

Interactions of an atomic force microscope tip with a reversed ferroelectric domain

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A theory of interactions between an atomic force microscope (AFM) tip and a ferroelectric domain that forms under its electric field is proposed. We show that even for low potentials these interactions are dominant compared to the van der Waals forces and the electrostatic forces, within a certain distance interval. This interval expands, almost linearly, with the applied voltage. Dependence of the critical voltage required for domain formation as a function of the tip-ferroelectric surface distance is defined. This interaction force drops abruptly with removal of the tip from the ferroelectric surface, increases with the applied voltage and the tip apex radius, and depends logarithmically weak on the tip cone length.

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Since the pioneering work of Saurebach and Terris,¹ the atomic force microscope (AFM) was widely used for fabrication and studying domain structures in ferroelectrics (FE) (see, e.g., Refs. 2–12, and references therein). FE domain structures, tailored by AFM in both low^{1–9} and high voltage^{10,11} regimes, have paved the way for advanced photonic and microelectronic devices. At small distances (≤ 0.5 nm), the major contribution to interaction forces between the tip and the surface is made by covalent forces, attributed to valence orbital overlapping of the tip and the surface constituent atoms in the region of contact.¹³ When the tip-sample distance extends beyond 0.5 nm, the interatomic connections are detached and the van der Waals forces take the major role, as long as the applied potential is sufficiently low. Van der Waals forces weaken much faster than the electrostatic forces when the tip is detracted from the sample surface. Thus at distances larger than half of the apex radius, the electrostatic force, which is due to the contact potential between the tip and the surface and exist even without external applied potential, exceeds the van der Waals forces.^{14,15} The electrostatic forces strongly increase with the applied potential. When a tip is placed in the vicinity of a FE, the electric fields emerging from the surface of the FE domains can considerably contribute to the force, as long as screening charges do not compensate the field.^{3,16} These considerations do not take into account the possibility of the FE domain structure to deform in the electric field of the AFM tip. However, experiments show that strong fields of the AFM tip are capable of forming new domains under the tip.^{4–11} Hereafter, such domains are referred to as “self-domains.” The interaction of a tip with a self-domain resembles to interaction of an electron with a polarizable lattice, which results in formation of polarons. An electron polarizes the surrounding crystal lattice and is attracted by the field of polarization, creating a polaron—a bound state of an electron and a polarized lattice.¹⁷ Similarly, a tip is attracted to the domain which created.

For simplicity we assume that the tip is located in vacuum. The tip is not in contact with the sample, so it does not assert any mechanical pressure on it. We also neglect the weak piezoelectric deformation of the ferroelectric surface. This satisfies the weak indentation situation, according to the

terminology proposed by Kalinin and Bonnell.¹⁸ To develop the theory of tip and self-domain interaction, we first find the free energy of the self-domain as a function of the tip-surface distance. The total domain energy W consists of the depolarization field energy W_D , the energy of the domain wall W_S , and the interaction energy W_T between the electric field of the tip with local changes of spontaneous polarization in the domain volume. Following Landauer¹⁹ we assume that the domain has a half-ellipsoid shape elongated in the polar direction, where the initial orientation of the spontaneous polarization vector P_S is perpendicular to the sample surface. The main axis of the half-ellipsoid domain is along the polar axis and the base area is in the surface plane, see Fig. 1.

Landauer¹⁹ has obtained the expression for the depolarization field energy of an elongated half-ellipsoidal domain:

$$W_D(r, l) = \frac{16\pi^2 P_s^2}{3\epsilon_c} r^2 l (\eta^2 - 1) \left[\frac{1}{2} \eta \ln \left(\frac{\eta + 1}{\eta - 1} \right) - 1 \right], \quad (1)$$

where $\eta = 1 / \sqrt{1 - (\epsilon_c / \epsilon_a)(r^2 / l^2)}$. r and l are the base radius and the length of the half-ellipsoid, respectively and ϵ_c and ϵ_a are the dielectric constants in directions parallel and perpendicular to the polar axis, respectively.

