Rado–Weertman Boundary Equation Revisited in Terms of the Free-Energy Density of a Thin Film

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Historically, the first boundary conditions to be formulated and used in the theory of ferromagnetic thin films, the Rado–Weertman (RW) conditions, have a general advantage of being a simple differential equation, $2A_{\rm ex}\frac{\partial m}{\partial n} - K_{\rm surf}m = 0$. A key role in this equation is played by the phenomenological quantity $K_{\rm surf}$ known as the surface anisotropy energy density; $A_{\rm ex}$ denotes the exchange stiffness constant, and m is the amplitude of the transverse component of dynamic magnetization. In the present paper we use a microscopic theory to demonstrate that the surface anisotropy energy density of a thin film is directly related with its free-energy density, a fact not observed in the literature to date. Using two local free-energy densities $F^{\rm surf}$ and $F^{\rm bulk}$, defined separately on the surface and in the bulk, respectively, we prove that $K_{\rm surf} = d\left(F^{\rm surf} - F^{\rm bulk}\right)$, where d is the lattice constant. The above equation allows to determine the explicit configuration dependence of the surface anisotropy constant $K_{\rm surf}$ on the direction cosines of the magnetization vector for any system with a known formula for the free energy. On the basis of this general formula the physical boundary conditions to be fulfilled for a fundamental uniform mode and surface modes to occur in a thin film are formulated as simple relations between the surface and bulk free-energy densities that apply under conditions of occurrence of specific modes.

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The Rado–Weertman (RW) boundary equation is the earliest boundary condition to have been proposed in the theory of thin-film magnetism [1, 2] with the aim of taking into account the specific dynamics of motion of the surface magnetization, as distinct from that of the bulk magnetization. The RW equation is based on a continuum model of magnetization and in the circular approximation reads

$$2A_{\rm ex}\left(\frac{\partial m}{\partial n}\right)_{\rm surf} - K_{\rm surf}\left(\vartheta,\varphi\right)m_{\rm surf} = 0, \tag{1}$$

where m is the amplitude of the transversal (dynamic) component of the magnetization, $A_{\rm ex}$ is the exchange stiffness constant, n denotes the direction normal to the surface of the film, $K_{\rm surf}\left(\vartheta,\varphi\right)$ is the *surface anisotropy energy density*, and magnetization angles φ and ϑ are azimuth and polar angles, respectively. The RW Eq. (1) is mostly used for the description of two extreme situations, defined by the conditions:

$$\left(\frac{\partial m}{\partial n}\right)_{\rm surf} = 0, \text{ or } m_{\rm surf} = 0. \tag{2}$$

The first condition (2) implies zero surface anisotropy constant, $K_{\rm surf}\left(\vartheta,\varphi\right) \equiv 0$; this is considered to correspond to *completely unpinned* surface spins. The fulfillment of the other condition (2) requires that $|K_{\rm surf}\left(\vartheta,\varphi\right)| \to \infty$, and an infinite value of the surface anisotropy constant is considered to result in a situation in which surface spins are completely *pinned*.

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We will now show that the differential form of the RW equation written above is equivalent to the microscopic boundary equation derived within the surface inhomogeneity (SI) model; the latter is based on a discrete model of magnetization and has the form of difference equation [3, 4]:

$$A_{\rm surf}m_0 = m_{-d}, \tag{3}$$

where $m_0 \equiv m_{\rm surf}$ is the surface amplitude of the transversal (dynamic) magnetization component m, and m_{-d} is its analytical continuation *beyond* the surface, denoting the amplitude in the first fictitious layer parallel to the surface, separated from it by one lattice constant d. On putting

$$\left(\frac{\partial m}{\partial n}\right)_{\rm surf} \equiv \frac{1}{d}\left(m_{-d} - m_0\right); \quad m_0 \equiv m_{\rm surf}, \tag{4}$$

we can rewrite the differential Eq. (1) in the difference equation form

$$m_0\left[1 + \frac{K_{\rm surf}\left(\vartheta,\varphi\right)}{2A_{\rm ex}/d}\right] = m_{-d}, \tag{5}$$

equivalent to Eq. (3) with *the surface pinning parameter* $A_{\rm surf}$ given as

$$A_{\rm surf} = 1 + \frac{K_{\rm surf}\left(\vartheta,\varphi\right)}{2A_{\rm ex}/d}. \tag{6}$$

