Loss of elastic stability and formation of inhomogeneous states at phase transitions in thin films on substrates

A. P. Levanyuk [1] , S. A. Minyukov [2] , I. B. Misirlioglu [3]

[1] *University of Washington, Department of Physics, Seattle, WA 98105 USA*

[2] *Shubnikov Institute of Crystallography of Federal Scientific Research Centre "Crystallography and Photonics" of Russian Academy of Sciences, Moscow 119333, Russia*

[3] *Faculty of Engineering and Natural Sciences, Sabanci University, Tuzla/Orhanli 34956 Istanbul, Turkey*

Within the Landau-like approach we study stability of homogeneous states near phase transitions in thin films on substrates. The order parameter is electrically neutral in order to exclude the effects of the depolarizing fields and concentrate on the elasticity effects. We consider the case where the first-order transition in free crystal would convert into a second order when in the film on a substrate if the system remained homogeneous. Limit of stability of the homogeneous state is found analytically, though approximately. Numerical simulations provide qualitatively similar results and reveal temperature evolution of the arising inhomogeneities

Author to whom correspondence should be addressed: A. P. Levanyuk, levanyuk@u.washington.edu

1. Introduction

All the known ferroelectric phase transitions in perovskite crystals are of the first order, i.e. discontinuous. However, in thin perovskite films on substrates the same phase transitions look continuous and fairly smeared. There is no consensus about the reason of this difference. Most of the researchers seem to agree with th**e** conclusion of Pertsev et al. [1] that partial clamping of the film material by the substrate converts the first order transition in $BaTiO_3$ and $PbTiO_3$ crystals into a second order one similar to the prediction of Devonshire [2] for a clamped $BaTiO_3$ crystal. Then the smearing of the phase transitions could be ascribed to different defects just as for bulk transitions. A disagreement with this conclusion has been voiced by Roytburd earlier [3] who pointed out that first order phase transitions in constrained systems procced normally through inhomogeneous two-phase states while only the homogeneous states were supposed by the above authors. However, Roytburd's specific arguments [4,5] were relevant for sufficiently thick films with strong first order transitions while thin films of perovskites whose first order transitions in the bulk are mainly relatively weak [6] are of the main current interest. These thin films are the focus of our attention.

We demonstrate that apart from the two-phase state formation because of possibility of the energy gain there is another mechanism leading to the inhomogeneity: loss of elastic stability due to specific anomalies of elastic moduli [7] which exist in homogeneous state of the low symmetry phase (LSP) in clamped films. These anomalies are especially pronounced if the continuous phase transition expected according to the theory [2,1] coincides with the tricritical point. Here we shall consider this case only, i.e. tricritical phase transitions**.** We shall use continuous medium Landau-like approach. A somewhat similar approach has been already used for treating two-phase states in partially clamped systems with weak first order transitions in bulk crystals [8] but presence of a substrate was not taken into account, i.e. virtually it was considered a slab clamped laterally but with free upper and lower surfaces. We shall show that the account for substrate changes the results qualitatively.

Moreover, we shall show that there are other inhomogeneous states which cannot be classified as two-phase ones. An exhaustive study of macroscopic inhomogeneities in thin films on substrates seems to be well ahead. In this paper we try to single out the effects of the stability loss. The limit of stability of homogeneous state with respect to any, including infinitesimal perturbations can be, in principle, found analytically. This is the only analytical part of the work. The further evolution of the inhomogeneous state as well as its detailed maps was studied by numerical simulations. Finding the limits of stability of the homogeneous state involves a lot of quite cumbersome algebra even if one makes reasonable approximations and is aimed to obtain qualitative results first of all as we do in this work. That is why we concentrate here on the simplest case of a one-component electrically neutral order parameter, isotropy of the elastic properties, not very thin films, and an infinitely rigid substrate.

The paper is organized as follows. In Sec.2 we describe the anomaly of the bulk elastic moduli near a tricritical phase transition in a thin film on a substrate supposing that the film remains homogeneous. This is to show that this supposition is dubious since conditions of elastic stability seem to be violated due to the anomaly. In Sec 3 we discuss qualitatively the meaning of this finding. In Sec.4 we report results obtained from our analytical study of conditions of elastic stability for a thin film on a substrate with the above mentioned restrictions. In Sec.5 we report the results of the numerical simulations aimed to define the appearance and the nature of the inhomogeneous state whose inevitability under certain conditions has been shown in Sec.3. In Sec.6 we discuss the obtained results and outline further studies in this field.

