Electronic Supplementary Information

Ferroelectricity in thin films driven by charges accumulated at interfaces

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1. Interaction of charges and dipoles with other dipoles in a continuous model, cylindrical coordinates

The ferroelectric material is supposed concentrated inside an infinite plate with outer surfaces at $z' = Z$ and $z' = -Z$, z' being the coordinate oriented perpendicular to the plate with unit vector $\hat{\boldsymbol{z}}$, as represented in Figure SI-1. This volume will be noted by $\mathcal{D}$ in the following. The material has a polarization oriented along the positive direction of z, z', and in the most general case the polarization is function of z, $P(z)$.

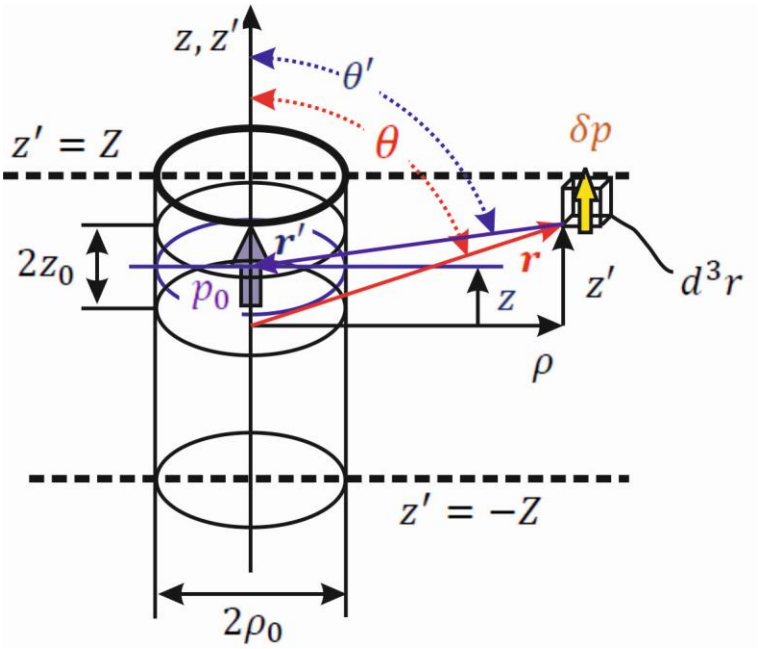

Figure SI-1. Geometry for evaluating the total electron-dipole and dipole-dipole interaction in a continuous model.

The problem will be treated in cylindrical coordinates (ρ, φ, z'). Suppose first that an electron is placed at the distance z from the central plane of the material $z' = 0$, i. e. at O': $(\rho = 0, (\varphi), z' = z)$. A volume element $d^3r = \rho d\rho d\varphi dz'$ carries a dipole moment $\delta\boldsymbol{p} = \hat{\boldsymbol{z}}P(z)d^3r$. Let $\boldsymbol{r}' = z\hat{\boldsymbol{z}} - \boldsymbol{r}$ be the vector oriented from the volume element d^3r towards the point O', $r'^2 = \rho^2 + (z' - z)^2$. The interaction energy between the electron placed in O' and the dipole $\delta\boldsymbol{p}$ is:

$$\delta\varepsilon_{e-d} = -\frac{e\delta\boldsymbol{p}\cdot\boldsymbol{r}'}{4\pi\epsilon_0\kappa r'^3} \qquad \text{(SI-1)}$$

where $-e$ is the electron charge, ϵ_0 the permittivity of vacuum, and κ the dielectric constant of the material. Assuming that the polarization is uniform $P(z) = P$:

$$\varepsilon_{e-d} = \frac{eP}{4\pi\epsilon_0\kappa}\int_{\mathcal{D}} \frac{\cos\theta'}{r'^2}\, d^3r = -\frac{ePz}{\epsilon_0\kappa} \tag{SI-2}$$

The above equation in fact evidences the "depolarization field" $-P/(\epsilon_0\kappa)$, oriented in the opposite direction with respect to the polarization. Adding the field due to the surface charges, see Figure 1 from the main text (positive charges at $z' = -Z$ and negative charges at $z' = Z$), the total field inside the material vanishes.

