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Phase Transitions and Domain Structures in Nanoferroelectrics.

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A review of the Landau-type theory of size effects in ferroelectric phase transitions will be presented. An aspect of this theory, a question about the "critical thickness" of ferroelectric thin films will be the main emphasis. This question can be reduced to that of the size dependence of temperature of ferroelectric phase transition by taking into account two possibilities for such a transition: formation of (i) single- or (ii) multi-domain ferroelectric state. In a defect-free sample, two factors would define which of these possibilities is realized: the depolarizing field and the specific features of the sample surface reflected in the boundary conditions for the Landau-type equations in addition to the conventional electrodynamics boundary conditions. The possibility of the transition into the single domain state strongly depends on a character of electrodes and the additional boundary conditions, while it is much less important for the multi-domain case. In realistic conditions, the transition would proceed into the multi-domain state, especially in near cubic ferroelectrics, e.g. films of cubic perovskites with an elastic mismatch between the film and a substrate. Importantly, the shift of a transition temperature with respect to a bulk is relatively small in this case. The message is that, while studying the question about the "critical thickness", multi-domain states rather than single domain ones should be considered first of all, contrary to the approach in some recent papers where only monodomain state was studied.. In particular, there is no definite indication of ultimate "critical thickness" for a multi domain ferroelectric state in nearly cubic samples. Along with ultra thin films the ferroelectric nanopowders are also intensively studied now. Here the size effects are more complicated because of long-range interaction between the particles. The problems which the theory faces here are briefly commented upon. It is worth mentioning that several important results in the theory of the size effects have been obtained long ago but, unfortunately, seem not to be well known by the ferroelectrics community. They will be exposed together with more recent results obtained in collaboration with A.Bratkovsky at Hewlett-Packard Laboratories, Palo Alto.