2. Anomaly of the bulk modulus at virtual tricritical transition in thin films on substrates. Violation of conditions of the elastic stability

The system, which we consider, is characterized by the Landau-like free energy:

$$F = \frac{\alpha}{2}\eta^2 + \frac{\beta}{4}\eta^4 + \frac{\gamma}{6}\eta^6 + r\eta^2\left(u_{11}+u_{22}+u_{33}\right) + \frac{\lambda+2\mu}{2}\left(u_{11}^2+u_{22}^2+u_{33}^2\right) + \lambda\left(u_{11}u_{22}+u_{11}u_{33}+u_{22}u_{33}\right) + 2\mu\left(u_{12}^2+u_{13}^2+u_{23}^2\right), \quad (1)$$

where η is the order parameter, λ and μ are, correspondingly, the Lame coefficient [9] and the shear modulus of the high-symmetry phase (HSP). This phase in absence of stresses is considered as the reference state for the strains. Only the coefficient α is supposed to depend on temperature changing its sign at the limit of stability of HSP (T_c).

Let us start with a free crystal. It is natural to assume that the equilibrium state of LSP is homogeneous, allowing us to easily find the equilibrium values of η and the strains as well as material parameters LSP. For a detailed explanation see [7]. The phase transition is of the first order if $\beta < 2r^2/K$, where K is the bulk modulus of the high-symmetry phase given as $K=\lambda+2\mu/3$. For a tricritical transition ($\beta = 2r^2/K$) and for the bulk modulus of the low-symmetry phase we have in this case:

$$\tilde{K} = \tilde{\lambda} + \frac{2\mu}{3} = K\frac{(K/r^2)\sqrt{-\alpha\gamma}}{1+(K/r^2)\sqrt{-\alpha\gamma}} \cong \frac{K^2}{r^2}\sqrt{-\alpha\gamma}\,, \quad (2)$$

i.e. that the bulk modulus is zero at the tricritical point (Fig. 1). This is a very old result obtained by Landau in 193**5** [10].

Consider now an epitaxial film on an isotropic substrate. The film plane contains axes 1 and 2. Assume (for a moment only!) that the phase transition is into homogeneous state. To calculate the equilibrium value of η and the strains we put all the strain components in Eq.1 to zero but u_{33}. The second order transitions are realized now if $\beta > 2r^2/(\lambda+2\mu) = 2r^2/\overline{K}$, where $\overline{K}$ is the longitudinal modulus of LSP. Since $\overline{K} > K$ it is possible that $2r^2/K > \beta > 2r^2/\overline{K}$, i. e. the phase transition which is of first order in a free crystal becomes second order in the film on a substrate (if the film remains homogeneous) which was concluded in [1] for $BaTiO_3$ and $PbTiO_3$. Tricritical transition mentioned in the title of this Section corresponds to $\beta = 2r^2/\overline{K}$.

To calculate the elastic moduli of LSP we should take into account all the components of the strain tensor since we are now interested in strains and stresses which are local. By the same method as for the free crystal we find [7]:

$$\tilde{\overline{K}} = \tilde{\lambda} + 2\mu = \overline{K}\frac{(\overline{K}/r^2)\sqrt{-\alpha\gamma}}{1+(\overline{K}/r^2)\sqrt{-\alpha\gamma}} \cong \frac{\overline{K}^2}{r^2}\sqrt{-\alpha\gamma}\,, \quad (3)$$

i.e. at the tricritical transition in a thin film on a substrate the longitudinal modulus behaves in the same way as the bulk modulus in a free crystal. For the bulk modulus of LSP we have now:

$$\tilde{K} = \tilde{\lambda} + \frac{2\mu}{3} = \frac{-4\mu/3+(K\overline{K}/r^2)\sqrt{-\alpha\gamma}}{1+(\overline{K}/r^2)\sqrt{-\alpha\gamma}} \cong \frac{-4\mu}{3} + \frac{K\overline{K}}{r^2}\sqrt{-\alpha\gamma}\,, \quad (4)$$

i.e., the bulk modulus is negative ($\widetilde{K} = -4\mu/3$) at the transition and, naturally, in some vicinity of it (Fig. 2). What this means is discussed in the next Section.