The interaction of an electric dipole $\boldsymbol{p}_0$ placed in O' with the dipole $\delta\boldsymbol{p}$ starts with:

$$\delta\varepsilon_{d-d} = -\frac{3\left(\boldsymbol{p}_0\cdot\widehat{\boldsymbol{r}'}\right)\left(\delta\boldsymbol{p}\cdot\widehat{\boldsymbol{r}'}\right) - \delta\boldsymbol{p}\cdot\boldsymbol{p}_0}{4\pi\epsilon_0\kappa r'^3} \tag{SI-3}$$

and, using $P(z) = n_0\tilde{p}p_{\mathrm{B}}\langle\xi\rangle$, where p_{B} is the "Bohr electon", $\tilde{p}$ the maximum value of the dipole moment of an unit cell expressed in p_{B} units, $\langle\xi\rangle$ with $|\langle\xi\rangle| < 1$ the average value of the order parameter and n_0 the density of dipoles in the material (inverse of the volume of a unit cell), and with $p_0 = \tilde{p}p_{\mathrm{B}}\xi$, $\Omega_0 = 4\pi {a_0}^3/3$ and ε_0 the energy unit defined by eq. (3) from the main text:

$$\varepsilon_{d-d} = -\frac{\varepsilon_0\tilde{p}^2 n_0\Omega_0}{4\pi\kappa}\xi\int_{\mathcal{D}-\mathcal{D}_0}\frac{3\cos^2\theta' - 1}{r'^3}\langle\xi\rangle d^3r \tag{SI-4}$$

One can easily demonstrate (see also below) that, if $\langle\xi\rangle = \mathrm{Const.}$ and the integral is performed over the whole material $(-Z \le z' \le Z; 0 < \rho < \infty)$ the dipole-dipole interaction energy cancels with the interaction energy of the dipole $\boldsymbol{p}_0$ with the accumulated charges at the extremal surfaces $z' = \pm Z$. But in fact one has to eliminate from the integral a volume $\mathcal{D}_0$ corresponding to the dipole $\boldsymbol{p}_0$, in order to exclude self-interaction. $\mathcal{D}_0$ is defined as $(z - z_0 \le z' \le z + z_0; 0 < \rho < \rho_0)$, see Figure SI-1. Eq. (SI-4) becomes:

$$\begin{aligned}\varepsilon^{(0)}_{d-d}(z) &= -\frac{\varepsilon_0\tilde{p}^2 n_0\Omega_0}{2\kappa}\xi(z)\int_{-Z}^{Z}\langle\xi(z')\rangle dz'\int_{\rho_0}^{\infty}\rho d\rho\left\{\frac{3(z'-z)^2}{[\rho^2+(z'-z)^2]^{\frac{5}{2}}} - \frac{1}{[\rho^2+(z'-z)^2]^{\frac{3}{2}}}\right\}\\ &= \frac{\varepsilon_0\tilde{p}^2 n_0\Omega_0}{2\kappa}{\rho_0}^2\xi(z)\int_{-Z}^{Z}\frac{\langle\xi(z')\rangle}{[{\rho_0}^2+(z'-z)^2]^{\frac{3}{2}}}dz'\end{aligned} \tag{SI-5}$$

In the above integral, a cylinder of radius ρ_0 is excluded, so one needs to add a one dimensional integral from $-Z$ to Z where one excludes the range $z - z_0 \le z' \le z + z_0$. This adds the following term, for $-Z + z_0 \le z \le Z - z_0$:

$$\varepsilon^{(1)}_{d-d}(z) = -\frac{\varepsilon_0\tilde{p}^2 n_0\Omega_0}{2\kappa}{\rho_0}^2\xi(z)\left\{\int_{-Z}^{z-z_0} + \int_{z+z_0}^{Z}\right\}\frac{\langle\xi(z')\rangle dz'}{|z'-z|^3} \tag{SI-6}$$

For $-Z + z_0 > z$ the first integral is not considered, and for $Z - z_0 < z$ the second integral is not considered.