The half-ellipsoidal shape of the domain surface can be considered as a continuous set of planes with different orientations. Since the domain wall surface energy density σ_w depends on the wall orientation, its value will vary with the local coordinates on the domain wall. Such dependence is unknown for the considered lithium niobate domains. Hence we conduct our calculations in the framework of Landauer's¹⁹ model, which employs a single intermediate value for the domain wall surface energy density σ_w . Accordingly, the energy of the domain wall is

$$W_S(r, l) = \sigma_w S(r, l) \quad (2)$$

and $S(r, l)$ is the surface area of the elongated half-ellipsoid

$$S(r, l) = \pi r \left(r + \frac{l}{\sqrt{1 - \frac{r^2}{l^2}}} \arcsin \sqrt{1 - \frac{r^2}{l^2}} \right).$$

The tip will be considered as a truncated vertical cone with a spherical apex.^{14,15} Let us determine the contribution of charges located on the tip apex, to the domain energy. For this matter, we shall use the spherical model in which a field of a tip apex is supposed to coincide with a field of a metallic sphere of radius R , which is the curvature radius of the tip apex. We will use a somewhat general model,¹⁸ proposed by Kalinin and Bonnell. This model takes into account charge distribution in the apex of the tip, which is located near an anisotropic dielectric. The charge $q_0=RU$ is generated in the center of curvature of the tip apex under applied voltage U . In addition, infinite series of image charges q_n is located at a distance r_n from the center of the sphere:

$$q_{n+1} = RU \left(\frac{\sqrt{\varepsilon_c \varepsilon_a} - 1}{\sqrt{\varepsilon_c \varepsilon_a} + 1} \right)^n \frac{\sinh \alpha}{\sinh(n+1)\alpha},$$

$$r_{n+1} = R^2/[2(R + \delta) - r_n], \quad r_0 = 0, \quad (3)$$

where δ is the distance between the tip apex and the sample surface, α is defined by $\cosh \alpha = s/R$, and $s=R+\delta$ is the distance between the center of curvature of the tip apex and the sample surface.

The interaction energy W_{Tn} of the charges q_n with the local change of the spontaneous polarization inside the domain is²⁰

$$W_{Tn}^{\text{apex}}(r, l) = - \frac{8\pi q_n P_s}{(\sqrt{\varepsilon_c \varepsilon_a} + 1)\gamma} \left[l - \frac{s_n + \frac{l}{\gamma} - \sqrt{s_n^2 + r^2}}{\gamma \left(\frac{1}{\gamma^2} - \frac{r^2}{l^2} \right)} + \frac{\frac{s_n r^2}{l^2}}{\left(\frac{1}{\gamma^2} - \frac{r^2}{l^2} \right)^{3/2}} \ln \frac{\sqrt{\frac{1}{\gamma^2} - \frac{r^2}{l^2}} \left(s_n + \frac{l}{\gamma} \right) + l \left(\frac{1}{\gamma^2} - \frac{r^2}{l^2} \right) + \frac{s_n}{\gamma}}{\sqrt{\left(\frac{1}{\gamma^2} - \frac{r^2}{l^2} \right) (r^2 + l^2) + \frac{s_n}{\gamma}}} \right],$$

where $s_n = R + \delta - r_n$ is the distance between the charge q_n and the sample surface and $\gamma = \sqrt{\varepsilon_c / \varepsilon_a}$. The total interaction energy of charges on the tip apex with the domain is

$$W_T^{\text{apex}}(r, l) = \sum_{n=0}^{\infty} W_{Tn}^{\text{apex}}(r, l). \quad (4)$$

Sum (4) is made over all charges (3), concentrated in the tip apex.

As shown by Hudlet *et al.*^{14,15} and Belaidi *et al.*,²¹ the electric field in the vicinity of the tip apex is well described by the spherical model. However, at distances δ larger than $R/2$, the cone makes a noticeable contribution to domain energy. For this matter, we shall use the linear model proposed by Hao *et al.*²² According to Ref. 22, the electric field of the cone is approximated by an electric field of a line segment, having a linear charge density $\lambda = U/\beta$, where $\beta = \ln[(1 + \cos \theta)/(1 - \cos \theta)]$ and θ is the half-angle of the cone.

