

The Stress Driven Rearrangement Instabilities in Electronic Materials and in Helium Crystals

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ABSTRACT

At present, there is a consensus that various Stress Driven Rearrangement Instabilities (SDRI) are the implications of the mathematically rigorous theoretical Gibbs thermodynamics. Many applied researchers and practitioners believe that SDRI are also universal physical phenomena occurring over a large range of length scales and applied topics. There is a multitude of publications claiming experimental observation of the SDRI based phenomena. This opinion is challenged by other highly respected scholars claiming theoretical inconsistencies and multiple experimental counterexamples. Such an uncertainty is too costly for further progress on the SDRI topic. The ultimate goal of our project is to resolve this controversy.

The project includes experimental, theoretical, and numerical studies. Among various plausible manifestations of SDRI, the authors focused only on two most promising for which the validity of the SDRI has already been claimed by other researchers: a) stress driven corrugations of the solid-melt phase interface in macroscopic quantum ⁴He and b) the dislocation-free Stranski-Krastanov pattern of growth of semiconductor quantum dots. We devised a program and experimental set-ups for testing applicability of the SDRI mechanisms using the same physical systems as before but using implications of the SDRI theory for 2D patterning which have never been tested in the past.

INTRODUCTION

It is widely believed that the Gibbs variational paradigm (Gibbs, 1868, 1870) can be used as a reliable foundation of thermodynamics of heterogeneous systems allowing for the exploration of equilibrium and stability in these systems. Although universal stability conditions of such systems can be found in many textbooks on thermodynamics, they are, in fact, valid for the systems with liquid phases only. An adequate stability theory of heterogeneous systems with solid phases was suggested in 1982 and its basic results were summarized in a monograph (Grinfeld, 1991). The main conclusion of the theory was totally unexpected: contrary to the existing experimental data and observations, the theory claims that various morphological instabilities at the phase interfaces in heterogeneous systems should exist. Similarly to the consideration of Gibbs this general stability theory was based on the reliable foundation of nonlinear elasticity. Therefore, any possibility of artifacts, which are quite often generated by linear elasticity, was eliminated. Therefore, a difficult dilemma appeared: to accept the existence of multiple

undetected instabilities or to recognize the limited predictability potential of Gibbs classical paradigm. The controversy is still far from convincingly resolved. Physicists, however, took the possibility of multiple morphological instabilities seriously. They started to adopt the exact theory to their traditional techniques and look for potential experiments and existing data that would bring the results from the world of abstract ideas to the world of real physical phenomena. In addition to the experiments with the instability of “stressed crystal – melt” in ^4He , suggested by Grinfeld (1986), several other possibilities have been suggested (Nozieres, 1989, Carolis et al, 1989, Srolovitz, 1989, Leo and Sekerka, 1989, and many others later on). On the theoretical side, it was demonstrated that the many conclusions of the exact nonlinear theory of SDRI can be obtained on the basis of linear elasticity (Nozieres, 1989). That was quite an unexpected development since the classical theory of elastic stability cannot be based on linear elasticity, in principle: neither at finite nor at infinitesimal deformations. The analysis by Nozieres has changed the attitude of specialists regarding the earlier exciting paper of Asaro and Tiller (Asaro and Tiller, 1972) and has returned it to active life. Nozieres (Nozieres, 1989) made a remarkable effort to prove the “stressed crystal – melt” instability by appealing directly to a variational principle of minimum energy. Unfortunately, this part of Nozieres work, which is not based on assumption of linearity, still remains unappreciated by interested communities.

Of various SDRI effects, two plausible manifestations have received the most attention: i) stress driven corrugations of the solid-melt phase interface in macroscopic quantum ^4He and ii) the Stranski-Krastanov pattern of growth of semiconductor quantum dots. The first one was announced by Grinfeld (1986) and experimentally confirmed by Torii and Balibar (1992) and Thiel et al. (1992). The latter plausible manifestation was suggested by Srolovitz (1989) – its role has grown considerably after observation of the dislocation-free Stranski-Krastanow pattern of epitaxial growth of nanoscale solid films (Eaglesham and Cerullo, 1990, and LeGueus et al., 1990).