The stabilization energy (eq. (1) from the main text), i. e. the energy of interaction of $\boldsymbol{p}_0$ with the outer charge distribution will be written, by using the definition of the polarization, as:

$$\varepsilon_s(z) = -\frac{\varepsilon_0 \tilde{p}^2 n_0 \Omega_0}{\kappa} \xi(z) \frac{1}{2Z} \int_{-Z}^{Z} \langle \xi(z') \rangle dz' \tag{SI-7}$$

The total energy (stabilization + dipole-dipole interaction) is the sum of (SI-5), (SI-6) and (SI-7). The interaction with an external field and the associated statistics will be included later. For instance, one will suppose that $\langle \xi \rangle = \text{Const.}$, i. e. it does not depend on z. In this case, the total energy is written as:

$$\varepsilon_{\text{tot.}}(z) = \frac{\varepsilon_0 \tilde{p}^2 n_0 \Omega_0}{2\kappa} \xi \langle \xi \rangle \left\{ \frac{Z - z}{[(Z - z)^2 + {\rho_0}^2]^{1/2}} + \frac{Z + z}{[(Z + z)^2 + {\rho_0}^2]^{1/2}} - 2 + f(\rho_0, z_0, Z, z) \right\} \tag{SI-8a}$$

where:

$$f(\rho_0, z_0, Z, z) = \begin{cases} \dfrac{{\rho_0}^2}{2(Z - z)^2} + \dfrac{{\rho_0}^2}{2(Z + z)^2} - \dfrac{{\rho_0}^2}{{z_0}^2}, \text{for } -Z + z_0 \le z \le Z - z_0 \\ \dfrac{{\rho_0}^2}{2(Z - z)^2} - \dfrac{{\rho_0}^2}{2{z_0}^2}, \text{for } -Z \le z < -Z + z_0 \\ \dfrac{{\rho_0}^2}{2(Z + z)^2} - \dfrac{{\rho_0}^2}{2{z_0}^2}, \text{for } Z - z_0 < z \le Z \end{cases} \tag{SI-8b}$$

The corresponding dependencies with the out-of-plane oriented coordinate z are represented in Figure SI-2.