Note, on the other hand, that we have previously [3–5] expressed this surface parameter in the frame of the SI model by the following equation:

$$A_{\rm surf} = 1 - \frac{d}{2A_{\rm ex}/d}\left(\boldsymbol{K}_{\rm eff}^{\rm surf}\cdot\boldsymbol{M}\right), \tag{7}$$

where $\boldsymbol{K}_{\rm eff}^{\rm surf}$ means *the effective surface anisotropy field* acting additionally on surface spins, $\boldsymbol{M}$ is a sample magnetization, and d is a lattice constant.

By comparing (7) and (6) we find that the RW surface anisotropy constant is related with the effective surface anisotropy field by the equation

$$-K_{\rm surf}\left(\vartheta,\varphi\right)=d\left(\boldsymbol{K}_{\rm eff}^{\rm surf}\cdot\boldsymbol{M}\right). \tag{8}$$

However, we have defined the effective surface anisotropy field as the difference between the effective magnetic fields on the surface and in the bulk of a thin film: $\boldsymbol{K}_{\rm eff}^{\rm surf}\equiv\boldsymbol{H}_{\rm eff}^{\rm surf}-\boldsymbol{H}_{\rm eff}^{\rm bulk}$; considering this and the fact that the free-energy density is defined as $F=-\boldsymbol{M}\cdot\boldsymbol{H}_{\rm eff}$, we can rewrite the relation (8) as

$$K_{\rm surf}\left(\vartheta,\varphi\right)=d\left[F^{\rm surf}-F^{\rm bulk}\right], \tag{9}$$

where $F^{\rm bulk}$ and $F^{\rm surf}$ denote the bulk and surface free-energy densities, respectively. By the above-derived formula (9) the RW equation acquires a general character, becoming suitable for studying the configuration effects contained explicitly in the dependence $K_{\rm surf}\left(\vartheta,\varphi\right)$.

Thus, by Eq. (9) we have related the anisotropy constant $K_{\rm surf}\left(\vartheta,\varphi\right)$ figuring in the RW equation to the free energy of the system, a quantity we are generally able to determine for a studied thin film. Formula (9) allows to present *explicitly* the dependence of the surface anisotropy on the magnetization direction, i.e., on the spherical angles ϑ and φ, which is an extremely important information in the study of surface effects. Also, with Eq. (9) we easily get an insight into the physical sense of the RW boundary conditions described by Eq. (1). For example, by Eq. (9) the fulfillment of the first condition (2) $\left(\frac{\partial m}{\partial n}\right)_{\rm surf}=0$, implies $F^{\rm surf}=F^{\rm bulk}$, which corresponds to the particular situation that we have named the *natural pinning* ($A_{\rm surf}\equiv 1$, see Eq. (6)). In this situation surface spins only feel energetically the natural lack of that part of their neighbors of which they have been deprived by the formation of the surface, and do not experience at all the influence of the surface anisotropy field. This interpretation results from the way in which formula (7) is derived in the SI model: the breaking of the interaction between the surface spins and their eliminated neighbors is contained in the "unity" in Eq. (7), whereas all other surface perturbations are contained in the anisotropy field $K_{\rm eff}^{\rm surf}$. The natural pinning is a reference point with respect to which we consider other surface spin pinning situations. When $K_{\rm surf}\left(\vartheta,\varphi\right)>0$ (i.e. $A_{\rm surf}>1$), we say that surface spins are *unpinned*; when $K_{\rm surf}\left(\vartheta,\varphi\right)<0$ ($A_{\rm surf}<1$), the freedom of surface spins is constrained, and therefore we say they are *pinned*. The fulfillment of the second condition (2) corresponding to the *complete* pinning $m_{\rm surf}\equiv 0$, is, by Eq. (9), only possible when the surface free-energy density is much greater than the bulk free-energy density, $F^{\rm surf}\gg F^{\rm bulk}$.