3. Stability with respect to homogeneous and inhomogeneous perturbations

For a free body the negativeness of the bulk modulus means loss of stability with respect to homogeneous change of the volume. But for a film on substrate this is not possible and because of the clamping the only homogeneous strain which is possible here is changing of the thickness due to displacements perpendicular to the film plane. However this strain is controlled not by the bulk but by the longitunal modulus which is never negative and becomes zero just at the tricritical point (Eq.3). As a result for a tricritical transition (and, of course, for transitions which are not far from it) there is a temperature interval wherein the bulk modulus is negative but the elastic stability with respect to homogeneous strains is not lost.

This does not mean, however, that stability with respect to inhomogeneous perturbations is not lost either. Indeed, in inhomogeneous states any component of the strain tensor can be present, in principle though there are some restrictions for these components. For example, for a sinusoidal elastic inhomogeneity along axis 1 only one can easily see by different ways (including the Saint Venant conditions) that the strain components u_{22}, u_{12}, u_{13} are absent here. Looking for positive definiteness of the quadratic form

$$F = \frac{\widetilde{\lambda} + 2\mu}{2}\left(u_{11}^2 + u_{33}^2\right) + \widetilde{\lambda} u_{11} u_{33} + 2\mu u_{13}^2, \qquad (5)$$

which is obtained from Eq.1 after exclusion of η and putting to zero the three above mentioned strain components. The condition of positiveness of this quadratic form are μ>0 and

$$\widetilde{\lambda} + \mu > 0. \qquad (6)$$

We have singled out the last condition because in our case $\widetilde{\lambda} = -2\mu$ at the phase transition meaning that the condition (6) can actually be violated well before the phase transition. In our recent paper [7] we stated that the condition (6) defines the limit of the elastic stability with respect to inhomogeneous states. This was an error. In fact, it gives the limit of stability for extremely thick films only. Otherwise, one should take into account the boundary conditions as well as nonlocality of the elastic properties due to the term with gradient of η which has been omitted in Eq.1. Some results of the more consistent treatment are presented in the next Section.

4. Limit of elastic stability for thin films on infinitely rigid substrate

The method to find the limit of elastic stability is to find the value of a material constant ($\widetilde{\lambda}$ in our case) of the system of linearized governing equations for η along with the relevant displacements. In isotropic case all the directions are equivalent so we can limit ourselves to the x_1-axis so that the relevant displacements would be u_1, u_3. The equations are obtained from Eq.1 (with addition of the gradient energy term, $\delta(grad\eta)^2/2$) and the conditions of elastic equilibrium. Linearizing these equations close to equilibrium homogeneous values of η and the strains (η_e, u_{33e}), i.e. putting $\eta = \eta_e + \eta'$, $u_{33} = u_{33e} + u_{33}'$ etc. ($u_{11e} = 0$) and using the Fourrier expansion for the x_1-dependence: $\eta(x_1, x_3) = \sum_k \eta_k(x_3)\exp(ikx_1)$ etc. we obtain:

$$(\alpha + 3\beta\eta_e^2 + 5\gamma\eta_e^4 + 2ru_{33e} + \delta k^2)\eta' + 2r\eta_e\left(iku_{1k} + \frac{du'_{3k}}{dx_3}\right) - \delta\frac{d^2\eta}{dx_3^2} = 0, \quad (7)$$

$$\mu\frac{d^2u_{1k}}{dx_3^2} - (\lambda + 2\mu)k^2u_{1k} + ik(\lambda + \mu)\frac{du'_{3k}}{dx_3} + ik2r\eta_e\eta'_k = 0, \quad (8)$$

$$(\lambda + \mu)\frac{d^2u'_{3k}}{dx_3^2} - \mu k^2u'_{3k} + ik(\lambda + \mu)\frac{du'_{1k}}{dx_3} + ik2r\eta_e\eta'_k = 0. \quad (9)$$

The boundary conditions for Eqs (7-9) we write supposing that free surface of the film is at $x_3 = 0$ and the film/substrate interface is at $x_3 = l$. We have chosen $\frac{d\eta'_k}{dx_3}(0) = \frac{d\eta'_k}{dx_3}(l) = 0$, i.e. both surfaces are "neutral" with respect to η, $u_{1k}(l) = u'_{3k}(l) = 0$, meaning that the substrate is infinitely rigid while the standard free surface conditions for the strain tensor components are used.

