Final Technical Report for Award # DE-FG02-05ER46227; FRS #527017

Multiscale Studies of the Formation and Stability of Surface-based Nanostructures

DOE Computational Materials Science Network

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Referenced to the submitted proposal, my work on this award was related to background sections 4.1.2, 4.1.3, and 4.1.5 on step energetics and dynamics, island nucleation and growth, and quantum size effects in growth of ultrathin metal films, respectively. Generically this is work on complex morphology and nanostructures at surfaces and interfaces.

Regarding proposed work, my efforts were directed toward sections on kinetic Monte Carlo (KMC) and step dynamics, with some attention to continuum modeling, focused on islands and quantum dots on flat and stepped surfaces. In some cases, long-range interactions, both elastic and electronic, were involved. The relevant sections are 4.2.1.3-4 and 4.2.2.2.

Collaborations fostered by this CMSN award:

Consistent with the goals of this program, this award led to several collaborations with other members of the team. Most notably, I interacted repeatedly with James W. Evans and his group at Iowa State on work to characterize capture zones (proximity cells) around growing islands. This led to their performing detailed simulations which uncovered shortcomings in our mean-field analysis, which led us to improve our analytic treatment of the problem. Specifically, this research eventually led to a comment by them and a reply by my group:
Reply to Comment by M. Li, Y. Han, and J.W. Evans on "Capture-Zone Scaling in Island Nucleation: Universal Fluctuation Behavior", Alberto Pimpinelli and T.L. Einstein, Phys. Rev. Lett. 104, 149602 [1p.] (2010) **DOI**: 10.1103/PhysRevLett.104.149602.
The essence of this work is that new islands due not nucleate randomly but rather form preferential near the borders between capture zones, where newly deposited atoms are least likely to diffuse quickly to a preexisting island.

As a result of several discussions with Michael Tringides at Iowa State, he applied our capture zone analysis to his extensive data on islands (Pb on Si) with heights determined by quantum size effects. We are still working on analysis of his data.

Over the years I have had many interactions with K.-M. Ho and C.-Z. Wang on a wide range of topics, including my belief that quantum islands extend down to the substrate rather than riding on the wetting layer that is known to permeate between the islands, an idea that they later confirmed with painstaking calculations.

Over the years I have had broad and continued discussions with Zhenyu Zhang at U. of Tennessee and formerly at ORNL, most notably on quantum size effects (which after many iterations led to a Phys. Rev. Letter, cited below), but also on adsorption on graphene, electromigration, and other topics. I had arranged for a graduate student to spend some weeks at ORNL and currently my postdoc is being supported through U. of Tennessee.
The PRL showed that Friedel oscillations on Pb(111) decay more slowly than for other metal surfaces, due to the unusual shape of lead's Fermi surface. The paper carefully characterizes the oscillatory behavior of electron density and displacements as a function of distance from the

surface, but also the superoscillatory behavior of the envelope. It provides for the first time a lucid explanation of why quantum oscillations are exceptionally robust in Pb(111) films.

I submitted nuggets on correlations in nano-scale step fluctuations, comparing simulation and experiments, and on edge stiffness of islands as a function of edge orientation.

Many projects (in particular, the PRL about quantum size effects in Pb(111) films) begun under this award came to fruition only later on under subsequent funding from the CMCSN program.

6a: Publications acknowledging CMSN support:

Correlations in Nanoscale Step Fluctuations: Comparison of Simulation and Experiments, F. Szalma, D.B. Dougherty, Ellen D. Williams, Michael I. Haftel, and T.L. Einstein, Phys. Rev. B 73, 115413 [10 pp.] (2006). **DOI:** 10.1103/PhysRevB.73.115413

Extended Lattice Gas Interactions of Cu on Cu(111) and Cu(001): Ab-Initio Evaluation and Implications, T. J. Stasevich, T.L. Einstein, and S. Stolbov, Phys. Rev. B 73, 115426 [7 pp.] (2006). **DOI:** 10.1103/PhysRevB.73.115426

Analytic Formulas for the Orientation Dependence of Step Stiffness and Line Tension: Key Ingredients for Numerical Modeling, T.J. Stasevich and T.L. Einstein, [SIAM-]Multiscale Model. Simul. 6, 90–100 (2007) [cond-mat/0609237] **DOI:** 10.1137/060662861

Capture-Zone Scaling in Island Nucleation: Universal Fluctuation Behavior, Alberto Pimpinelli and T.L. Einstein, Phys. Rev. Lett. 99, 226102 [4pp.] (2007) **DOI:** 10.1103/PhysRevLett.99.226102 [cond-mat/0612471].

