac{1}{\theta_{\text{c bulk}}} \right).
\end{equation}

Since $E_\rho$ with $\rho \leq 2$ are expected to change not so strongly as $E_1(\theta)$ at the temperature interval $\theta_{\text{c bulk}} - \theta$, the quantity $\Sigma_N$ can be expected to be subdominant in comparison to other parts of Eq. (3.2).

For the simple cubic lattice, $P_2$ is the Green function of the square lattice which is given by
\begin{equation}
P_2(X) \sim \left( \frac{1}{\pi} \right) \ln\left[ \frac{8}{1 - X} \right] \quad \text{for} \quad X \sim 1.
\end{equation}

Adopting this in Eq. (3.2) and exponentiating yields
\begin{equation}
E_1(\theta) \cong C_N(\theta) \exp \left[ -\frac{2\pi N}{3} \left( \frac{1}{\theta} - \frac{1}{\theta_{\text{c bulk}}} \right) \right],
\end{equation}
where
\begin{equation}
C_N(\theta) = E_1(\theta_{\text{c bulk}}) \prod_{\rho=2}^N \frac{E_\rho(\theta_{\text{c bulk}})}{E_\rho(\theta)}.
\end{equation}

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 $\theta$ close to $\theta_{\text{c bulk}}$ and thus the corresponding numerators and denominators in Eq. (3.4) cancel each other. The low-lying eigenvalues also cannot change significantly in this temperature interval, thus the product in Eq. (3.4) should be of order unity. This leads to the order-of-magnitude estimation
\begin{equation}
C_N \sim E_1(\theta_{\text{c bulk}}) \sim C/N^2,
\end{equation}
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 Eq. (3.5) can be justified as follows. For thick films at the bulk criticality, $G_n$ is close to 1 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 $E_1(\theta_{\text{c bulk}}) \sim E_1^{\text{MFA}}(\theta_{\text{c bulk}})$. Solution of the Schrödinger equation (2.16) with the potential $V_n = 0$ yields eigenvalues
\begin{equation}
E_\rho^{\text{MFA}}(\theta_{\text{c bulk}}) = 2(1 - \cos q_\rho), \quad q_\rho = \pi \rho/(N + 1).
\end{equation}

[so that $E_1^{\text{MFA}}(\theta_{\text{c bulk}}) \sim 1/N^2$ for $N \gg 1$] and eigenfunctions
\begin{equation}
\psi_{n\rho} = C_{N\rho} \sin(nq_\rho), \quad C_{N\rho} \sim 1/\sqrt{N},
\end{equation}
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 Fig. 4. The latter were performed for the continuous-dimension model in $d = 3.0$. The dashed line in Fig. 4 represents Eq. (3.3), where the transition from the sc lattice to the $d = 3.0$ lattice is done by the replacement $\pi \Rightarrow 2$, according to the general rule which can be found in Refs. [3, 4]. The constant $C$ in Eq. (3.3) fits to 8 in $d = 3.0$ dimensions.
Fig. 4: Temperature dependence of the three lowest eigenvalues $E_\rho$ for the isotropic film in $d = 3.0$ dimensions. Dashed lines represent Eq. (3.3) with $\pi \Rightarrow 2$ and $c_N = 8/N^2$.

One can ask how 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 Eq. (2.3) immediately follows that $b_1 = b_N = 1/2$ and $b_n \approx 1$ inside the film. This yields

$$G_n \approx \begin{cases} 
2d/(2d-1), & n = 1, N \\
1, & n \neq 1, N 
\end{cases} \quad (3.8)$$

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

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

These eigenvalues are all shifted downwards with respect to those of Eq. (3.6), and the lowest eigenvalue is exactly zero, in accord with Eq. (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 Eq. (3.9) and Eq. (3.6) in Eq. (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 Eq. (3.3) does not help much. Linearization at $\theta \ll 1$ shows that deviations of $G_n$ from the zero-temperature result of Eq. (3.8) are linear in temperature. A compact analytical solution can be only obtained for the triayer.