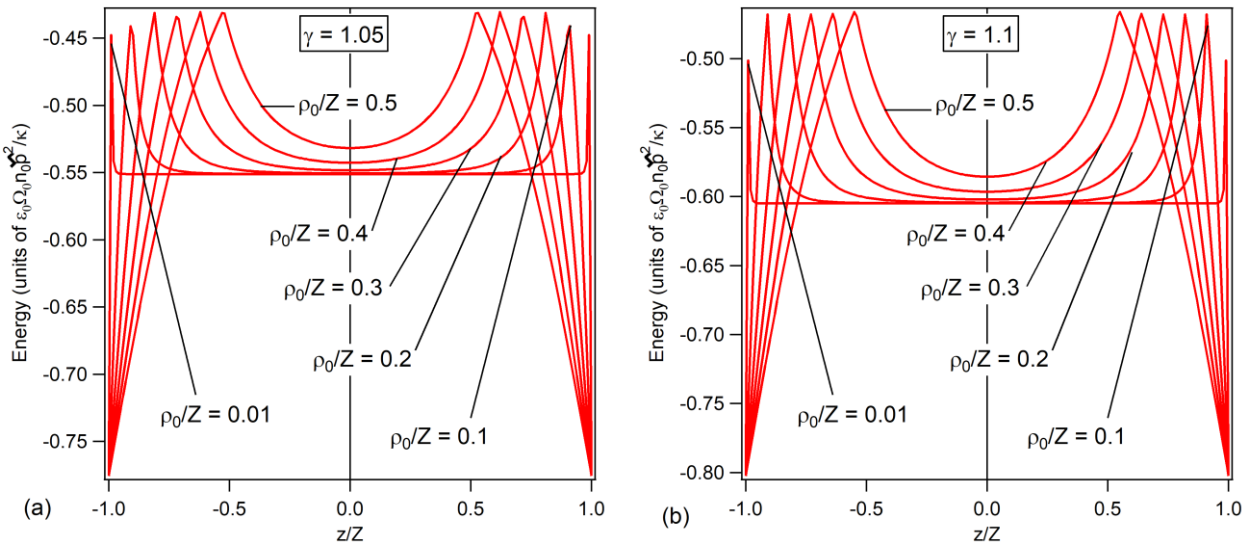

Figure SI-2. Total energies (ordering + dipole-dipole) computed as function of the coordinate z, for several values of the cutoff parameters ρ_0 (divided by half of the film thickness, Z) and for $\gamma = \rho_0/z_0$ = 1.05 (a) and 1.1 (b).

For $z = 0$, i. e. in the middle plane of the material:

$$\varepsilon_{\text{tot.}}(0) = \frac{\varepsilon_0 \tilde{p}^2 n_0 \Omega_0}{2\kappa} \xi\langle\xi\rangle \left\{ \frac{2Z}{[Z^2 + {\rho_0}^2]^{1/2}} - 2 + \frac{{\rho_0}^2}{Z^2} - \frac{{\rho_0}^2}{{z_0}^2} \right\} \tag{SI-9}$$

and one observes that, if $\rho_0 \to 0$ with $z_0 \neq 0$ the total energy vanishes in this middle plane. It follows that the stabilization character (i. e. negative value) of the total energy is defined by the ratio $\gamma \equiv \rho_0/z_0$. In the following, this ratio will be connected with the geometrical characteristics of the unit cell of the perovskite material. One starts with the asssumption that the cylinder of radius ρ_0 and height $2z_0$ represents a cell corresponding to the formula unit ABO_3, whose basis has an area a^2 and whose height is c, with c/a the tetragonality factor. Then, it is natural to suppose that $2z_0 = c$ and $\pi{\rho_0}^2 = a^2$. In this case, let $\Theta = 2Z/c$ be the number of unit cells comprised in the total thickness $2Z$ (twice the number of atomic layers). The parameter γ is connected to the tetragonality by $\gamma = (2/\sqrt{\pi})(c/a)^{-1}$. With these assumptions, eq. (SI-9) may be written by using more 'physical' parameters as:

$$\varepsilon_{\text{tot.}}(0) = \frac{\varepsilon_0 \tilde{p}^2 n_0 \Omega_0}{2\kappa} \xi\langle\xi\rangle \left\{ \frac{2}{\left(1 + \frac{\gamma^2}{4\Theta^2}\right)^{\frac{1}{2}}} - 2 + \frac{\gamma^2}{4\Theta^2} - \gamma^2 \right\} \to -\frac{\gamma^2}{2} \frac{\varepsilon_0 \tilde{p}^2 n_0 \Omega_0}{\kappa} \equiv -\frac{G \varepsilon_0 \tilde{p}^2 n_0 \Omega_0}{\kappa}$$

(when $\Theta \to \infty$) (SI-10)

The above formula justifies the geometry factor $G(< 1)$ discussed in the main text. In fact, since for practical cases the tetragonality $c/a \approx 1.05 - 1.1$, the parameter γ is close to unity, then G is close to 1/2. Figure SI-3 presents the geometry factor for different thicknesses of the ferroelectric film, for different values of γ, as function on the film thickness Θ.