Effect of Impurities on Pentacene Island Nucleation, B.R. Conrad, Elba Gomar-Nadal, W.G. Cullen, A. Pimpinelli, T.L. Einstein, and E.D. Williams, Phys. Rev. B 77, 205328 [5pp.] (2008) **DOI:** 10.1103/PhysRevB.77.205328.

Relaxation of Terrace-width Distributions: Physical Information from Fokker-Planck Time, Ajmi BH. Hamouda, Alberto Pimpinelli, and T.L. Einstein, Surface Sci. 602, 3569–3577 (2008) **DOI:** 10.1016/j.susc.2008.09.041

Strong Quantum Size Effects in Pb(111) Thin Films Mediated by Anomalous Friedel Oscillations, Yu Jia, Biao Wu, Chong Li, T.L. Einstein, H. H. Weitering, and Zhenyu Zhang, Phys. Rev. Lett. 105, 066101 [4 pp] (2010) **DOI**: 10.1103/PhysRevLett.105.066101.

Invited talks benefiting from this CMSN award:

CMSN Workshop, Madison, WI, Oct. 2005: Straddling Atomistic/Discrete and Nano/Mesoscale Perspectives on Vicinal Surfaces: Using the Step-Continuum Model to Study the Statistical Mechanics of Steps

IPAM, Los Angeles, Nov. 2005: Straddling Atomistic/Discrete/Lattice Gas and Nano/Mesoscale Perspectives on Islanded and Vicinal Surfaces: Using the Step-Continuum Model to Study the Statistical Mechanics of Steps (poster since post-deadline)

U. Blaise-Pascal, Clermont-2, Aubière, France, Jan. 2006: Manière de Regarder des Marches sur les Surfaces Cristallines: Une Physique Familière sous une Nouvelle Apparence (in French)

2nd International Workshop on Physics and Technology of Thin Films (IWTF2), Prague, Czech Republic, June 2006: Going Beyond Minimal Models of Step Fluctuations and Lattice-Gas Interactions: Confronting Reality in the Step-Continuum Model

CMSN Workshop, College Park, MD, Oct. 2006: Scaling of Capture-Zone Distributions: Applying Ideas from Universality of Fluctuation Phenomena to Islanding

Nonequilibrium Interface Dynamics: Theory and Simulation from Atomistic to Continuum Scales (nid07), U. Maryland, April 2007: Application of the Wigner Distribution to Non-equilibrium Problems at Surfaces: Relaxation, Growth, and Scaling of Capture Zones

U. New Hampshire, Durham, NH, April 2007: Steps on Crystalline Surfaces: From Elementary Models to Universal Fluctuation Phenomena

Fluctuations and Scaling in Materials, Todi, Umbria, Italy, satellite meeting to Statphys23, July 2007: Fluctuations and Scaling of Steps on Crystal Surfaces: Revelations from Random Matrix Theory

CMSN Workshop, Iowa State U, Ames, IA, Oct. 2007: Impurity Decoration for Crystal Shape Control: C_{60} on Ag(111)

Cargèse Summer School on NanoSteps: Self-organized nanostructures on crystal surfaces, Corsica, France, July 2008: 1) Interactions Between Steps: Entropic, Elastic, and Electronic, and Implications for Spatial Correlations 2) Step Fluctuations in Equilibrium 3) Applications of the Generalized Wigner Distribution to Nanostructures on Surfaces: Universal Fluctuation Phenomena (with Alberto Pimpinelli, Rajesh Sathiyanarayanan, Ajmi BHadj Hammouda, and Kwangmoo Kim) 4) Influence of Impurities on Capture Zones and Scaling in Thin-film Growth (with Ajmi BH. Hamouda, R. Sathiyanarayanan, A. Pimpinelli), 5) Effects of Short-range Behavior on Interaction Strength Measurements: A Study Using Monte Carlo Simulations (with Rajesh Sathiyanarayanan, Ajmi BHadj Hammouda, and Alberto Pimpinelli)

CMSN Workshop, Gatlinburg, TN, Oct. 2008: Small Pyramidal Mounds on Cu(001): Role of Impurities in Growth

Hebrew University, Jerusalem, May 2009: Evolution of Size Distributions during Relaxation and Growth on Surfaces

Technion, Haifa, Israel, June 2009: Evolution of Size Distributions during Relaxation and Growth on Surfaces

Virginia Tech, Blacksburg, Aug. 2009: Steps on Surfaces and Their Evolution: From Elementary Models to Universal Fluctuation Phenomena: What does the time between buses in Cuernavaca have to do with step separations?