Even for this simplified formulation the analytical treatment is quite laborious. The general solution of the system (7-9) has six arbitrary constants which should satisfy six boundary conditions. The resulting system of six homogeneous equations can have non-trivial solutions if the 6×6 determinant of the coefficients is zero which signals loss of stability for the given value of k. Since the only temperature-dependent coefficient is α the solutions of the transcendental equation which results from equating to zero the determinant give a function $\alpha_{ls}(k)$, where the subscript "ls" means "loss of stability" so that the function provides the value of α corresponding to the stability loss with respect to perturbations with the given k. Minimizing this function with respect to k we obtain the temperature of the real stability loss as well as the value of k for the "most dangerous" perturbation. This procedure is fairly standard and was repeatedly reviewed (see, e.g., [11]).

At the moment we have only preliminary results of the above described procedure. The main conclusion is that they are qualitatively similar to the results of even a more simplified treatment when the last term in Eq. (7) is omitted and η' can be excluded from Eqs.(8,9). The determinant becomes 4×4 and its analysis is relatively simple. The main findings are:

1. For the "most dangerous" perturbations the value of k is somewhat (not strongly) larger than l^{-1}, i.e. the sinusoidal inhomogeneity which arises after the stability loss has the period not very different from the film thickness.
2. Temperature of the stability loss (T_{ls}) increases when the film thickness decreases so that $T_c - T_{ls} \cong T_c - T_{ls}(l = \infty) - al^{-2}$, where a is a constant.
3. The value of a is very sensitive to the value of r, approximately $a \propto r^4$.
4. There is a "critical thickness" below which the stability loss does not occur.

5. Numerical simulations

We solved numerically the same equations of state as in the analytical treatment but with only difference that they were non-linearized. The non-linear part put limits to the effects of the stability loss allowing to obtain the amplitude of the arising modulation and not only to reveal the fact of the loss of stability as the linear theory does. In addition, their account allows revealing situations where inhomogeneous states are more energetically profitable than the homogeneous state despite the latter are stable with respect to small perturbations, i.e. metastable. Appearance of such states prevents from observing the loss of stability and to observe the latter one has to hamper the nucleation, which is necessary to a transformation of a metastable state into the stable one. One of

the ways of hampering the nucleation was to consider the inhomogeneities along one axis only which is also convenient technically since allows us to consider a 2D system. Being unsure that this excludes the nucleation completely we also tried different initial states for the simulations both homogeneous and randomly inhomogeneous ones. No difference in the temperatures of appearance of inhomogeneous state beyond the error margin of the simulations has been detected (±0.25°C). This allows us to hope that the formation of inhomogeneous states in the simulations was due to the stability loss.

In the numerical simulations we used Gauss-Seidel iterative scheme. substrate. The number of iterations was kept to 20K after which we did not observe any significant evolution of the system. All the differential equations were discretized to fit into a finite difference form and the equations for the stresses were expressed in terms of displacements u_1, u_3, which were then found simultaneously with η for a given temperature. The boundary conditions were taken as the same as for the analytical treatment mentioned in the previous sections. The numerical values of the material constants where chosen to be close to those of $BaTiO_3$.

The results for temperature of arising of inhomogeneous states are presented in Fig.3 together with the theoretical curve for the loss of stability of homogeneous states obtained from the simplified approach described above. The transcendental equations which appear in the analytical treatment were solved numerically. Despite of approximate character of the theoretical curve it has the same shape as the experimental one.

The most remarkable result of the numerical simulations is, probably, the maps of the order parameter and the strains. (Fig. 4). They are qualitatively different from what was considered both by Roytburd [4,5] and by Tselev et al. [8] where piece-wise homogeneous states were supposed to exist when the system consists of regions of symmetrical or non-symmetrical phases with boundaries of negligible thickness between them. Unlike these structures we observe fairly smooth distributions of the order parameter which are more like sinusoidal modulations of the homogeneous state rather than composite structures consisting of one of the two phases elements. Also interesting is evolution of the inhomogeneous structure with temperature (Fig.5). We see that the period of the sinusoidal distribution increases and its form changes becoming similar to periodically situated small inclusions of the low-symmetry phase. Remarkably, the inhomogeneous structure exists also in the region of stability of the high-symmetry phase this time similarly to what was found in [8] though the periodicity did not appear in their treatment.