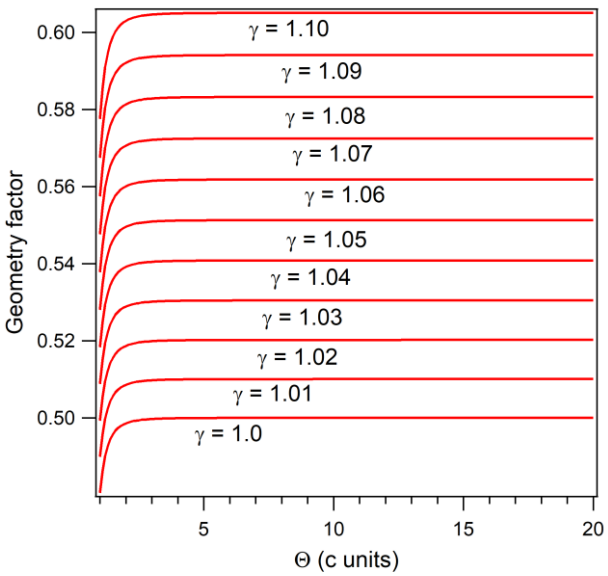

Figure SI-3. Geometry factors obtained from eq. (SI-10) for films of different thicknesses and values of the parameter $\gamma = \rho_0/z_0$.

The following step is to treat the case of a non-uniform polarization as function of z. The first step is to write down the sum of eq. (SI-5), (SI-6) and (SI-7) such as:

$$\varepsilon_{\text{tot.}}(z) = -\frac{\varepsilon_0 \tilde{p}^2 n_0 \Omega_0}{2\kappa} \xi \hat{\alpha}(\gamma, \Theta, z; \langle\xi(z)\rangle)$$

(SI-11)

where $\hat{\alpha}$ is an integral operator, since the function $\langle\xi(z)\rangle$ intervenes in the integrals of all equations (SI-5), (SI-6) and (SI-7). For each point z one may then apply the statistics of a two-state system, in applied field h, yielding the equation:

$$\langle\xi(z)\rangle = \tanh\{-\beta\varepsilon_{\text{tot.}}(z) + \beta\varepsilon_0\tilde{p}h\} = \tanh\left\{\frac{\varepsilon_0\tilde{p}^2 n_0\Omega_0}{2\kappa k_B T}\left(\hat{\alpha}(\gamma,\Theta,z;\langle\xi(z)\rangle) + \frac{2\kappa h}{n_0\Omega_0\tilde{p}}\right)\right\} \tag{SI-12}$$

and this equation may be solved by iterations, i. e. one starts with $\langle\xi(z)\rangle$ in the right hand side term, evaluate a new $\langle\xi(z)\rangle$ by using the equation, replace again in the right hand side term, and so on. From now on, $h' = 2\kappa h/(n_0\Omega_0\tilde{p})$ and a simple evaluation yields that this corrected field is in the range of unity. Also, one defines a 'reduced temperature' $t = T/T_0$, with

$$k_B T_0 = \frac{\varepsilon_0\tilde{p}^2 n_0\Omega_0}{2\kappa} \tag{SI-13}$$

and, working in the reduced coordinate $x = z/Z$, with a straighforward redefinition of $\langle\xi(x)\rangle$, eq. (SI-12) becomes:

$$\langle\xi(x)\rangle = \tanh\left\{\frac{\hat{\alpha}(\gamma,\Theta,z;\langle\xi(x)\rangle) + h'}{t}\right\} \tag{SI-14}$$

and, exploiting an obvious symmetry $\langle\xi(x)\rangle = \langle\xi(-x)\rangle$:

$$\begin{aligned}
&\hat{\alpha}(\gamma,\Theta,z;\langle\xi(x)\rangle) \\
&= 2\int_0^1 \langle\xi(x')\rangle dx' - \left(\frac{\gamma}{2\Theta}\right)^2 \left\{\int_0^1 \frac{\langle\xi(x')\rangle dx'}{\left[\left(\frac{\gamma}{2\Theta}\right)^2 + (x'+x)^2\right]^{\frac{3}{2}}} + \int_0^1 \frac{\langle\xi(x')\rangle dx'}{\left[\left(\frac{\gamma}{2\Theta}\right)^2 + (x'-x)^2\right]^{\frac{3}{2}}}\right\} \\
&+ \left(\frac{\gamma}{2\Theta}\right)^2 \begin{cases} \displaystyle\int_{\frac{1}{2\Theta}+x}^1 \frac{\langle\xi(x')\rangle dx'}{(x'-x)^3} + \int_{\frac{1}{2\Theta}-x}^1 \frac{\langle\xi(x')\rangle dx'}{(x'+x)^3}, \text{ for } 0 \le x \le \dfrac{1}{2\Theta} \\ \displaystyle\int_{\frac{1}{2\Theta}+x}^1 \frac{\langle\xi(x')\rangle dx'}{(x'-x)^3} - \int_0^{x-\frac{1}{2\Theta}} \frac{\langle\xi(x')\rangle dx'}{(x'-x)^3} + \int_0^1 \frac{\langle\xi(x')\rangle dx'}{(x'+x)^3}, \text{ for } \dfrac{1}{2\Theta} \le x \le 1 - \dfrac{1}{2\Theta} \\ \displaystyle\int_0^1 \frac{\langle\xi(x')\rangle dx'}{(x'+x)^3} - \int_0^{x-\frac{1}{2\Theta}} \frac{\langle\xi(x')\rangle dx'}{(x'-x)^3}, \text{ for } x > 1 - \dfrac{1}{2\Theta} \end{cases}
\end{aligned} \tag{SI-15}$$

Eqs. (SI-14 – 15) are solved by iterations (maximum 20 iterations are needed) and produced the data represented in Figure 3, main text.

In the case of a finite cylindrical domain with maximum radius $\rho_{\text{max.}}$, the total energy, eq. (SI-8a) is written as:

$$\varepsilon_{\text{tot.}}(z) = \frac{\varepsilon_0 \tilde{p}^2 n_0 \Omega_0}{2\kappa} \xi\langle\xi\rangle \left\{ \frac{Z-z}{[(Z-z)^2+{\rho_0}^2]^{1/2}} + \frac{Z+z}{[(Z+z)^2+{\rho_0}^2]^{1/2}} - \frac{Z-z}{[(Z-z)^2+{\rho_{\text{max.}}}^2]^{\frac{1}{2}}} - \frac{Z+z}{[(Z+z)^2+{\rho_{\text{max.}}}^2]^{1/2}} - 2 + f(\rho_0, z_0, Z, z) \right\} \quad \text{(SI-16)}$$

with $f(\rho_0, z_0, Z, z)$ given by eq. (SI-8b). Thus, the formation of domains introduces negative terms yielding to an enhancement of the stability of the FE state.