CMSN Workshop, Denver, Oct. 2009: Adsorption contours, interactions, and assembly of benzene on Cu(111): Application of van der Waals DFT and of surface-state-mediated interactions en route to study of quinone photovoltaics

German Physical Society (DPG), Symposium on Crystal Growth Kinetics, Regensburg, Germany, March 2010: Modeling the Role of Co-deposited Impurities in Growth: What Causes the Distinctive Step Meandering and Pyramidal Mounds on Cu(001)

Appendices on following pages: Continuation reports submitted in 2006 and 2007 for this award.

2006 CONTINUATION REQUEST FOR
DOE GRANT DE-FG02-05ER426226

COMPUTATIONAL MATERIALS SCIENCE NETWORK
Cooperative Research Team on *"Multiscale studies of the formation and stability of surface-based nanostructures"*

PROGRESS REPORT

The team at University of Maryland, led by Prof. Theodore L. Einstein, is principally one postdoctoral associate, Dr. Ferenc Szalma, working about half time on the project, with contributions from graduate students Timothy J. Stasevich and Rajesh Sathiyanarayanan.

The work performed so far includes three related but distinct topics:

(a) characterization of fluctuations on island edges, with applications to Pb(111)
(b) characterization of orientation dependence of stiffness, the inertial parameter of steps
(c) calculation of characteristic energies to parametrize lattice-gas models of surface phenomena, with emphasis on role of multisite interactions

Accomplishments

a) Since fluctuations become progressively a larger fraction of cluster motion as size decreases, detailed understanding is an important ingredient to describing nanoscale phenomena. Our work to date has focused on structures on Pb(111), for which there is abundant data at Maryland. We have confronted experimental autocorrelations using kinetic Monte Carlo simulations, finding good agreement at room temperature and evidence of new processes at higher temperature [1]. b) Since step stiffness is the "inertial parameter" that weights the response of steps to driving forces, it plays a crucial role in the dynamics of nanoscale structures. We have shown that the typical assumption of isotropy is poor, especially near facet directions, and have developed remarkably simple formulas to describe the angular dependence at most orientations on the two principal faces of fcc metals [2,3]. c) While lattice-gas models have long been invoked to describe the energetics of atoms on surfaces, it has only recently become possible to calculate reliably these energies to verify that phenomenologically-derived parameters correspond to actual values. We have calculated such energies in conjunction with computation of the step stiffness based on such models [4]. The results we find are generally consistent with the values we estimated based on using statistical mechanical models to fit experimental data for the dependence of step stiffness on orientation and temperature.

Current and future work

In area a) we are collaborating with Ho, Wang, and Tringides at Iowa State to understand behavior of nanoscale structures on Pb(111). We will investigate how our work on single-layer islands generalizes to multilayer islands that are stabilized by quantum size effects. Our experiences on island properties, rooted in the step continuum model, will add new perspectives to this effort. We will consider how the key property of stiffness is altered by the higher, quantum-dominated islands. For islands on Si(111) there have been estimates of how this change scales with height. We have also considered the role of

microfacets and edges on pyramidal islands [5], and will apply our thinking to this metallic system. With regard to thrusts b) and c), we will characterize the stiffness and free-energy anisotropies of the island edges. In particular, the latter suggests that if one is to include influential relaxations when casting the problem into a lattice gas model, it is important to include multi-site interactions, as we have been investigating for various fcc metals.

In our lattice models we will collaborate with Evans at Iowa State, as well as Zhang at Oak Ridge and Liu at Utah. We are eager to see how the elastic effects that they are studying will affect our parametrization scheme. We will also continue to do kinetic Monte Carlo simulations [1] in conjunction with their investigations. We are currently verifying the power of our analytic formulation of the step stiffness [5]: steps that are initially pinned in strikingly irregular configurations in experiments at Maryland—discussed in part by Prof. E. D. Williams at the CMSN coordination meeting in October 2005 (U. of Wisconsin, Madison)—on Ag(111) are monitored as the steps are depinned and relax toward equilibrium. In parallel, finite element simulations are being carried out by collaborators at Cesar in Germany using our analytic expression. The correspondence is excellent. We will work with Shenoy at Brown, an expert in continuum modeling, to generalize this procedure, which we expect to be of interest to all members of the CMSN collaboration.

