e.g. in works of Refs. 3,4,24,25. For 180° walls, the polarization profile associated with SPP is sometimes denoted as the Ising-type wall. In contrast, the CPP solutions with non-zero $P_{\rm s}$, $P_{\rm t}$ are often considered as Néel and Bloch-like,[25] even though, in contrast with magnetism, the modulus of $\mathbf{P}$ is far from being conserved along the wall normal $\mathbf{s}$.

We have previously considered non-constant $P_{\rm s}$ component of polarization in the 90° wall with explicit treatment of electrostatic interaction and realized that the deviations from SPP approximation are quite negligible.[4] In general, non-constant $P_{\rm s}$ would lead to non-vanishing $\nabla \cdot \mathrm{P}$ and finite local charge density, which in a perfect dielectric causes a severe energy penalty. The same situation is expected for all domain wall species. However, there is no such penalty for non-constant $P_{\rm t}$-solutions. It was previously argued[3] that the Bloch-like (with a considerable magnitude of $P_{\rm t}$ at the domain wall center) solutions could occur in orthorhombic $\mathrm{BaTiO_3}$. Therefore, it is interesting to systematically check for existence of such solutions using our model.

In order to study such Bloch-like solutions, we have calculated Euler-Lagrange potential in the order-parameter plane $P_{\rm s} = P_{\rm s}(\pm\infty)$ by integrating Euler-Lagrange equations (Eqn. 13 and 14) for all domain wall species from Table III similarly as e.g. in the Refs. 1,3. Resulting 2D Euler-Lagrange potential surfaces (ELPS) are displayed in Fig. 7. In each ELPS, the bold lines indicate numerically obtained domain-wall solution with the lowest energy. The spatial step was chosen as 0.1 nm, $P_{\rm r}$ and $P_{\rm t}$ were fixed to boundary conditions in sufficient distance from domain wall (6 nm) and initial conditions for $P_{\rm t}$ were chosen so that the polarization path bypasses the energy maximum of the ELPS, and the system was relaxed to the equilibrium.

Among the twelve treated wall species, there are six cases where only the SPP solutions with $P_{\rm t}$=const exist: T180{001}, T180{011}, T90, O180{1$\bar{1}$0}, O90, and R71. These solutions are clearly "Ising-like". In all these cases, the ($P_{\rm r} = 0$, $P_{\rm t} = 0$) point is the only saddle point of the ELPS. In the other six cases – O180{001}, O60, O120, R180{1$\bar{1}$0}, R180{$\bar{2}$11}, and R109 – the ELPS has a maximum at the ($P_{\rm r} = 0$, $P_{\rm t} = 0$), and the lowest energy solutions correspond to curved polarization paths. This suggests that the previously discussed SPP description may not necessarily be the proper approximation for these walls. Nevertheless, in the case of O60 and O120 walls the deviations from the SPP model are marginal, and only the remaining four solutions exhibit strong Bloch-like behavior. Moreover, the energy differences between SPP and CPP solutions were found to be almost negligible, except for R180, where the CPP energy is by about 10% lower in the entire temperature range of stability of the rhombohedral phase. Therefore, it is quite possible that in the case of O180{001}, R180{1$\bar{1}$0}, R180{$\bar{2}$11}, and R109 walls both Bloch-like and Ising-like solutions may be realized.

The deviations from SPP in the case of the almost Ising-like O60 and O120 walls are associated with the fact that ELPS is not symmetric with respect to $P_{\rm t} = P_{\rm t}(\pm\infty)$ mirror plane. In these cases not only the polarization path and wall energies, but also domain wall thicknesses of the SPP and CPP counterpart solutions are very similar. This is demonstrated in Fig. 8, which shows polarization profiles of both SPP and CPP solutions for the O60 wall.

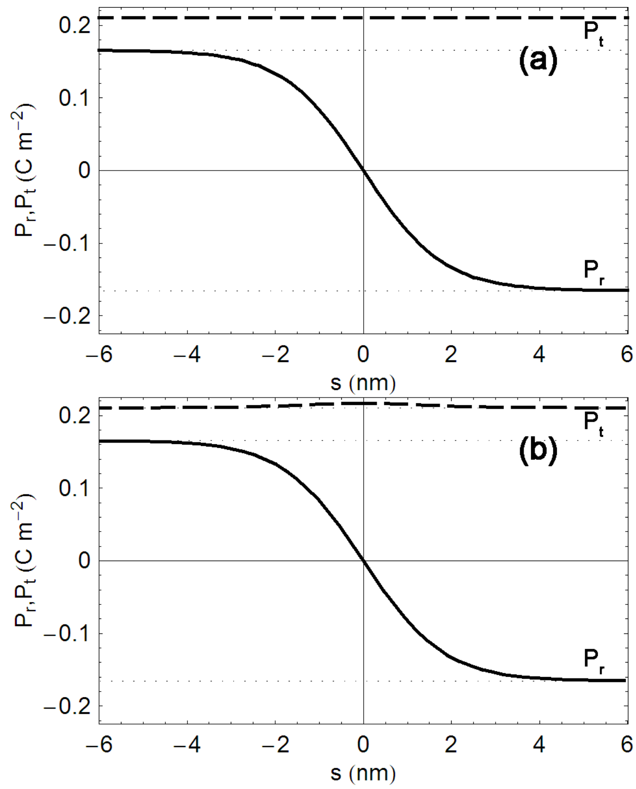

FIG. 8: Predicted profiles of polarization components for O60 domain wall in $\mathrm{BaTiO_3}$ at $T = 208\,\mathrm{K}$. Full line stands for the $P_{\rm r}$ component of polarization vector, broken line for the $P_{\rm t}$ one. Analytically obtained SPP solution (a) practically does not differ from the numerically obtained CPP solution (b) with an unconstrained $P_{\rm t}$ component in this case.

Much more pronounced difference between domain wall profiles of SPP and CPP solutions are found in case of O180{001}, R180{1$\bar{1}$0}, R180{$\bar{2}$11}, and R109 Bloch-like walls where the CPP trajectories bypass the ($P_{\rm r} = 0$, $P_{\rm t} = 0$) maximum near the additional minima, which originate from 'intermediate' domain states either of the same phase or even of the different ferroelectric phases. In these cases, the inadequacy of SPP approximation is obvious. For example, the CPP of R180{$\bar{2}$11} wall seems to pass through a additional minimum corresponding to an 'orthorhombic' polarization state (consult corresponding inset in the Fig. 2). As expected, the profile of such CPP solution deviates strongly from *tanh* shape and even definition of the wall thickness would be problematic (see Fig. 9).