2. The Clausius-Mossotti relation in spherical and cylindrical coordinates

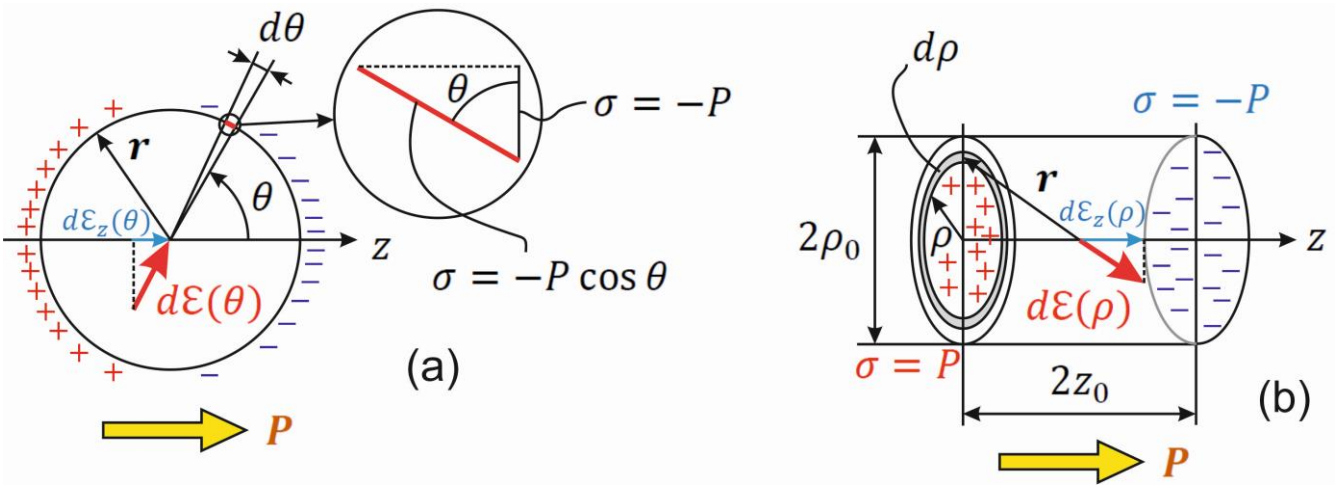

Figure SI-4. Geometries of a spherical cavity (a) and of a cylindrical cavity (b) for calculating the internal field.

The first step is to compute the internal field inside a vacuum cavity performed in the material by removing a piece of the poled material. The remaining charges accumulated on the inner surfaces are as represented in Figure SI-4.

(a) For spherical coordinates, the total field is obtained by integrating the projections on the axis z for any charge element on the inner surface, which is proportional to $\sigma r^2 d\Omega$, where $d\Omega = \sin\theta \, d\theta d\varphi$ is the solid angle. The surface charge density varies with the angle θ such that $\sigma(\theta) = -P\cos\theta$, see the enlarged part of Figure SI-4(a). Consequently:

$$d\mathcal{E}_z(\theta) = d\mathcal{E}(\theta)\cos\theta = -\frac{\sigma(\theta) r^2 d\Omega}{4\pi\epsilon_0 r^2}\cos\theta = \frac{P\cos^2\theta \sin\theta \, d\theta d\varphi}{4\pi\epsilon_0} \quad \text{(SI-17)}$$

It is easy to demonstrate that the components normal to z are cancelled by integration. Integrating the above equation over θ and φ yields:

$$\mathcal{E}_z = \frac{P}{3\epsilon_0} \quad \text{(SI-18)}$$

Therefore, in presence of an external field $\mathcal{E}_0$ the total field in the center of the cavity is $\mathcal{E}_z + \mathcal{E}_0$. The Clausius-Mossotti equation is obtained by introducing the polarizability α of an elemental dipole placed

in the center of the cavity, whose dipole moment will be $\alpha(\mathcal{E}_z + \mathcal{E}_0)$. Therefore, the polarization is n_0 times this dipole moment, where n_0 is the density of dipoles:

$$P = n_0\alpha\left(\mathcal{E}_0 + \frac{P}{3\epsilon_0}\right) \tag{SI-19}$$

At the same time, the polarization is proportional to the applied field

$$P = (\kappa - 1)\epsilon_0\mathcal{E}_0 \tag{SI-20}$$

Extracting the terms with P in eq. (SI-9) and using eq. (SI-20) one obtains the Clausius-Mossotti equation:

$$\frac{\kappa - 1}{\kappa + 2} = \frac{n_0\alpha}{3\epsilon_0} \tag{SI-21}$$

(b) For cylindrical coordinates, one extracts from the material a cylinder-shaped cavity with radius ρ_0 and height $2z_0$, see Figure SI-4(b). Each lateral face of the cylinder has this time an uniform charge density $\sigma = \pm P$. The distance from a point on the external face placed at the distance ρ from the center of the face to the middle of the cylinder is $r = (\rho^2 + {z_0}^2)^{1/2}$. One needs then to integrate

$$d\mathcal{E}_z(\rho) = d\mathcal{E}(\rho)\frac{z_0}{r} = \frac{P\rho z_0 d\rho d\varphi}{4\pi\epsilon_0 r^3} \tag{SI-22}$$

and to multiply by 2, since one needs to sum the contribution from both positively and negatively charged lateral faces.