The interaction energy of the cone with the domain was calculated in Ref. 23:

$$W_T^{\text{cone}}(r, l) = - \frac{8\pi P_s \lambda}{(\sqrt{\varepsilon_c \varepsilon_a} + 1)} \int_0^r \ln \left(\frac{[s + L + \sqrt{\rho^2 + (s+L)^2}] \left[s + \frac{z_m(\rho)}{\gamma} + \sqrt{\rho^2 + \left(s + \frac{z_m(\rho)}{\gamma} \right)^2} \right]}{[s + \sqrt{\rho^2 + s^2}] \left[s + L + \frac{z_m(\rho)}{\gamma} + \sqrt{\rho^2 + \left(s + L + \frac{z_m(\rho)}{\gamma} \right)^2} \right]} \right) \rho d\rho, \quad (5)$$

where ρ and z are cylindrical coordinates and $z_m(\rho) = l\sqrt{1 - \rho^2/r^2}$ is the distance between the FE surface and the ellipsoidal face of the domain at point ρ . The complete energy of the domain is determined by sum of energies (1), (2), (4), and (5)

$$W_{\text{dom}}(r, l) = W_S(r, l) + W_D(r, l) + W_T^{\text{apex}}(r, l) + W_T^{\text{cone}}(r, l). \quad (6)$$

Domain energy (6) includes positive (W_D, W_S) and negative ($W_T^{\text{apex}}, W_T^{\text{cone}}$) terms. The formed domain is stable if its total energy is negative. This suggests the existence of a minimal threshold potential U_{th} , necessary for domain formation. Experiments confirm this conclusion. Threshold for domain formation in barium titanate and triglycine sulfate single crystals was measured by Abplanalp⁹ and Hong *et al.*²⁴ Calculations of this threshold were conducted in Refs. 9 and 23. However, it was assumed that the tip is in direct contact with the surface.

The field of the tip strongly decreases with removal of the tip from the surface. Therefore, it is expected that U_{th} will increase when increasing the distance. All further calculations will be performed for lithium niobate, for which $P_s = 75 \mu\text{C}/\text{cm}^2$, $\varepsilon_c = 34$, $\varepsilon_a = 80$. Since the domain wall surface energy density is unknown for lithium niobate we will use $\sigma_w = 15 \text{ mJ}/\text{m}^2$ which is in the range of measured $\sigma_w = 10 - 35 \text{ mJ}/\text{m}^2$ for lithium tantalite, which has similar ferroelectric properties.²⁵ Calculation results of the threshold distance for domain formation δ_{th} as a function of the applied voltage are brought in Fig. 2. It can be seen that the threshold distance δ_{th} , at which the domain formation is possible, increases with U and R . Obviously, the interaction force F_{dom} has a meaning only if the tip-surface distance is $\delta \leq \delta_{\text{th}}$.

Energies W_T^{apex} and W_T^{cone} depend directly on the distance δ . The domain equilibrium sizes r_m and l_m , which correspond to a minimum of functional (6), depend on δ as a parameter.

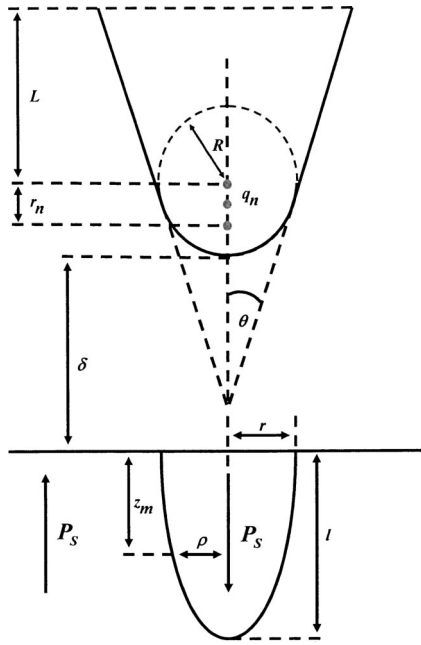


FIG. 1. Schematics of the used model.

Therefore W_S and W_D also depend on δ through the equilibrium domain sizes. Hence, all the terms in the domain energy depend, directly or indirectly, on δ , so when deriving the interaction force

$$F_{\text{dom}}(\delta) = -\partial W_{\text{dom}}/\partial \delta \quad (7)$$

it is necessary to take into account the entire domain energy (6).

We have calculated forces of a tip interaction with a self-domain for different values of R , L , θ , and U . The full energy functional of the domain (6) was minimized for fixed values of δ , R , L , θ , and U . This allowed obtaining $W_{\text{dom}}(\delta)$ as a function of the distance δ . Equation (7) defines the tip-self domain interaction force.