The deviation of the gap parameter from the bulk value, which is defined by $G_{1n} \equiv G_n - G$, is shown in Fig. 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

$$G_n \approx 1 + \frac{1 - \mu^2}{2dn^2}, \quad \mu = \frac{d - 3}{2}, \quad 1 \ll n \ll N/4, \quad (3.10)$$
for $2 < d < 4$, as for the semi-infinite model [10, 11]. This yields the large-distance form

$$V_n \approx -\left(1 - \mu^2\right)/n^2, \quad 1 \ll n \ll N/4,$$

(3.11)

for potential $V_n$ in Eq. (2.16). Note that in Refs. [10, 11], the quantity $V(z) \equiv -(G_n - 1) \approx 2dV_n$ was used. For models with finite number of spin components, the energy-density profiles in critical films were calculated with the help of the $\epsilon$ expansion [15, 16]. 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 Eq. (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 Eq. (3.3) is already $-10$, thus $E_1$ is very small and further 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 seen above, in isotropic films in $d \leq 3$ 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 $\sigma_{nn'}$, Eqs. (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 to 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 done 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 Eq. (2.10), since this term creates a gap in the transverse CF $\sigma_{nn}$ and it should be essential at small wave vectors. After that, defining $G_n^{(0)}$ as the solution of the isotropic problem, one immediately
Fig. 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 behavior at small $n$ is in accord with Eq. (3.15). The mean-field result of Eq. (3.7) is shown by the dotted line.

finds that $G_n$ adjusts so that $b_n$ retains its isotropic value, i.e.,

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

(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 Eq. (2.16)

$$V_n = V_n^{(0)} + V_n^{(1)},$$

where

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

(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 in 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 Eq. (3.13) will be absorbed into analytically unknown numerical factors.

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

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

(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 Eq. (3.14) can be done at $T = T_c^{\text{bulk}}$. Here not too close to the surfaces and to the middle of the film one should consider the Schrödinger equation (2.10) with the potential $V_n$ given by Eq. (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 labeled with the wave vector taking continuous values from the interval $(0, \infty)$ [10, 11, 13, 14]. In the
For comparison, the MFA solution of Eq. (3.7) yields
\[ \psi \text{ the surface in the isotropic model at any temperatures.} \]

Thus for using \( J_\mu(z) \sim z^\mu, \ z \ll 1 \), one obtains
\[ \psi_{n,1}^2 \sim n^{1+2\mu}/N^{2(1+\mu)}, \quad \psi_{1,1}^2 \sim 1/N^{2(1+\mu)}. \]  

For comparison, the MFA solution of Eq. (3.7) yields \( \psi_{1,1}^2 \sim 1/N^3 \). Strong increase of the probability of finding the particle near the boundaries for \( N \gg 1 \) in our case, which is illustrated in Fig. [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 Eq. (3.8), this effect becomes even stronger: \( \psi_{n,1}^2 \equiv 1/N \). But there are no bound states near the surface in the isotropic model at any temperatures.

Now, from Eq. (3.14) one obtains for the surface- and bulk-anisotropy models
\[ E_1^{(1,\text{surface})} \sim -\kappa_s^2/\mu, \quad E_1^{(1,\text{bulk})} \equiv -\kappa_c^2, \] where in the bulk case \( G_n(0) \equiv 1 \) 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 Eq. (2.18) in the form \( E_1^{(0)} + E_1^{(1)} = 0 \), where \( E_1^{(0)} \) is given for \( d = 3 \) by Eqs. (3.3) and (3.4). Explicitly, one has
\[ \begin{cases} \frac{\kappa_s^2}{(\kappa_c N)^2} \sim \exp \left[-\frac{2\pi N}{3} \left( \frac{1}{\theta_c} - \frac{1}{\theta_{c,\text{bulk}}} \right) \right] \end{cases} \]  