References

1. "Correlations in nanoscale step fluctuations: Comparison of simulation and experiments," F. Szalma, D. B. Dougherty, M. Degawa, Ellen D. Williams, Michael I. Haftel, and T. L. Einstein, Phys. Rev. B **73**, 115413 (2006) (citing DOE-CMSN support).

2. "The Effects of Next-Nearest-Neighbor Interactions on the Orientation Dependence of Step Stiffness: Reconciling Theory with Experiment for Cu(001)**,"**T. J. Stasevich, T. L. Einstein, R. K. P. Zia, M. Giesen, H. Ibach, and F. Szalma, Phys. Rev. B **70**, 245404 (2004).

3. "Low-Temperature Orientation Dependence of Step Stiffness on {111} Surfaces," T. J. Stasevich, H. Gebremariam, T. L. Einstein, M. Giesen, C. Steimer, and H. Ibach, Phys. Rev. B **71**, 245414 (2005).

4. "Extended lattice gas interactions of Cu on Cu(111) and Cu(001): Ab initio evaluation and implications," T. J. Stasevich, T. L. Einstein, and Sergey Stolbov, Phys. Rev. B **73**, 115426 (2006).

5. "Accurate Explicit Analytic Expressions for the Orientation Dependence of Step Line Tension and Stiffness: Key Ingredient for Numerical Modeling," T. J. Stasevich and T. L. Einstein, in preparation.

2007 CONTINUATION REQUEST FOR
DOE GRANT DE-FG02-05ER46227

COMPUTATIONAL MATERIALS SCIENCE NETWORK
Cooperative Research Team on *"Multiscale studies of the formation and stability of surface-based nanostructures"*

PROGRESS REPORT

The team at University of Maryland, led by Prof. Theodore L. Einstein, is principally a postdoctoral associate, Dr. Ferenc Szalma, and graduate student, Rajesh Sathiyanarayanan, working about 1/3 time on the project, with assistance from starting graduate student Suriyanarayanan Vaikuntanathan and recent graduate Dr. Timothy J. Stasevich (now a postdoctoral fellow at the National Cancer Institute at NIH, applying similar thinking to biological systems).

The work performed so far includes three related but distinct topics:

(d) characterization of fluctuations on island edges, with applications to Pb(111)
(e) characterization of orientation dependence of stiffness, the inertial parameter of steps
(f) calculation of characteristic energies to parametrize lattice-gas models of surface phenomena, with emphasis on role of multisite interactions

Accomplishments

a) Since fluctuations become progressively a larger fraction of cluster motion as size decreases, detailed understanding is an important ingredient to describing nanoscale phenomena. Last year we focused on structures on Pb(111), for which there was abundant data at Maryland. This year we are collaborating with an experimental group in Hong Kong to investigate similar effects on structures on Si(111) at high-temperature [1].
b) We completed our theoretical investigation of step stiffness, which weights the response of steps to driving forces and thereby plays a crucial role in the dynamics of nanoscale structures [2]. We have derived analytic expressions for the stiffness anisotropy; though complicated, they can be straightforwardly used as input for finite-element simulations. In addition, we have applied this perspective to analyze the effect of a necklace of C_{60} decorating islands on Ag(111) [3,4].
c) While lattice-gas models have long been invoked to describe the energetics of atoms on surfaces, it has only recently become possible to calculate reliably these energies to verify that phenomenologically-derived parameters correspond to actual values. Using VASP we have calculated such energies in conjunction with computation of the step stiffness based on such models [5]. The results we find are generally consistent with the values we estimated based on using statistical mechanical models to fit experimental data for the dependence of step stiffness on orientation and temperature. We are investigating the role of relaxation and of multi-site interactions in forming a full description [6].
d) We have extended our analysis of fluctuations of steps on surfaces from equilibrium to non-equilibrium situations [7-9].
e) Extending my work decades ago on indirect interactions between adsorbed atoms, I have been studying interactions mediated by metallic surface states [10]. Since such states are free-electron-like in the plane, the propagators can be handled analytically, and the much slower decay and longer wavelength make the effects more dramatic.

f) Capitalizing on formal theoretical arguments by Spohn and coworkers that the spatial correlations of fluctuations of the edges of facets should have novel, distinctive behavior, we rederived the results in a more intuitive fashion and obtained the temporal correlation function (also novel) as well [11]. Although STM is to slow to obtain a snapshot of large regions of the surface at the same instant, using pseudoimages (repeated scans over the same position) we could measure our newly-found dynamic behavior, confirming the picture.