6. Conclusions

We hope that we have convincingly demonstrated that the so-called second order phase transitions in thin films on substrates obtained from “weak” first order transitions due to the clamping may well be, in fact, much more complicated phenomena involving two phase transitions, one of them with the limit of overheating (loss of stability) and the other (to the symmetrical phase) whose nature has to be revealed. Formation of heterophase structures at the considered transitions has been suspected before this work [3] but we started a systematic study of the topic revealing both the perspectives and the difficulties. Now we are just in the beginning of a long way which, hopefully, will lead us to a better understanding of reasons of apparent smearing of ferroelectric phase transitions in the perovskite thin films. Taking into account a realistic substrate, the crystalline anisotropic elasticity, the depolarizing electric fields including interaction between the elastic inhomogeneities and the ferroelectric ones (domains) should give an idea about challenges which should be met before being in position to discuss quantitatively the experiment. We think, however, it does not seem impossible to meet these challenges with modern computational analysis tools.

Figure Captions

Figure 1. [7] Plot of the bulk modulus near tricritical transition in a stress-free isotropic body. The axes are normalized with respect to λ and the temperature of the tricritical transition, T_{tc}, $\lambda = 2.5\ \mu$. Vertical dashed line indicates T_{tc}. We do not consider the temperature dependence of the modulus in the HSP region and assume it is constant. LSP: Low symmetry phase, HSP: High symmetry phase.

Figure 2. [7] Plot of the normalized bulk modulus (red line) and the longitudinal modulus (blue line) of the isotropic film laterally restricted near the tricritical transition under the assumption of the homogeneous state. The axes are normalized with respect to λ and the temperature of the tricritical transition, T_{tc}, $\lambda = 2.5\ \mu$.Vertical dashed line is to indicate T_{tc}. The shaded region is the range of temperature where bulk modulus of the film is negative. We do not consider the temperature dependence of the moduli in the HSP region and assume it is constant. LSP: Low symmetry phase, HSP: High symmetry phase.

Figure 3. Thickness dependence of temperature of the transition from the homogeneous to inhomogeneous state (during heating). Both theoretical approximate curve and the numerical results are given.

Figure 4. Maps of η and the strains, u_{11} and u_{33} for the 8 nm (left) and 20 nm (right) films near the homogeneous-inhomogeneous transition temperature.

Figure 5. Maps to reveal the dependence of the period of the inhomogeneity on temperature in the 8 nm film on a rigid substrate, $r=1.5 \times 10^{10}$. Note that we have 131°C for the last map which is about a degree below the upper limit of existence of the inhomogeneous state (order parameter slowly relaxes to zero at 132°C) Also note that this is well below the temperature of thermodynamic first order transition in a free crystal (140°C) which is expected to signal appearance of the two-phase state according to [5,8].

Acknowledgement

A. L. is grateful to A. L. Roytburd for stimulating discussions.

References

1. Pertsev NA, Zembilgotov AG, and Tagantsev AK: Effect of Mechanical Boundary Conditions on Phase Diagrams of Epitaxial Ferroelectric Thin Films, Phys. Rev. Lett. 1998; 80: 1988-1991.
2. Devonshire AF: Theory of barium titanate. Phil Mag. 1949; 40: 1040-1063; Theory of barium titanate-Part II. Phil Mag. 1951; 42: 1065-1079.
3. Roytburd AL, Abstracts of Workshop on Fundamental Physics of Ferroelectrics, Washington DC; 2014.
4. Roitburd AL: Equilibrium structure of epitaxial layers. Phys. Status Solidi (a). 1976; 37: 329-339; Martensitic transformation as a typical phase transformation in solids. Solid State Physics, 1978; 33: 317-390.
5. Roytburd AL: Thermodynamics of polydomain heterostructures II. Effect of microstresses. J Appl Phys. 1998; 83**:** 239-245.
6. We consider as “weak” those first order transitions which transform at clamping into second order ones according to the theory [2,1].
7. Levanyuk AP, Minyukov SA, Misirlioglu IB: Negative bulk modulus and possibility of loss of