for the surface- and bulk-anisotropy models, respectively. This results in Eqs. (2.23) 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 \( \theta_c \) works if the argument of the exponential above is large. The method evidently breaks down for the bulk-anisotropy model, if \( \kappa_c N \gg 1 \). Here the result for \( \theta_c \) crosses over to the finite-size-scaling solution of Eq. (1.1) with \( \lambda = 2 \) and \( A \sim 1/\kappa_c \) (3.14). For the model with surface anisotropy, Eq. (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 \( \psi_{n,1}^2 \equiv 1/N \) and in Eq. (3.3) \( C_N = O(1) \) [see comment after Eq. (3.8)]. This yields
\[ \theta_c^{-1}(N) \equiv \frac{3}{\pi N} \ln \frac{\sqrt{N}}{\kappa_s}, \quad \theta_c^{-1}(N) \equiv \frac{3}{\pi N} \ln \frac{1}{\kappa_c} \]  

for the surface- and bulk-anisotropy models, respectively, in accord with Eqs. (1.3) and (1.2). It should be stressed that the applicability conditions for the formulae above are difficult to fulfill for thick films, \( N \gg 1 \). For the latter, the shift of the Curie temperature is typically small and Eqs. (2.23) and (2.26) are relevant.

Let us consider now ferromagnetic films in dimensions lower than three. For the continuous-dimension model [3] the lattice Green function of layers, \( P_d \), is given by
\[ P_d(X) = \frac{d'}{A_d} \int_0^A \frac{q^{d'-1} dq}{1 - X \lambda_q}, \quad \lambda_q' \equiv 1 - q^2/(2d'). \]

For \( X \) close to 1 this yields
\[ P_d(X) \equiv \begin{cases} C_d/\kappa_{d'}^2, & d' < 2 \\
W_d + C_d \kappa_{d'}^2, & d' > 2, \end{cases} \]

\[ \kappa_{d'} \equiv \sqrt{2d'(1/X - 1)} \ll 1, \]
where the Watson integral \( W_{d'} \) and the coefficient \( C_{d'} \) are given by

\[
W_{d'} = \frac{(d')^2}{(d')^2 - 4}, \quad C_{d'} = \frac{d'}{\Lambda^{d'}} \frac{\pi d'}{\sin((2 - d')\pi/2)}.
\]  

(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 Eq. (3.2) is of order \( 1/E_1^{(3-d)/2} \) and it dominates over \( \Sigma_N \). 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 will be retained in the formulae in order to provide correct limiting transition \( d \to 3 \). Using Eq. (3.22) and equating \( E_1 \) to the anisotropic correction \( E_1^{(1)} \) with the opposite sign, one obtains

\[
\theta_c^{-1} \approx \theta_{c,bulk}^{-1} + \frac{dC_{d'}}{dN} \left( \frac{1}{(-E_1^{(1)})^{(3-d)/2}} - \frac{\Sigma_N}{C_{d'}} \right).
\]  

(3.23)

Inserting here expressions for \( E_1^{(1)} \) from Eq. (3.17) and using the value of \( \mu \) from Eq. (3.10), one arrives at the final results

\[
\theta_c^{-1} \approx \theta_{c,bulk}^{-1} + \frac{d'}{\Lambda^{d'}} \frac{\pi d'}{\sin((3 - d')\pi/2)} \left(1 - (c_{dK_a})^{3-d} N^{(3-d)/2} \right) \]

(3.24)

for the surface-anisotropy model and

\[
\theta_c^{-1} \approx \theta_{c,bulk}^{-1} + \frac{d'}{\Lambda^{d'}} \frac{\pi d'}{\sin((3 - d')\pi/2)} \left(1 - (a_{dK_c} N)^{3-d} \right) \kappa_{c}^{3-d} N
\]  