Since the successful experiments (Torii and Balibar, 1992 and Thiel et al, 1992) there has been no other published experimental work on the SDRI “stress crystal – melt” during the past 14 years. According to Nozieres (Nozieres, 1993), there is a conceptual problem with the SDRI-based interpretation of the dislocation free Stranski-Krastanow pattern of epitaxial growth. In the authors’ opinion these circumstances demand a more careful experimental verification of the SDRI-based interpretation of the two phenomena. Therefore, we suggest some new experiments with helium crystals and nanoscale solid thin films based on other conclusions of the SDRI theory. This combined effort is the main thrust of our research and of this paper.

Because of natural page limitation of this short paper neither of the aspects of the SDRI topic can be discussed in a detailed manner here. A much more complete description of the connection between the topics of Helium crystals and quantum dots can be found in Grinfeld (1993, 1994, 1995) (in particular, interested readers can find there a detailed derivation of the key formula (1) of this project). The advantages of using experiments with Helium crystals for studies of various materials science systems have been discussed in the special paper “Helium crystals as a probe in materials science” of Balibar and Nozieres (1994). Currently, both areas have the same main goal: it is to demonstrate the SDRI is not just a theoretical artifact of Gibbs thermodynamics but also a physical reality. A lot can be gained by studying the two phenomena in parallel.

Similarity in observed patterns would be strong evidence that both phenomena are indeed based on the same SDRI mechanism. Strong differences in the observed patterns would show that, at least, one of the phenomena has nothing in common with the SDRI mechanism (the Nozieres conjecture of 1993).

THE MORPHOLOGICAL INSTABILITY OF EPITAXIAL FILM VIA NOZIERES METHOD

Since Nozieres method is based on linear elasticity, it cannot be treated as a reliable thermodynamically acceptable proof of the SDRI. But it seems to be extremely convincing for a majority of physicists, and it is a very useful shortcut for getting the main quantitative results quickly. Let us consider a thin crystalline film of a thickness H coherently attached to a solid crystalline substrate with mismatch in the lattice parameters. It is the typical situation in various applications (epitaxial crystal growth, "coating" with thin films, engineering of interfaces and composites, etc...) that the films appear to be highly stressed. The stresses can be produced, say, by the misfit in the lattice parameters of the epitaxial film and the substrate or by the thermal stresses due to a discrepancy in the expansion coefficients of the film and the substrate. We use the notation T_1, T_2 for the in-plane principal misfit stresses generated in the unbounded film of uniform thickness. These parameters (together with the directions of the principal stresses) completely characterize the stressed state of the film with flat boundary since the upper boundary of the film is traction-free. The stressed crystalline film accumulates a certain amount of energy, E , consisting of two parts: the bulk (elastic) energy E^e and the surface energy E^{surf} . A corrugated film with the thickness deviation described by the function $\varepsilon M(x^1, x^2)$ of the in-plane coordinates x^1, x^2 will accumulate less elastic energy (E_{corr}^e), compared with the energy of a flat film (E_{flat}^e), which was calculated explicitly for the case of isotropic elastic substances by Nozieres (1989) and Grinfeld (1993, 1994, 1995). Referring interested readers to these publications for details, we present only a typical result for the case when the film and substrate have the same shear modulus μ and Poisson ratio ν :

$$E_{flat}^e - E_{corr}^e = -\frac{\varepsilon^2}{2\mu_f} \int_{-\infty}^{+\infty} dk_1 dk_2 |\vec{k}| |\Delta(\vec{k}) \Delta^*(-\vec{k})| [(1-\nu)T_n^2 + T_t^2] \quad (1)$$