$$\mathcal{E}_z = \frac{Pz_0}{\epsilon_0}\int_0^{\rho_0}\frac{\rho d\rho}{(\rho^2 + {z_0}^2)^{3/2}} = \frac{P}{\epsilon_0}\left\{1 - \frac{1}{(1+\gamma^2)^{1/2}}\right\} \tag{SI-23}$$

with $\gamma = \rho_0/z_0$ (see also the above considerations, after eq. (Si-9)). As a consequence, in this case, the Clausius=Mossotti equation results as:

$$\frac{n_0\alpha}{\epsilon_0} = \frac{(\kappa-1)(1+\gamma^2)^{1/2}}{\kappa\{(1+\gamma^2)^{1/2} - 1\} + 1} = \begin{cases} \kappa - 1, & \text{for } \gamma \to 0 \\ \dfrac{\kappa - 1}{\kappa}, & \text{for } \gamma \to \infty \end{cases} \tag{SI-24}$$

As a consequence, different Clausius-Mossotti factors are obtained for cavities of different shapes.

3. The approximation for the inverse Langevin function proposed by A. Cohen [*Rheol. Acta* **30**, 270–273 (1991).]

Remember that

$$\mathcal{L}(x) = \coth x - \frac{1}{x}$$

$$\mathcal{L}^{-1}(x) \approx \frac{3x - x^3}{1 - x^2}$$

(eq. (11))

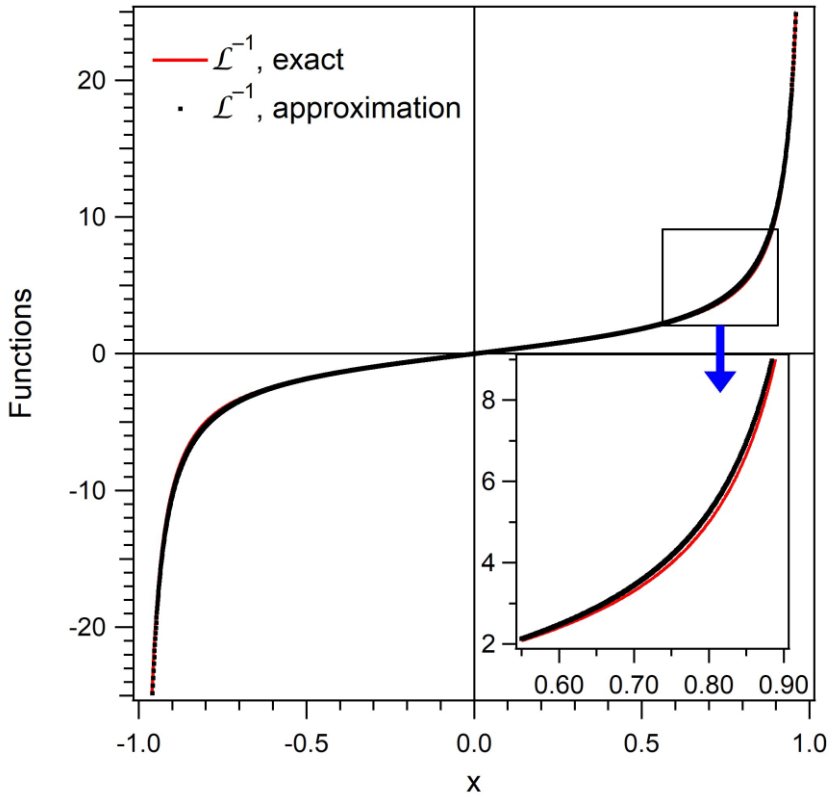

Figure SI-5. Inverse Langevin function, exact and approximation given by eq. (11).