Electronic Supplementary Information

Self-consistently derived sample permittivity in stabilization of ferroelectricity due to charge accumulated at interfaces

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1. List of symbols utilized in the manuscript, and of their meaning

(in order of occurrence)

P = electric polarization of the material

ϵ_0 = the permittivity of vacuum

κ_0 = "pseudo-dielectric constant", considered constant in Ref. 1

p_0 = microscopic electric dipole moment inside the material

E = applied (external) electric field

ε = total interaction energy of a dipole with the applied field and with the field created in the material

ε_s = stabilization energy, due to the interaction of a dipole p_0 with charges accumulated at interfaces, including also the dipole-dipole interaction

ε_f = energy of interaction of the dipole p_0 with the external field

G = "geometry factor", takes into account the decrease of the stabilization energy due to dipole-dipole interactions

T = absolute temperature

c = the lattice parameter in the polarization direction (perpendicular to the surface of the film)

a = the lattice parameter in the plane of the film

$p_0^{(max.)}$ = the maximum value allowed for p_0

n_0 = the density of elemental (electric or magnetic) dipoles

$\kappa(P,T)$ = dielectric constant written as function of polarization and temperature

$\varepsilon_{micro.}$ = microscopic energy corresponding to the interaction of a dipole p_0

ε_a = front factor for the stabilization energy written in terms of the order parameter

ξ = order parameter, ranging from – 1 to + 1

$\langle \xi \rangle$ = average value of the order parameter

ε_b = front factor for the energy of interaction with the applied field, written with the order parameter

h = applied field in reduced units E_0 or B_0 (for electric or magnetic fields, respectively)

$E_0 = p_B/(\epsilon_0 \Omega_0) \approx 5.6\ MV/m$ = unit for applied electric fields

$B_0 = \mu_0\mu_B/\Omega_0 \approx 18.8\ T$ = unit for applied magnetic fields

μ_0 = the vacuum permeability

$\Omega_0 \approx 0.62\ \text{Å}^{-3}$ = the volume of a sphere with Bohr radius

$\mu_B \approx 9.3 \times 10^{-24}\ Am^2$ = the Bohr magneton

$p_B = \mu_B/c \approx 3.1 \times 10^{-31}\ Cm$ = the Bohr 'electon' (atomic unit for electric dipole moments, see Ref. 1)

c = the speed of light in vacuum

p_s = saturation value of elemental electric dipole moment

μ_s = saturation value of elemental magnetic dipole moment

p = electric dipole moment

μ = magnetic dipole moment

M = magnetization of the material

J = the exchange integral between nearest-neighbors

η = the number of nearest neighbors

S = the maximum allowed value of the spin projection on the field axis

$\varepsilon_0 = E_0 p_B = B_0\mu_B \approx 1.09\ meV$ = a relevant energy unit

$P_s = n_0 p_s$ = saturation polarization

Θ = the film thickness in c units

$W = F - (E p_{tot.}\ or\ B\mu_{tot.})$ = thermodynamic potential, Legendre transform of the free energy with respect to the polarization (magnetization) times the applied electric (magnetic) field.

F_0 = free energy

$W_1 = -W/(Nk_BT)$ = thermodynamic potential, in dimensionless (reduced) units

$p_{tot.}$ = total electric dipole moment of the material

$\mu_{tot.}$ = total magnetic dipole moment of the material

$p_{tot.,s} = Np_s$ = saturation value of the total electric dipole moment

$\mu_{tot.,s} = N\mu_s$ = saturation value of the total magnetic dipole moment

k_B = the Bolzmann constant

N = total number of dipoles

$a = \varepsilon_a/\varepsilon_b$ = dimensionless parameter proportional to the stabilization energy

$t = k_BT/\varepsilon_b$ = dimensionless parameter proportional to the temperature

$F(x)$ = the function resulting from the ratio of the two sums from eq. (12): Langevin, Brillouin or tanh function, depending on the summation method used for the order parameter

$L(x) = \coth x - 1/x$ = Langevin function

$B_S(x) = (2S + 1)/(2S)\coth\{(2S + 1)x/(2S)\} - 1/(2S)\coth\{x/(2S)\}$ = Brillouin function

χ_d = differential susceptibility

χ_g = global susceptibility

$p_r = n_0 \Omega_0 (p_s/p_B \ or \ \mu_s/\mu_B)$ = dimensionless parameter proportional to the saturation dipole (electric or magnetic) moment

$a_1 = a/t = \varepsilon_a/(k_B T)$ = dimensionless parameter, proportional to the ratio between the stabilization and the thermal energy