The following additional notation is used in (1): $\Delta(\vec{k}) = \Delta(k_1, k_2)$ is the Fourier component of the surface corrugation $M(x^1, x^2)$ with the in-plane wave-vector \vec{k} ; we use the notation k and θ for the module of \vec{k} and the angle between \vec{k} and the principal direction of the in-plane stress T_1 ; then, e_a and q_a are the unit in-plane vectors parallel and orthogonal \vec{k} , respectively; $T_n = T_1 \cos^2 \theta + T_2 \sin^2 \theta$ and $T_t = (T_1 - T_2) \sin \theta \cos \theta$ are the normal and tangential components of the stress $\vec{T}_{\vec{k}}$ acting at the cross-section orthogonal to the wave-vector \vec{k} ; T_n and T_t are functions of the wave-vector \vec{k} . Formula (1) shows that the minimum energy surface pattern changes dramatically i) with changing external stresses T_1 and T_2 , as in the quantum helium experiments or ii) for different

lattice mismatch epitaxial systems, as in the quantum dot experiments. Experimental verification of this very implication of the SDRI theory is one of the central thrusts of our project.

THE EXPERIMENTS WITH QUANTUM ^4He

As is well known, ^4He remains in liquid state down to absolute zero. If the liquid ^4He is pressurized to 25 bars, it crystallizes into hcp solid phase at temperatures below 1.5 K. The liquid/solid interface of ^4He at low temperatures has many advantages in the study of SDRI such as small latent heat in liquid/solid conversion, rapid melting and freezing and efficient normal/superfluid convective heat flow. The length scale involved in the spatial variation in SDRI on ^4He solid is truly macroscopic (on the order of millimeters). The small magnitudes of both the surface tension and the shear modulus lead to relatively small critical uniaxial stress for the onset of SDRI.

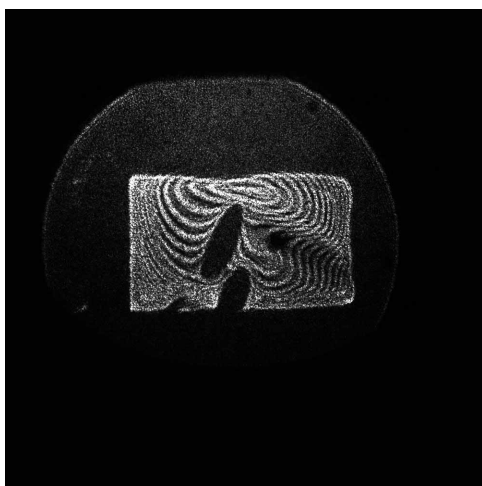


Figure 1. Interference pattern in solid helium-melt interface with externally applied stress.

As it was already mentioned, the SDRI “stressed crystal – melt” was experimentally confirmed by Torii and Balibar (1992) and Thiel et al. (1992). In order to make further studies we built a cryogenic optical interferometer apparatus including piezoelectric transducers for applying 2D-stresses to the ^4He crystal. Such a setup permits experimental verification of different surface patterns implied by the formula (1) and others announced in Grinfeld (1993 - 1995) and Kassner et al (2003).

An example of an interference pattern is shown in Figure 1. Here, the chamber is cooled to 1.25 K and pressurized to the melting pressure of 25 bars. After a solid seed appears, its size is decreased to less than 0.5 mm by removing helium from the chamber. When applied stress exceeds the threshold value for the sample, spectacular localized and irregular patterns begin to develop. The high values of applied stress induce several regions to form deep valleys whose nascent stages can be seen by the dense curled up interference line pattern (indicating rapid change in solid height). The lines become so dense as to produce dark patches in several regions. The relaxation phenomenon is a topic of future studies. Our observations indicate that the critical threshold strain is in a range which is fairly close to the theoretical predictions. Since our interference pattern does not show any periodicity, it is not possible to make comparison with the predicted critical wavelength. In view of our observation that the strain is not uniformly applied onto the sample, it may not be unreasonable that the instability does not form regular periodic pattern. Further optimization of this experiment is necessary in order to unambiguously verify the SDRI in the quantum Helium case.