The force F_{dom} depends on cone length L very weakly. Curves of the forces $F_{\text{dom}}(\delta)$ for different cone lengths $L = 5 \mu\text{m}$ and $10 \mu\text{m}$, where $U = 50 \text{ V}$ and $R = 50 \text{ nm}$, practically coincide. For reasonable values of $\theta = 10^\circ - 15^\circ$, the force magnitude F_{dom} weakly depends on the cone half-angle. Therefore all further calculations were conducted under fixed values of $L = 10 \mu\text{m}$ and $\theta = 12^\circ$. Figure 3 shows $F_{\text{dom}}(\delta)$. It is seen that the force F_{dom} sharply drops with increase of the distance and increases with the applied voltage U and the apex radius R . The characteristic decay distance of the force is about the apex radius R . As the force F_{dom} strengthens with the applied potential, it would be particularly strong under conditions of the so-called ‘‘domain breakdown’’ phenomenon, recently observed by Rosenman *et al.*^{10,11}—formation of elongated stringlike domains, under large applied potentials, superficially similar to electrical breakdown channels.

Let us compare the interaction force between the tip and the self-domain with other forces between the tip and the FE surface. Usually experiments are conducted in air. In this case ionic charge is adsorbed on the surface, which almost totally compensates the field of the spontaneous polarization

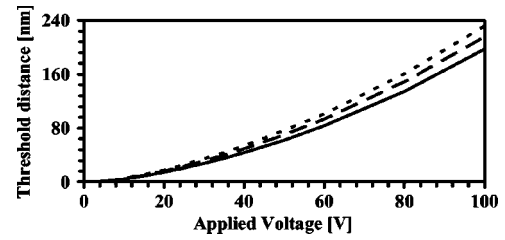


FIG. 2. Threshold distance δ_{th} at which the tip is capable of forming a domain in lithium niobate as a function of the applied voltage for different tip apex radii: $R = 30 \text{ nm}$ (solid curve), $R = 40 \text{ nm}$ (dashed curve), and $R = 50 \text{ nm}$ (dotted curve).

outside the crystal.¹⁸ Hence, the remaining Coulomb interaction of the tip with the domains^{3,16} can be neglected. In addition, from the same considerations, the field arising from bound charges on the domain base is discarded when calculating the depolarization energy (1) and only the bound charges near the apex of the domain are considered.

We shall compare various forces at distances $\delta > 0.5 \text{ nm}$, for which the interatomic forces are negligible.¹³ Previously, it was considered that at such distances the tip-sample interaction is exclusively governed by van der Waals and capacitive forces. For distances exceeding a few nanometers, the retarded effect must be taken into account in van der Waals forces.²⁶ As already shown by Saint Jean *et al.*,¹⁵ the van der Waals force, including the retarded effect, is given by

$$F_{\text{vdW}} = -\frac{H^{\text{ret}}}{30} \left\{ \frac{1 + \text{tg}^2 \theta}{[\delta + R(1 - \sin \theta)]^2} + \frac{2R - \delta}{\delta^3} \right\}, \quad (8)$$

where H^{ret} is the retarded Hamaker constant. The magnitude of H^{ret} increases with the polarizability of interacting

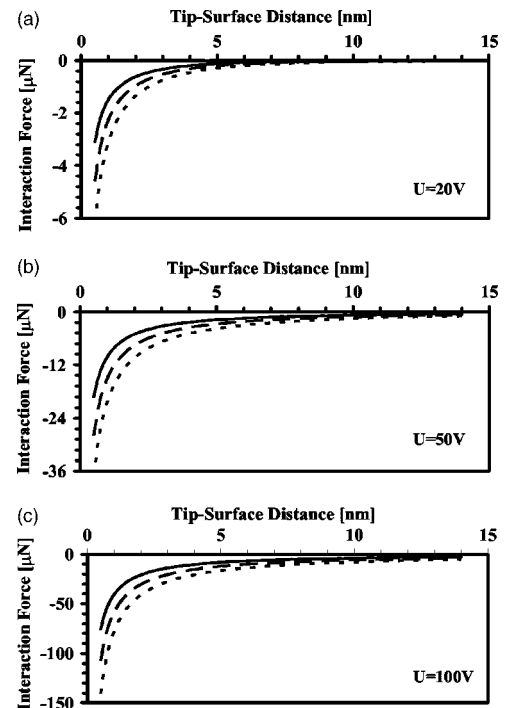


FIG. 3. Force F_{dom} as a function of the tip-surface distance for different tip apex radii and applied voltages (a) $U = 20 \text{ V}$, (b) $U = 50 \text{ V}$, and (c) $U = 100 \text{ V}$, where $R = 30 \text{ nm}$ (solid curve), $R = 40 \text{ nm}$ (dashed curve), and $R = 50 \text{ nm}$ (dotted curve).