$h_1 = h/t = (Ep_s \ or \ B\mu_s)/(k_B T)$ = dimensionless parameter, proportional to the ratio between the energy corresponding to the applied field and the thermal energy

$p_1 = p_r/t = p_s^2 n_0/(\epsilon_0 k_B T) \ or \ \mu_0 \mu_s^2 n_0/(k_B T)$ = dimensionless parameter, proportional to the ratio between the energy corresponding to the maximum dipole moment in the field units defined above and the thermal energy

$F^{-1}(x)$ = the inverse of the function $F(x)$

$\alpha = F'(0)$ = the derivative in the origin ($\alpha = 1$ for $\tanh x$, $\alpha = 1/3$ for the Langevin function, $\alpha = (S+1)/(3S)$ for the Brillouin function)

T_C = Curie temperature

$\langle \xi_c \rangle$ = value of the order parameter corresponding to the coercive field

h_{1c} = coercive field in reduced units, normalized with respect to the thermal energy ($E_c p_s/(E_0 k_B T)$ or $B_c \mu_s/(B_0 k_B T)$)

$h_{1c}^{(0)}$ = coercive field in reduced units, normalized with respect to the thermal energy, at $T = 0$

$h_c^{(0)}$ = coercive field in reduced units (E_c/E_0 or B_c/B_0) at $T = 0$

E_c = coercive electric field

B_c = coercive magnetic field

$E_c^{(0)}$ = coercive electric field at zero absolute temperature

$B_c^{(0)}$ = coercive magnetic field at zero absolute temperature

$p_{1,c}$ = value of the parameter p_1 corresponding to the Curie temperature

$E_c(T)$ = dependence of the electric coercive field on the temperature

$\chi(0)$ = differential or global susceptibility at zero polarization, in the models of Subsecs. 3.1 and 3.2

$\chi_{\pm}(0)$ = solution of eqs. (36) and (37) for the susceptibilities at zero polarization, Subsecs. 3.1. and 3.2.

$\langle \xi \rangle (h_1)$ = dependence of the order parameter on the applied field, in reduced units, starting with an unpolarized system

$\langle \xi \rangle (h_1)$ = dependence of the order parameter on the applied field, in reduced units, for the polarized system

$\tilde{\chi}_d$ = differential susceptibility for the curve of first polarization

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$\tilde{\chi}_g$ = global susceptibility for the curve of first polarization

h_{10} = bias field

$F^{-1\prime}(\langle\xi\rangle)$ = the derivative of $F^{-1}(\langle\xi\rangle)$ with respect to $\langle\xi\rangle$

$\epsilon_1 \equiv \epsilon_0\kappa_1$ = modified permittivity to allow reasonable values of the coercive fields and Curie temperatures

κ_1 = "background" dielectric constant

$h_1^{(0)}(\langle\xi\rangle)$ = initial guess for iterative solving of the differential equation (51)

$h_1^{(1)}(\langle\xi\rangle)$, $h_1^{(2)}(\langle\xi\rangle)$, etc. = consecutive iterative solutions

$L^{-1}(\langle\xi\rangle)$ = inverse of the Langevin function

β = fitting parameter assuming that the coercive field h_{1c} is proportional to the parameter p_1

$\gamma \approx 1.1$ = fitting parameter for the dependence of the reduced coercive field on the parameter p_1

V_p = polarizability of the unit cell, expressed in volume units (the real polarizability, i. e. the ratio between the induced dipole moment and the applied electric field is $4\pi\epsilon_0 V_p$)

V_0 = volume of the unit cell

$C_{tot.}$ = total capacitace of a ferroelectric capacitor

C_{bulk} = capacitance corresponding to the bulk of a ferroelectric capacitor

$C_{interface}$ = capacitance corresponding to the interface regions of a ferroelectric capacitor

2. Proof that the average value of the polarization is obtained as a partial derivative of the thermodynamic potential with respect to the field, and that the field and the polarization can be considered as independent variables in this treatment.

One has to prove that $\langle\xi\rangle = \partial W_1/\partial h_1$ and not $\langle\xi\rangle = dW_1/dh_1 = \partial W_1/\partial h_1 + (\partial W_1/\partial\langle\xi\rangle)(\partial\langle\xi\rangle/\partial h_1)$. Although this should be clear from textbook statistical mechanics, this possibility is, however, investigated in relation with ferroic systems, to rule out definitely the possibility of extra terms related to $\partial\langle\xi\rangle/\partial h_1$.