(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 Eqs. (3.25) 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 Eqs. (3.24) and (3.25) cross over to the single result \( \theta_c^{-1} - \theta_{c,bulk}^{-1} \sim 1/N^{d-2} \) \([17, 4]\) in dimensions above 3, 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 longitudinal susceptibility \( \chi_{zn} = \sigma_{zn}^z(\mathbf{q} = 0)/\theta \) [see Eq. (2.17)] in the boundary region, where the eigenfunction \( \psi_{n1} \) is localized. An example of the surface bound states is shown in Fig. 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 Fig. 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 accommodate a bound state. The well known result in quantum mechanics (see, e.g., Ref. [18]) is that in one dimension a whatever small potential well creates a bound state with the energy quadratic in the volume of the well:

\[ E \sim -\frac{1}{4} \left[ \int_{-\infty}^{\infty} V(x) dx \right]^2 \]

for \( \hbar = 1 \) and \( m = 1/2 \). If, however, the potential well is situated near a potential hump or a 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

\[ E \sim -A(P - P_c)^\zeta + \text{const}, \tag{4.1} \]

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 \( P = aq, q = \sqrt{V_0}, P_c = \pi/2, \) and \( A = \pi^2/(2a)^2 \).

If the potential \( V(x) \) has a long tail, the situation becomes more complicated, and the exponent \( \zeta \) deviates from 2, as we shall see below.

Calculation of the critical strength \( P_c \) in Eq. (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 Eq. (3.11), the values of \( V_n \) for \( n \sim 1 \) can be only determined numerically [6]. Nevertheless, it can be shown that the isotropic semi-infinite model at the bulk criticality in \( d \leq 3 \) dimensions is in the critical state, \( P = P_c \). A whatever small surface anisotropy \( \eta'_s \) 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 [10, 11, 6]

\[
\sigma_{nn'}(q) = 2d\theta \left\{ \begin{array}{ll}
\sqrt{nn'}I_\mu(qn)K_{\mu}(qn'), & n \leq n' \\
\sqrt{nn'}I_\mu(qn')K_{\mu}(qn), & n' \leq n,
\end{array} \right.
\]

\[
\tag{4.2}
\]
with $\mu$ defined by Eq. (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 $n, n' \sim 1$ Eq. (4.2) is modified by nonsingular factors of order unity. 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 whatever small perturbation of $V_n$ changes the wave functions with $E \to 0$ in a nonperturbative way, which leads to formation of bound states for attractive perturbations. To analyze the semi-infinite problem, one can use

\[ I_\mu(z) \approx \frac{1}{\Gamma(1+\mu)} \left( \frac{z}{2} \right)^\mu [1 + O(z^2)], \quad z \ll 1 \]

\[ K_\mu(z) = \frac{\pi}{2\sin(\pi\mu)} [I_{-\mu}(z) - I_\mu(z)] \]

for the modified Bessel and MacDonald functions. One can see that for $\mu \leq 0$ (i.e., $d \leq 3$) 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 $d \leq 3$ one has $\eta_{s,c} = 0$.

Different behavior 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 Eq. (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 Fig. 1(b) of Ref. [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 Eq. (3.8), which corresponds to $V_1 = V_N = -1, V_n = 0$ ($n \neq 1, N$). It can be checked directly that a whatever 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 Eq. (4.2), which has different forms for \( d > 3 \) and \( d < 3 \) and contains the relevant information, without explicitly analyzing the region \( n \sim 1 \).

Now let us analyze 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 Eq. (2.16), a continuous Schrödinger equation

\[-\psi'' + V(x)\psi = E\psi \]

with the potential \( V(x) \) modelled as

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

[cf Eq. (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 tells nothing about the critical value of the surface anisotropy, but allows the determination of the exponent \( \zeta \) in Eq. (4.3). The bound solution of the problem above, if it exists, has the form

\[
\psi(x) = \begin{cases} 
C_1 \sin(q_\lambda x), & 0 \leq x \leq a \\
C_2 \sqrt{\kappa_\mu} K_\mu(\kappa_\mu x), & x > a 
\end{cases} \tag{4.5}
\]