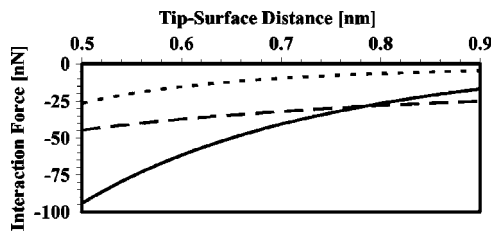


FIG. 4. Comparison of various tip-surface interaction forces: tip with self-domain interaction force F_{dom} (solid curve), capacitive force F_C (dashed curve) and van der Waals force F_{vdW} (dotted curve). Applied potential is $U=4$ V and the tip apex radius is $R=50$ nm.

bodies.²⁶ Typical values of H^{ret} is on the order of 10^{-28} J m for dielectrics²⁶ and up to 10^{-27} J m for metals.¹⁵ The tip is usually metallic or heavily doped semiconductor and the FE is considered to be a dielectric. Therefore, it is expected that the Hamaker constant of the tip-FE system is between the two values. In calculations of force (8) we used the Hamaker constant value $H^{\text{ret}}=10^{-27}$ J m for metals. This allows evaluating an upper bound to van der Waals forces.

An expression for the capacitive force was found by Hudlet *et al.*^{14,15} for the case of a metallic tip interacting with a metallic surface. Analogously we evaluate the interaction of a tip with an anisotropic dielectric

$$F_C(\delta) = -\frac{(\sqrt{\epsilon_c \epsilon_a} - 1)}{4(\sqrt{\epsilon_c \epsilon_a} + 1)} \left\{ \frac{R^2(1 - \sin \theta)}{\delta[\delta + R(1 - \sin \theta)]} + \frac{1}{[\ln \text{tg}(\theta/2)]^2} \left[\ln \frac{L}{\delta + R(1 - \sin \theta)} - 1 + \frac{R \cos^2 \theta / \sin \theta}{\delta + R(1 - \sin \theta)} \right] \right\} U^2. \quad (9)$$

Contrary to forces (7) and (9), which strongly increase with the applied potential, the van der Waals force (8) does

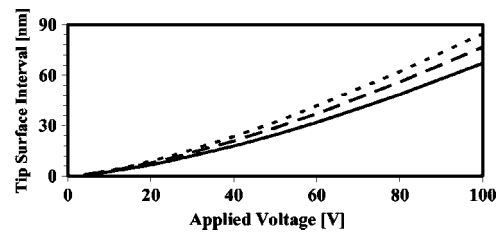


FIG. 5. Interval δ_{dom} for which the force F_{dom} exceeds F_C , as a function of the applied voltage. $R=30$ nm (solid curve), $R=40$ nm (dashed curve), and $R=50$ nm (dotted curve).

not depend on the potential U . Therefore, it influences the interaction only at low potentials and small tip-surface distances. At $U > 10$ V its relative contribution is so small that it can be neglected. Thus we will compare only forces F_{dom} and F_C . Calculations show that even for small potentials, there is an interval of distances between the tip and the surface δ_{dom} , for which the force F_{dom} exceeds F_C , see Fig. 4. Hence, it is necessary to take into account the interaction force of a tip with a self-domain when considering experiments, in which potentials higher than the threshold U_{th} are applied. As seen in Fig. 5, the interval δ_{dom} expands almost linearly with the applied potential.

Our calculations show that the interaction force between a tip and a self-domain increases with the applied potential. Even at low values of the applied potential, F_{dom} is the most significant interaction force between a tip and a ferroelectric surface at distances, between the tip and the surface, smaller than δ_{dom} . Hence, this force must be considered when studying interactions between the atomic force microscope tip and ferroelectrics.

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