THE DISLOCATION-FREE PATTERN OF EPITAXIAL GROWTH IN SEMICONDUCTOR NANO-FILMS

Another manifestation of SDRI as implied by formula (1) relates to the dislocation-free-Stranski-Krastanov (DFSK) growth of quantum dots. ARL's interest in the DFSK pattern of epitaxial growth of solid nanofilms goes well beyond the more limited goals of this project. With increasingly reduced dimensions of electronic devices, it will be necessary to explore quantum size effects in materials and devices at the nano-scale. Thus, the experimental and theoretical results offered by this project are extremely valuable and easily transferable at a later stage to the wide variety of strain-induced self-assembling nanostructures and devices. We wish to explore the question (Nozieres, 1993) on the validity of SDRI mechanism of DFSK pattern for materials that are of particular interest (e.g. InAs, GaAs, SiGe, etc).

Hundreds of experimental papers relating to III-V quantum dots have been published over 10-15 years. They have been reviewed in recent monographs (Bimberg, Grundmann, and Ledentsov, 1999; Yao and Woo, 2001). We refer interested readers to these comprehensive reviews. Contrary to our project, however, none of the experiments mentioned in these reviews has been designed from the standpoint of verification of applicability of the SDRI mechanism.

Our experimental work involves the growth of a series of strained-layer samples and the subsequent characterization of the morphology and the nanostructure using atomic force and transmission electron microscopy. An example experiment is a comparison of InAs grown on GaAs substrates (a system currently being used to form quantum dots as shown in Figure 2) with GaAs grown on InAs substrates (with a potential to form quantum antidots). These are binary semiconductors in which the strain induced in the thin epitaxial films would be equal in magnitude but opposite in sign (compressive for the former and tensile for the latter). This is an ideal system for testing

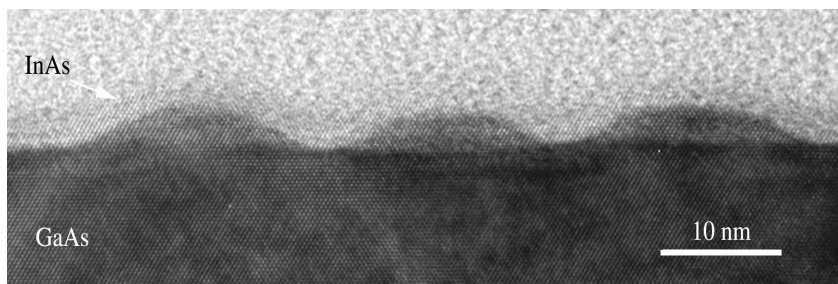


Figure 2 Cross sectional transmission electron micrograph of defect-free InAs quantum dots.

the predictions of the theoretical model. We have characterized the dependence on the growth temperature of the size, shape, and number density of a series of InAs quantum dots grown on GaAs substrates.

Complementary growths of GaAs films on InAs substrates are in progress. Another test experiment involves growth of the $\text{In}_{(x)}\text{Ga}_{(1-x)}\text{As}$ on InP substrates where the structure can be in tension or compression as a function of x . The results from the characterization of the morphology and nanostructure will be eventually correlated with the growth parameters and the theoretical studies and discussed in the light of the current theoretical views for the underlying mechanism.

NUMERICAL MODELING/VISUALIZATION OF DEFORMABLE STRESSED CRYSTALS

Computational work is based on numerical analysis of the mathematical problem formulated in the concluding section “The problem of equilibrium shape of deformable crystal” of the monograph (Grinfeld,1991) and analyzed further by Grinfeld (1991, 1993), Spencer and Tersoff (1997), Bonnetier et al. (1999) and others.

Multiple publications in physical literature related to numerical simulations of the SDRI effects appeared during last 10-15 years as well (we refer interested readers to the publications [21] and references therein). By its very nature, each scheme of numerical simulation brings one or numerical artifacts. The way to avoid these artifacts is to use a battery of various numerical schemes the hope that artifacts will be eventually eliminated by comparison.

Our numerical simulation of the quasi-static interface evolution is based on a combination of the level set method (Sethian, 1999, Osher and Fedkiv, 2002), the finite element procedure described in Fix and Strang (1974), and the moving mesh generation method of Strang and Persson (2005). The deformed interface is represented implicitly and propagated using the level set method. The elastostatic problem is discretized with a finite element method, using the same grid as the interface representation. A highly efficient matrix-free multigrid solver is used to solve the linear systems of equations, which allows us to use millions of degrees of freedom on a standard desktop computer.

