



Research Highlight

Seeing is believing: negative capacitance captured at both nano- and macro-scales

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The phenomenological theory of ferroelectrics was developed by Landau-Devonshire about 70 years ago in the 1940s [1], and the celebrated theory has been very successful in analyzing ferroelectric phase transitions [2,3], domain structures [4], as well as strain engineering [5,6]. Recently, it has been demonstrated that it is also capable of capturing emerging polarization textures such as a ferroelectric vortex [7], proving its wide applicability not only at phenomenological level, but also at the atomic scale. The idea is simple, that the internal energy density of a ferroelectric depends on polarization, the order parameter, and upon the phase transition, the energy becomes degenerate, corresponding to multiple ferroelectric variants arising from broken symmetry. Such behavior is captured well by a polynomial of polarization with temperature-dependent coefficient, as Devonshire originally demonstrated for barium titanate [1].

Hidden in such a Landau-Devonshire energy landscape is a region with negative capacitance, as shown in Fig. 1a, wherein the second derivative of internal energy density with respect to the polarization is negative, and thus the state is usually unstable and inaccessible [8]. This negative capacitance region arises naturally from the double energy well structure of the Landau-Devonshire polynomial with local maxima, though its implication has not been noted for quite a while. In 2008, it was suggested that such negative capacitance can actually be utilized to enhance the effective capacitance of ferroelectric-dielectric heterostructures, and thus help reducing operating voltage and power consumption in microelectronics, mitigating the so called Boltzmann tyranny [9]. This works because when a normal dielectric is connected in series with a ferroelectric having negative capacitance, the effective dielectric constant k^* of the heterostructure is governed by inverse of rule of mixture [10]

$$\frac{1}{k^*} = \frac{f_d}{k_d} + \frac{f_f}{k_f}, \quad (1)$$

wherein f and k are volume fraction and dielectric constant of constituent phases, and the subscripts d and f refer to dielectric and ferroelectric phases, respectively. When the dielectric constant of the

ferroelectric phase becomes negative, the effective dielectric constant of the heterostructure as well as its capacitance is enhanced. While the idea is straightforward, the direct observation of such negative capacitance remains elusive, despite some indirect experimental evidences.

In two recent papers published back to back in *Nature*, teams from USA and Germany have reported direct experimental observations of regions of negative capacitance in ferroelectric from two distinctive perspectives. The USA team, led by Sayeef Salahuddin [11], studied previously reported polar vortex structure in a SrTiO₃/PbTiO₃ superlattice in detail, and they successfully mapped the distribution of electric field and polarization simultaneously using advanced transmission electron microscopy (TEM) coupled with ab initio calculations. This enabled the team to reconstruct the distribution of internal energy density, as shown in Fig. 1b, wherein the region of negative capacitance is clearly identified near the vortex core, in good agreement with both phase field simulations and first-principles-based calculations. The key is that the energy density near vortex core is higher, but compensated by other energetic contributions and thus is stabilized, making it possible to access this negative capacitance region at atomic scale using TEM.

In a sense, the USA team took advantage of the high energy vortex core that is stabilized at the atomic scale, and thus gain temporal advance at the expense of spatial scale. The German team led by Michael Hoffmann [12], on the other hand, utilized brute force to track the transient polarization with high temporal resolution at the order of 100 ns. While losing spatial resolution, they have successfully captured reversible polarization of TiN/Ta₂O₅/Hf_{0.5}Zr_{0.5}O₂/TiN heterostructure at macroscopic scale in the unstable region of energy landscape during polarization switching, as shown in Fig. 1c, which reveals S-shape P - E curve as well as the energy barrier between the double wells, as originally envisioned by Devonshire!

It is quite remarkable that the simple phenomenological theory of Devonshire originally developed for macroscopic phenomenology not only captures the thermodynamic equilibrium of ferroelectrics well, but also predicts unstable energy landscape in good agreement with experiments. Even more impressive is that it captures the microscopic structure of such an unstable