elastic stability near tricritical transition in thin films on substrates. Ferroelectrics. 2016; 500: 116-128.
8. Tselev A, Strelcov E,.Luk'yanchuk IA, Budai JD, Tishler JZ, Ivanov IN, Jones K, Proksh R, Kalinin SV, and Kolmakov A: Interplay between Ferroelastic and Metal-Insulator Phase Transitions in Strained Quasi-Two-Dimensional VO_2 Platelets. Nano Lett. 2010; 10: 2003-2011.
9. Landau LD and Lifshitz EM: Theory of Elasticity. Oxford: Pergamon Press; 1970.
10. Landau LD: On the theory of specific heat anomalies. In: ter Haar D, ed. Collected Papers of L. D. Landau. London : Gordon and Breach; 1965: 96-100.
11. Bratkovsky AM and Levanyuk AP: Continuous Theory of Ferroelectric States in Ultrathin Films with Real Electrodes. J Comput Theor Nanosci. 2009; 6: 465-490.
12. The following material constants are used in calculations: $\alpha = 6.6(T - T_c) \times 10^5 \,\mathrm{JmC}^{-2}$, $T_c = 130°C$, $\gamma = 40 \times 10^9 \;\; Jm^9 C^{-6}$, $r = 1.2 \times 10^{10} \,\mathrm{JmC}^{-2}$,$1.5 \times 10^{10} \,\mathrm{JmC}^{-2}$, $\lambda = \mu = 8 \times 10^{10} \,\mathrm{Jm}^{-3}$, $\delta = 5 \times 10^{-11} \,\mathrm{J\,m}^3/\mathrm{C}^2$.