The prestraining $\varepsilon_x, \varepsilon_y$ is applied on the discretized system by writing the total displacement field as a sum of a given stretched field $U_0 = \varepsilon_x X + \varepsilon_y Y$ and an unknown, periodic perturbation U . We then solve for U in $KU = -KU_0$, where K is the stiffness matrix with boundary conditions incorporated.

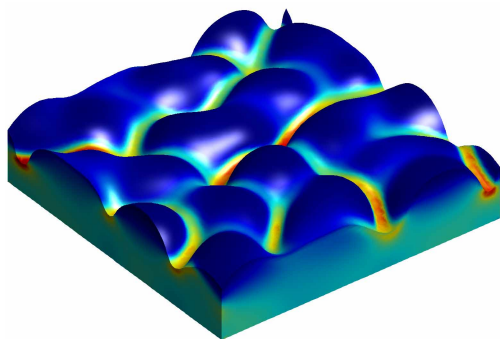


Figure 3. Morphology of the surface of stressed crystal - final configuration from the numerical modeling .

Figure 3 shows the results of a three dimensional simulation. Our computational domain is a block of dimensions $4 \times 4 \times 1$, discretized with a grid of size $193 \times 193 \times 49$ for a total of 1,825,201 nodes and 5,475,603 degrees of freedom. Initially, the surface is located a distance 0.66 from the bottom of the domain, and the height is perturbed at each node in the x^1, x^2 -plane by normally distributed random numbers with a standard deviation 0.0025. The material has Young's modulus $E = 1$, Poisson's ratio $\nu = 0.3$, and surface tension and $\sigma = 0.05$ in the simulation. Qualitatively, our pattern resembles the corrugation pattern obtained by

the McGill Advanced Materials group which can be found at www.miam.mcgill.ca/people.html.

The boundary conditions specify the displacement in the z -direction ($z = 0$ at the bottom face), and all displacements u_x, u_y, u_z are periodic at the left/right and the front/back faces. We use a timestep $\Delta t_1 = 0.05 \sigma$ for the curvature independent part, and

$\Delta t_2 = \Delta t_1/10$ for the motion by curvature. Animations of the quasi-static time evolution can be found at www-math.mit.edu/~persson/qdots.

CONCLUSIONS

The existence of various SDRI is an implication of Gibbs thermodynamics. Although there are several plausible physical manifestations of the SDRI it still remains unclear/unproved/challenged whether the SDRI is in fact the real physical mechanism of these phenomena. Currently, low temperature physics and solid-state nano-epitaxy physics have the same common goal regarding the SDRI: it is to demonstrate that the SDRI is not just a theoretical artifact of Gibbs thermodynamics but also a physical reality.

Experts of the SDRI topic in low temperature physics do not accept the SDRI as the underlying mechanism of the Dislocation-Free Stranski-Krastanov pattern of epitaxial growth (Nozieres, 1993). We do not completely share their opinion. We are certain, however, that criticism of low temperature physicists should not be ignored or silenced. On the contrary, we take this criticism seriously and think it should be discussed widely and openly. Yes, there are several plausible physical manifestations of the SDRI. But, there are also thousands of observations and experiments obviously contradicting predictions of the SDRI theory.

It would be naïve to expect that ultimate conclusion can be made overnight based on one single effort like ours. We strongly believe, however, that only carefully and meticulously designed multiple experiments are able to resolve the controversy of the two respectful groups of researchers. First fruits of the experimental program discussed above confirm the Nozieres (1993) conjecture to a certain extent. It would be premature, however, to make the ultimate decision of applicability of the SDRI mechanism for the Dislocation-Free Stranski-Krastanov pattern. It seems reasonable, however, to follow the advice of Nozieres and to begin thinking seriously about finding alternative physical mechanisms of nucleation and evolution of quantum dots.

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