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 Eq. (4.3). Then the boundary conditions at \( x = a \) result in the equation determining \( \kappa_\mu \):

\[
\tilde{q} a \cot \tilde{q} a = \frac{1}{2} - |\mu| - \frac{2|\mu|(\kappa_\mu)^{2|\mu|}}{1 - (\kappa_\mu)^{2|\mu|}}, \quad r_\mu = \frac{1}{2} \left[ \Gamma(1 - \mu) \Gamma(1 + \mu) \right]^{1/(2|\mu|)} \tag{4.6}
\]

Setting \( \kappa_\mu = 0 \) determines the critical value of the well strength \( P_c \), say, its depth \( V_0 \). For \( P \) slightly above \( P_c \), Eq. (4.4) can be represented in the form

\[
B(P - P_c) \approx \frac{|\mu|(\kappa_\mu)^{2|\mu|}}{1 - (\kappa_\mu)^{2|\mu|}} \tag{4.7}
\]

which yields

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

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

\[
E \approx -\left( \frac{2}{a_\gamma} \right)^2 \exp \left[ -\frac{1}{B(P - P_c)} \right], \quad \gamma = 0.5772 \tag{4.9}
\]

which resembles the well known result for the energy of the bound state in two dimensions [15]. Indeed, in two dimensions the radial part \( \psi(r) \) of the wave function \( \Psi(r, \phi) = r^{-1/2} \psi(r) \exp(\pm i m \phi) \), \( m = 0, 1, 2, \ldots \) for the problem without potential energy satisfies the one-dimensional Schrödinger equation with the effective potential energy written in Eq. (4.3) for \( x > a \), with \( \mu \Rightarrow m \) (see, e.g., Ref. [19]). 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 \( \eta_\mu \), thus one can replace in Eqs. (4.8) and (4.3) \( P - P_c \) by \( \eta_\mu - \eta_\mu^{(c)} \), where \( \eta_\mu^{(c)} = 0 \) for \( d \leq 3 \).
Fig. 9: Critical surface anisotropy vs film thickness (50 ≤ N ≤ 500 for d = 3, 3.0, 3.5 and 50 ≤ N ≤ 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.

The temperature of the surface phase transition, \( \theta_c \), can now be determined using the results above. At \( \theta_c \), which is slightly above \( \theta_{c, \text{bulk}} \), the energy of the bound state equals zero, but the bulk level of the potential, \( V_{\infty} \), slightly exceeds zero. The value of \( \theta_c \) can be found equating \( |E| \), which is given by Eq. (4.8), to \( V_{\infty} \):

\[
|E| = V_{\infty} \approx 1 - G \sim \kappa^2 \sim (\theta_c - \theta_{c, \text{bulk}})^{2\nu},
\]

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

\[
\theta_c - \theta_{c, \text{bulk}} \approx \left[ \frac{B(\eta_b' - \eta_{b,c})}{|\mu| + B(\eta_b' - \eta_{b,c})} \right]^{1/\Phi}, \quad \Phi = \frac{|d-3|}{d-2}.
\]

The critical index \( \Phi \) was calculated in Ref. [20] 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 Ref. [20] becomes \( \Phi = 1/2 - \varepsilon/4 - \varepsilon^2/8 + O(\varepsilon^3) \), which is in accord with Eq. (4.11).

Note, however, that the \( \varepsilon \) expansion fails below three dimensions for the model with 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 \( \eta_{b,c}(N) \) from the condition \( \theta_c(N, \eta_{b,c}) = \theta_{c, \text{bulk}} \). The value of \( \eta_{b,c}(N) \) can be found as the point of the intersection of the lowest eigenvalue \( E_1(N, \eta_b') \) with the zero level at the bulk criticality (see Fig. 8). For the model with symmetric surfaces, however, the second eigenvalue, \( E_2 \), also goes down, crosses the zero level at somewhat larger value of \( \eta_b' \) and then very fast 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. One more and 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 tunneling between the bound states across the film; only the lowest eigenvalue $E_1$ goes over to the bound state, whereas $E_2$ remains always 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 is the dependence $\eta'_c(N)$. This dependence can be obtained if one uses a potential of the type of Eq. (4.4) for a film, sets $\tilde{\kappa} = 0$ and imposes the symmetry condition on the wave function in the middle of the film, $x = L/2$. This yields Eq. (4.13) 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

$$\eta'_c(N) - \eta'_c(\infty) \sim \frac{2|\mu|N^{-2|\mu|}}{1 - N^{-2|\mu|}} \Rightarrow \frac{1}{\ln N} \quad (d = 3). \quad (4.12)$$