Now, let us have a look at an example of expansion of the surface anisotropy energy density $K_{\rm surf}\left(\vartheta,\varphi\right)$ into a series of anisotropy components with the aid of Eq. (9), which we will apply to a cubic crystal.

The free energy of a sample is expressed as a series of terms related to different symmetries; usually the series is limited to low-order terms related to the cubic and uniaxial symmetries. In this equation the terms of the series are expressed by the coordinates n_x, n_y and n_z of the unit vector $\widehat{\boldsymbol{M}}\equiv\boldsymbol{M}/M$ oriented along the magnetization $\boldsymbol{M}$ of the sample $n_x=\cos\varphi\sin\vartheta$, $n_y=\sin\varphi\sin\vartheta$, and $n_z=\cos\vartheta$, where the angles φ and ϑ are measured with respect to the [100] and [001] axes, respectively [6, 7]. The equation reads

$$F(\widehat{\boldsymbol{M}})=F_0+K_{\rm c1}\left(n_x^2n_y^2+n_x^2n_z^2+n_y^2n_z^2\right)$$
$$-K_{[001]}n_z^2-K_{[100]}n_y^2, \tag{10}$$

where F_0 is an isotropic term expressed by an angle-independent constant. The cubic anisotropy is described by the term invariant under permutation of the coordinate indexes x, y and z: $K_{\rm c1}\left(n_x^2n_y^2+n_x^2n_z^2+n_y^2n_z^2\right)$, where $K_{\rm c1}$ is a first-order cubic energy density coefficient. Along with the cubic anisotropy different types of uniaxial anisotropy originating in lattice strains are described by the last two terms of Eq. (10). The term $-K_{[001]}n_z^2$ refers to the perpendicular-to-plane uniaxial anisotropy energy, while the term $-K_{[100]}n_y^2$ refers to the in-plane uniaxial anisotropy along the *main* crystal axes. Using Eqs. (9) and (10) we obtain

$$K_{\rm surf}\left(\vartheta,\varphi\right)=d\left(K_{\rm c1}^{\rm surf}-K_{\rm c1}^{\rm bulk}\right)\left(n_x^2n_y^2+n_x^2n_z^2+n_y^2n_z^2\right)$$
$$+d\left(K_{[001]}^{\rm bulk}-K_{[001]}^{\rm surf}\right)n_z^2+d\left(K_{[100]}^{\rm bulk}-K_{[100]}^{\rm surf}\right)n_y^2. \tag{11}$$

Considering that (n_x,n_y,n_z) are the direction cosines of the magnetization $\boldsymbol{M}$ with respect to the principal crystal axes, Eq. (11) reveals the angular configuration dependence of the pinning coefficient $K_{\rm surf}\left(\vartheta,\varphi\right)$ figuring in the Rado–Weertman equation. A major advantage of Eq. (9) we have derived above is that by using an expression for the free energy in this equation we will obtain full information on the angular configuration dependence of the surface pinning, as is demonstrated by Eq. (11). Note that this information was not provided directly by the initial boundary Eq. (1) alone since it contained the surface anisotropy energy density $K_{\rm surf}\left(\vartheta,\varphi\right)$ expressed by the unspecified effective surface anisotropy field $\boldsymbol{K}_{\rm eff}^{\rm surf}$. In this context it is particularly important to relate the surface pinning parameter of a material with the expression for its free energy. Note that the standard method for the description of ferromagnetic properties of thin films is always based on an appropriately constructed expression for the free energy of the sample. However, its boundary conditions are commonly formulated with the aid of a variously defined, depending on the context, quantity referred to as the surface anisotropy, by no means related to the basic characteristic of the bulk material, which is its free energy.

In the present study we have managed to fill this conceptual gap by finding a relatively simple bridge connecting the surface free energy with the surface boundary, or pinning, conditions.

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