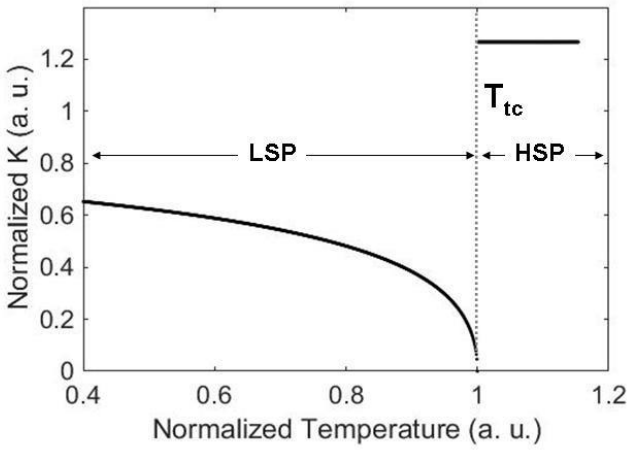

Figure 1

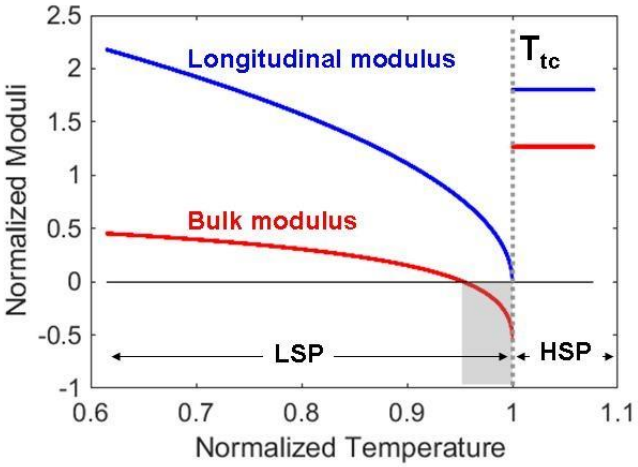

Figure 2

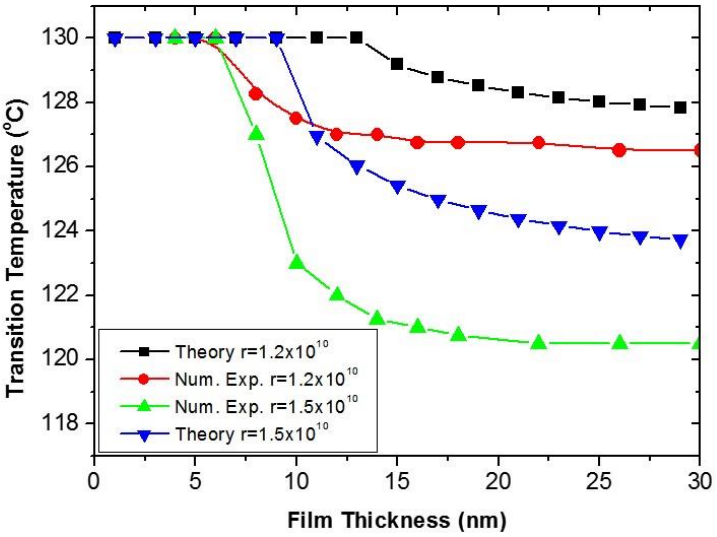

Figure 3

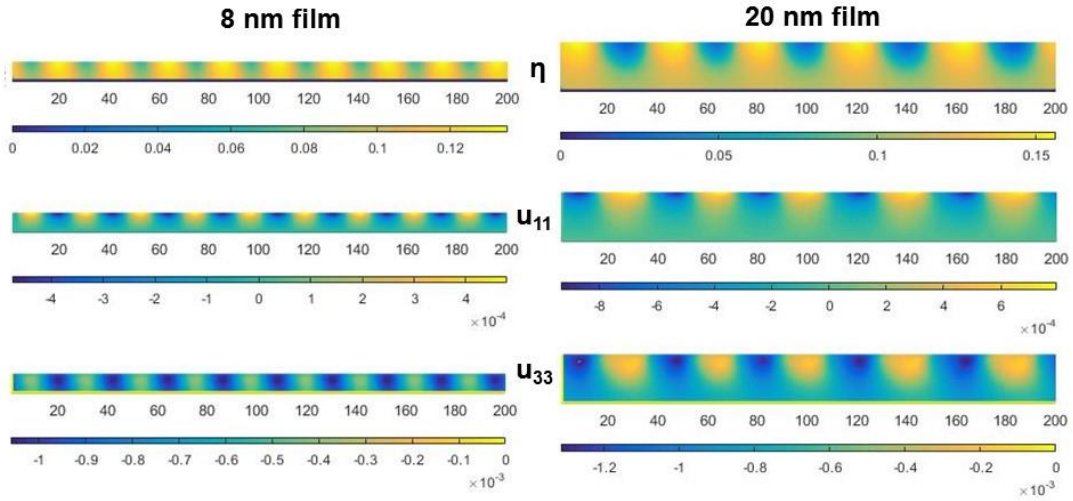

Figure 4

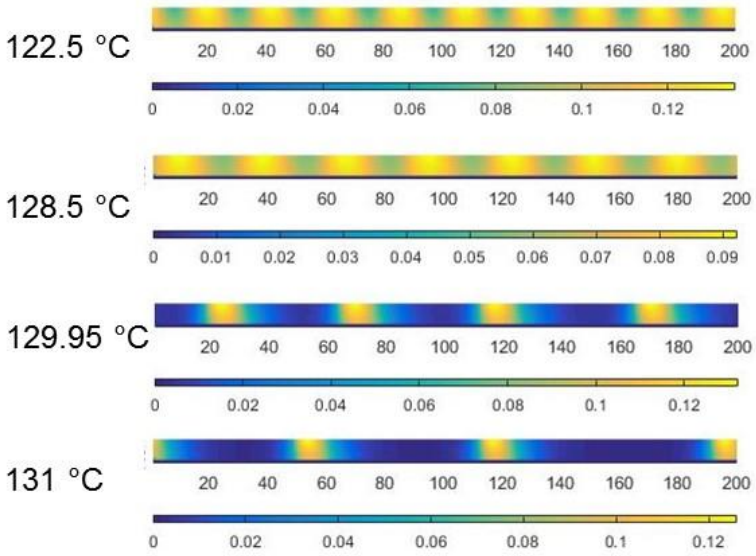
122.5 °C
20 40 60 80 100 120 140 160 180 200
0 0.02 0.04 0.06 0.08 0.1 0.12
128.5 °C
20 40 60 80 100 120 140 160 180 200
0 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09
129.95 °C
20 40 60 80 100 120 140 160 180 200
0 0.02 0.04 0.06 0.08 0.1 0.12
131 °C
20 40 60 80 100 120 140 160 180 200
0 0.02 0.04 0.06 0.08 0.1 0.12

Figure 5