Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

The variation in the space-charge potential at grain boundaries in $SrTiO_3$: the effects of two restricted equilibria

— Supplemental Information —

Adrian L. Usler, Fabian Ketter, Roger A. De Souza

S1 Explanations of the temperature dependence of Φ_0

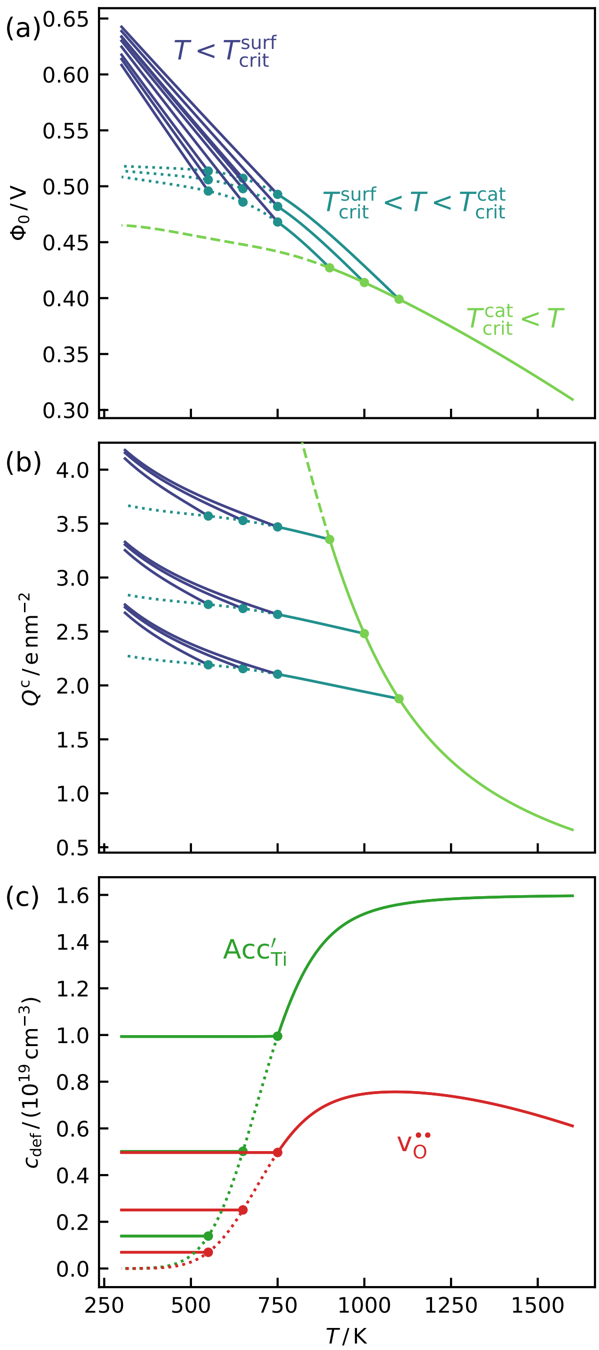

Figure S1: Temperature dependence of (a) the space-charge potential, Φ_0; (b) the grain-boundary core charge, Q^c; and (c) the bulk defect concentrations of Acc'_{Ti} and $v_O^{\bullet\bullet}$, with the temperature range encompassing the full-equilibrium (FE) as well as one restricted-equilibrium (1RE) and two restricted-equilibria (2RE) scenarios.

$\Phi_0(T)$ steepens both at T_{crit}^{cat} and T_{crit}^{surf}, but the reasons in both cases are quite different. The steepening below T_{crit}^{surf} may be attributed to a steeper increase in the grain-boundary core charge, $Q^c(T)$. The abrupt change in the core charge's behaviour may be explained with $c^b(v_O^{\bullet\bullet})$ abruptly staying constant below T_{crit}^{cat}, at a value that is much higher than the chemical equilibrium concentrations for $T < T_{crit}^{cat}$. Larger Q^c generally have an enhancing effect on Φ_0. Consistently, the Φ_0 values at a specific temperature are higher in the 2RE regime than in the 1RE regime. The abrupt steepening in $\Phi_0(T)$ at T_{crit}^{cat}, in contrast, stands opposed to an abrupt flattening in $Q^c(T)$. Increases in Q^c can be accomodated much more effectively in the FE regime than in the RE regimes, where an enrichment in Acc'_{Ti} is possible only by a valence change. Owing to this weaker shielding capability, the space-charge layer reacts, in the 1RE regime, much more sensitively to increases in Q^c than it does in the FE regime, and hence, Φ_0 increases more steeply despite the flatter increase in Q^c.

S2 Different grain-boundary parameters

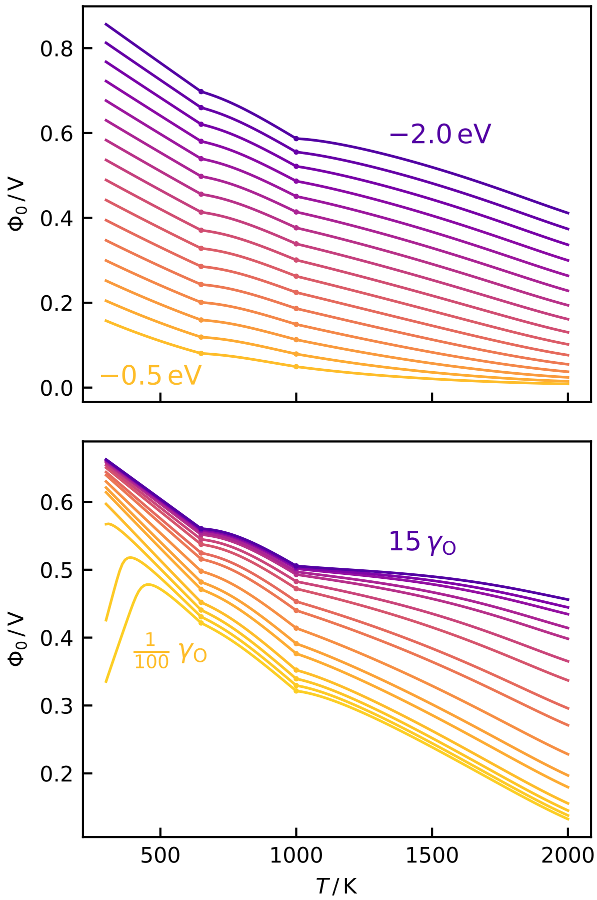

Figure S2: Temperature dependence of the space-charge potential, Φ_0, for different grain-boundary parameters: (a) different values of the $v_\text{O}^{\bullet\bullet}$ segregation energy, $\Delta\mu_\text{v}^{\ominus}$ (with $\gamma_\text{O}^\text{c} = \gamma_\text{O}/20$; (b) different values of the core oxygen-site density, γ_O^c (with $\Delta\mu_\text{v}^{\ominus} = -1.5\,\text{eV}$). In all cases, we set $T_\text{crit}^\text{cat} = 1000\,\text{K}$ and $T_\text{crit}^\text{surf} = 650\,\text{K}$.

Clearly, the non-trivial temperature dependence of Φ_0 with kinks at the critical temperatures applies over a wide range of grain-boundary core properties, i.e., the differences that are due to different temperature ranges must be expected to be encountered across different grain-boundary types.