If, from eq. (14) rewritten as:

$$\langle\xi\rangle = \frac{dW_1}{dh_1} = F(a_1\langle\xi\rangle + h_1)\frac{\partial}{\partial h_1}(a_1\langle\xi\rangle + h_1)$$

(S1)

one doesn't neglect $\partial\langle\xi\rangle/\partial h_1$, by computing the derivative:

$$\frac{\chi_d}{p_1} = \frac{\partial\langle\xi\rangle}{\partial h_1} = F'(a_1\langle\xi\rangle + h_1)\left(a_1\frac{\partial\langle\xi\rangle}{\partial h_1} + 1\right)^2 + F(a_1\langle\xi\rangle + h_1)a_1\frac{\partial^2\langle\xi\rangle}{\partial h_1^2}$$

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and evaluating it near the origin:

$$\frac{\chi_d(0)}{p_1} = \left(\frac{\partial \langle \xi \rangle}{\partial h_1}\right)_0 = F'(0)\left(\frac{a_1}{p_1}\chi_d(0) + 1\right)^2$$

This equation for $\chi_d(0)$ simply doesn't admit any negative solution, therefore no ferroicity is allowed by such a model. It turns out that when computing the average value of moments from the derivative of the thermodynamic potential one needs to treat the average value of the moment $\langle \xi \rangle$ and the field h as really independent variables.

This can be derived also in a more general case: assume:

$$W_1 = \log \sum_{\xi} \exp\left\{\xi f(\langle \xi \rangle, h_1)\right\}$$

with $f(0,0) = 0$, and for a while admit that $\langle \xi \rangle$ and h_1 are not independent. Then, applying eq. (S1) and using a *total* derivative:

$$\langle \xi \rangle = F\big(f(\langle \xi \rangle, h_1)\big)\left(\frac{\partial f}{\partial h_1} + \frac{\partial f}{\partial \langle \xi \rangle}\frac{d\langle \xi \rangle}{dh_1}\right)$$

The differential susceptibility is then computed as:

$$\chi_d = p_1\frac{d\langle \xi \rangle}{dh_1} = p_1 F'\big(f(\langle \xi \rangle, h_1)\big)\left(\frac{\partial f}{\partial h_1} + \frac{\partial f}{\partial \langle \xi \rangle}\frac{d\langle \xi \rangle}{dh_1}\right)^2 + p_1 F\big(f(\langle \xi \rangle, h_1)\big)\left\{\frac{\partial^2 f}{\partial h_1^2} + \frac{\partial^2 f}{\partial h_1 \partial \langle \xi \rangle}\frac{d\langle \xi \rangle}{dh_1} + \frac{\partial f}{\partial \langle \xi \rangle}\frac{d^2\langle \xi \rangle}{dh_1^2}\right\}$$

and, if no singularity occurs near the origin in the derivatives from the last parenthesis, the susceptibility near the origin cannot be negative:

$$\frac{\chi_d(0)}{p_1} = \alpha\left\{\left(\frac{\partial f}{\partial h_1}\right)_0 + \left(\frac{\partial f}{\partial \langle \xi \rangle}\right)_0\frac{\chi_d(0)}{p_1}\right\}^2$$

It follows then that eq. (S1) must be applied by using a partial derivative, or, equivalently, that the second term in the parenthesis of eq.(S5) must not be taken into account. Then, the differential susceptibility is given by:

$$\chi_d = p_1 F'(f(\langle\xi\rangle,h_1)) \left(\frac{\partial f}{\partial h_1} + \frac{\partial f}{\partial\langle\xi\rangle}\frac{d\langle\xi\rangle}{dh_1}\right)\frac{\partial f}{\partial h_1} + p_1 F(f(\langle\xi\rangle,h_1))\frac{\partial^2 f}{\partial h_1^2}$$

(S8)

Near the origin $F(f(0,0)) = 0$ and:

$$\frac{\chi_d(0)}{p_1} = \alpha\left\{\left(\frac{\partial f}{\partial h_1}\right)_0 + \left(\frac{\partial f}{\partial\langle\xi\rangle}\right)_0\frac{\chi_d(0)}{p_1}\right\}\left(\frac{\partial f}{\partial h_1}\right)_0$$

(S9)

with a single solution:

$$\chi_d(0) = p_1\alpha\left(\frac{\partial f}{\partial h_1}\right)_0^2\left\{1 - \alpha\left(\frac{\partial f}{\partial h_1}\right)_0\left(\frac{\partial f}{\partial\langle\xi\rangle}\right)_0\right\}^{-1}$$

(S10)

This solution is negative when the parenthesis is negative. For $f(\langle\xi\rangle,h_1) = a_1\langle\xi\rangle + h_1$ one retrieves the condition $\alpha a_1 > 1$.