This result, as well as the conjecture $\eta'_c(\infty) = 0$ for $d \leq 3$ made at the beginning of this section, are confirmed by numerical calculations the results of which are shown in Fig. 9.

Positive values of $\eta'_c(N)$, even for $d \leq 3$, 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 Eqs. (2.22) and (2.24) is $\eta'_s \ll \eta'_c(N)$. For $d \leq 3$, Eqs. (2.22) and (2.24) break down for whatever small surface anisotropy $\eta'_s$, if the film thickness $N$ is large enough. One can see that in three dimensions $\eta'_c(N)$ decreases logarithmically slowly, thus Eq. (2.23) works in a wide range $N \lesssim \exp(1/\eta'_s)$ for small surface anisotropies. The applicability range of Eq. (3.24) shrinks fast with the decrease 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, Eq. (1.1), which seems to be the only theoretical tool for interpretation of experiments (see, e.g., Ref. 14), describes in fact only one of several regimes. For the model with bulk anisotropy, the situation depends on ratio of the film thickness $N$ and the transverse correlation length $\xi_{c\perp}$, which is usually ignored as a noncritical variable. For $N\kappa_c \geq 1$, where $\kappa_c \equiv 1/\xi_{c\perp}$ at criticality, a different regime described by Eq. (2.26) is realized instead of Eq. (1.1). For the model with surface anisotropy, which is present in many experimentally investigated films, Eq. (1.1) never appears. Instead, the $T_c$ shift follows Eq. (2.27) in three dimensions for the surface anisotropy small enough. If surface anisotropy exceeds the critical value, $\eta'_s > \eta'_c(N)$, Eq. (2.27) breaks down and the film orders via the surface phase transition above the bulk Curie temperature (see Fig. 1). A remarkable result is that $\eta'_c(N)$ goes to zero in the semi-infinite limit, $N \to \infty$, for $d \leq 3$ (see Fig. 1). That is, a whatever small surface anisotropy leads to the surface phase transition in the bulk-isotropic semi-infinite model. This contrasts the isotropic model with enhanced surface exchange, which does not show any surface phase transition for $d \leq 3$. In three dimensions, $\eta'_c(N) \sim 1/\ln N$, thus Eq. (2.23) 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 model with $D \geq 2$. On the other hand, the nonlinear coupling of fluctuations, which arises for finite number of spin components $D$, suppresses fluctuations to some extent. This can be already seen from the fact that in the bulk $\theta_c \equiv T_c/T_{c}^{\text{MFA}}$ monotonically decreases with $D$ and reaches its minimum in the spherical limit $D = \infty$ (strongest fluctuations). For the semi-infinite problem, the surface susceptibility $\chi_{11}$ at the ordinary phase transition diverges for $d \leq 3$ (i.e., $\gamma^{\text{ord}}_{11} > 0$ for $d < 3$), if $D = \infty$. For finite $D$ the second-order $\varepsilon$ expansion (see, e.g., Ref. [20] and references therein, or, for a review, Ref. [21]) suggests that $\gamma^{\text{ord}}_{11}$ remains positive at $d = 3$ (no divergence of the surface susceptibility) and probably changes sign at some critical dimension lower than 3. 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 Sec. 4. Computing this critical value of the surface anisotropy with the help of MC simulations or other methods, as well as search for the regimes for the $T_c$ shift in films established above (or rather for their analogues for the Heisenberg model), seems to be an interesting problem.

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