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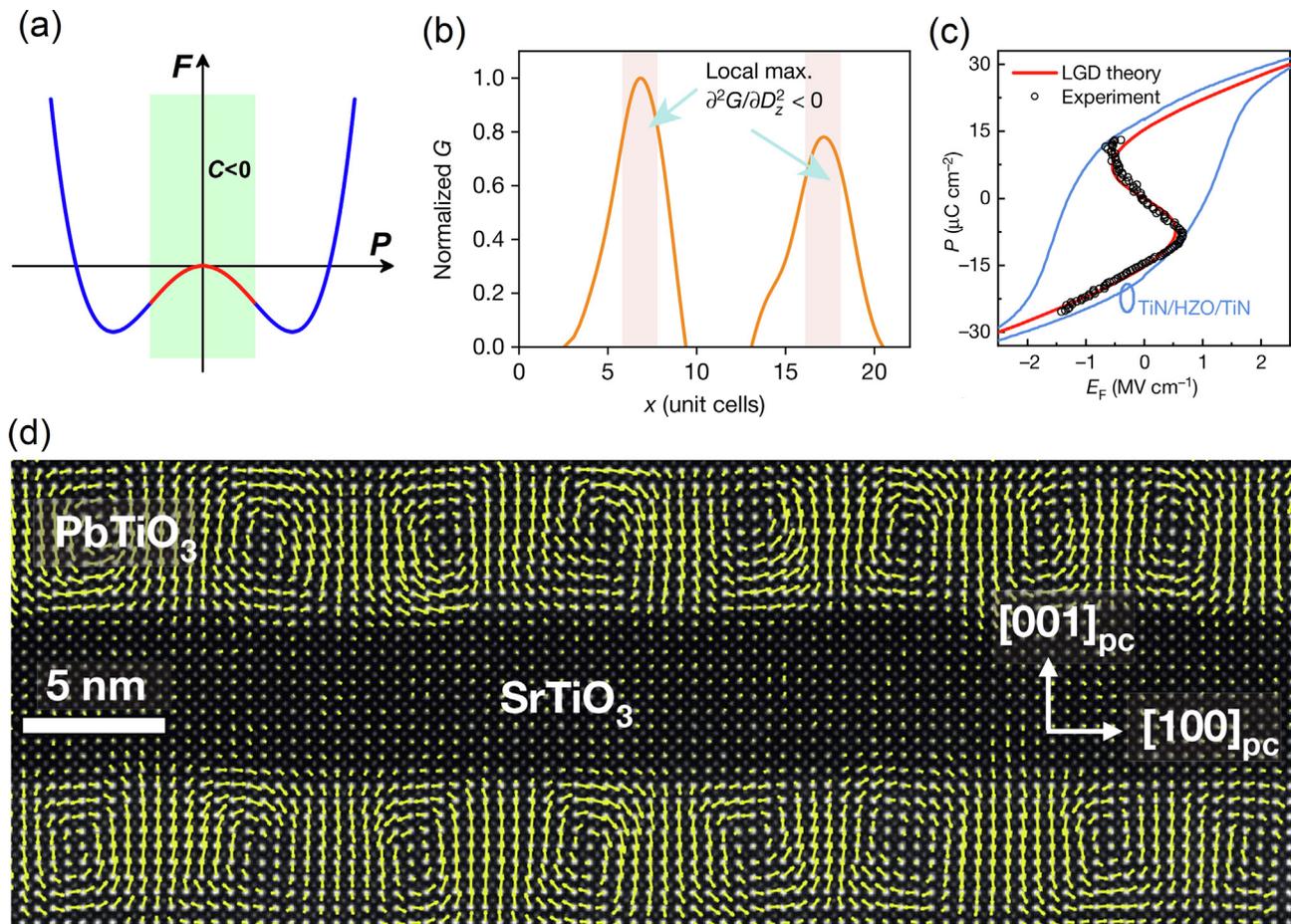


Fig. 1. (Color online) Negative capacitance captured at both nano- and macro-scales. (a) Schematic of Landau-Devonshire energy landscape with double energy wells, in which the green shading region can show negative capacitance effect with $C < 0$. (b) Local energy density near vortex core in SrTiO₃/PbTiO₃ superlattice, wherein the double derivative of internal energy density is negative, corresponding to negative capacitance. Reprinted with permission from Ref. [11]. Copyright © 2019, Springer Nature. (c) S-shape P - E curve of Hf_{0.5}Zr_{0.5}O₂ layer from both experiment and Landau-Devonshire theory. Reprinted with permission from Ref. [12]. Copyright © 2019, Springer Nature. (d) Array of ferroelectric vortex in SrTiO₃/PbTiO₃ superlattice. Reprinted with permission from ref. [7]. Copyright © 2016, Springer Nature.

negative capacitance region at atomic scale, suggesting that the theory is deep and elegant in microscopic mechanism as well. We expect that more direct evidences of such negative capacitance will be discovered with the advance of experimental techniques, and practical applications of such phenomenon may emerge on the horizon. It remains a big challenge to realize and control such negative capacitance for realistic device applications, and in this regard, the array of ferroelectric vortex in SrTiO₃/PbTiO₃ superlattice [7], as shown in Fig. 1d, provides a viable option. Note that such vortex structure is stable, and when arranged in parallel with each other as shown in Fig. 1d, the effective dielectric constant of the ferroelectric layer would be equivalent to that of individual vortex. The key then is to control and engineer the thickness and periodicity of the superlattice, so that the size of the vortex is decreased and thus the vortex core dominates, making the dielectric constant of individual vortex, and thus the ferroelectric layer, negative. If this is realized, then the effective dielectric constant of superlattice structure will be enhanced, which can be easily verified in capacitance structure. While there is substantial technical obstacle, these two works pave a way for such exciting opportunities.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

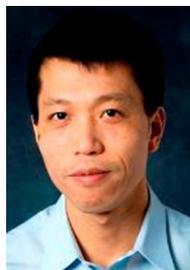
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