Current and future work

In area d) we have noticed that the general form describing distributions of fluctuating quantities, the so-called generalized Wigner surmise [12], can be used to understand the long-standing problem, in epitaxial growth studies, of the distribution of island sizes, or more fruitfully, of the capture zones of these islands. We have posted a paper on cond-mat and are making revisions for a Phys. Rev. Letter [9]. J.W. Evans and his team, arguably the world's leading group on this topic, are revisiting their simulations of island sizes and capture zones to investigate the validity of our results. This joint effort has been strongly fostered by CMSN collaboration and the workshops, which provided an early and effective way to exchange results.

In area e) Z. Zhang and I have common interests in the role of metallic surface states in creating large-scale patterns on surfaces such as Ru(0001). His coworker Prof. Yu Jia will come to Maryland for several days before our CSCAMM/MRSEC workshop nid07 in April, and he and Zhang (an invited speaker at nid07) and I will continue our interactions during the workshop. We also plan for Rajesh Sathiyanarayanan to visit Oak Ridge.

In area a) we continue to interact with Ho, Wang, and Tringides at Iowa State to understand behavior of nanoscale structures on Pb(111). The issue is how our work on single-layer islands generalizes to multilayer islands that are stabilized by quantum size effects. Our experiences on island properties, rooted in the step continuum model, will add new perspectives to this effort. We will consider how the key property of stiffness is altered by the higher, quantum-dominated islands. For islands on Si(111) there have been estimates of how this change scales with height. We have also considered the role of microfacets and edges on pyramidal islands [5], and will apply our thinking to this metallic system. With regard to thrusts b) and c), we will characterize the stiffness and free-energy anisotropies of the island edges. In particular, the latter suggests that if one is to include influential relaxations when casting the problem into a lattice gas model, it is important to include multi-site interactions, as we have been investigating for various fcc metals [5-6].

Tringides at AmesLab is looking for the fluctuations of rings on the top of mesa QSE islands on Pb(111), seeking the exponents we found for the facets on mounds in area f). There are great differences between rings on Pb islands with an even and with an odd number of layers. This work will also involve Ho and Wang at Iowa State.

In our lattice models we will collaborate with Evans at Iowa State, as well as Zhang at Oak Ridge and Liu at Utah. We are eager to see how the elastic effects that they are studying will affect our parametrization scheme. We have convinced K. Fichthorn of Penn State (invitee at the most recent CMSN meeting) of the importance of quarto (4-adatom non-pairwise or trio) interactions, and will make our case to CMSN team members as well. We will also continue to do kinetic Monte Carlo simulations

[1] in conjunction with their investigations. We are currently verifying the power of our analytic formulation of the step stiffness [5]: steps that are initially pinned in strikingly irregular configurations in experiments at Maryland—discussed in part by Prof. E. D. Williams at the CMSN coordination meeting in October 2005 (U. of Wisconsin, Madison)—on Ag(111) are monitored as the steps are depinned and relax toward equilibrium.

References

1. "Thermodynamics of the Si(111) (1x1) Surface: Step Line Tension and Island Decay," K.L. Man, A. Pang, M.S. Altman, T.J. Stasevich, F. Szalma, and T. L. Einstein, readable draft.

2. "Analytic Formulas for the Orientation Dependence of Step Stiffness and Line Tension: Key Ingredients for Numerical Modeling," T.J. Stasevich and T. L. Einstein, [SIAM-]Multiscale Model. Simul. 6, 90–100 (2007) [cond-mat/0609237] doi: 10.1137/060662861 (citing DOE-CMSN support).

3. "Metal/Molecule Interface Fluctuations," C.G. Tao, T.J. Stasevich, T. L. Einstein, and E.D. Williams, Nanoletters, in press. online as doi:10.1021/nl070210a S1530-6984(07)00210-X, highlighted in Nature 446, 472 (2007).

4. "A Quantitative Model for Step Decoration: C_{60} on Ag(111)," T. J. Stasevich, Chenggang Tao, William G. Cullen, Ellen D. Williams, and T. L. Einstein, in preparation, readable draft (citing DOE-CMSN support).

5. "Extended lattice gas interactions of Cu on Cu(111) and Cu(001): Ab initio evaluation and implications," T. J. Stasevich, T. L. Einstein, and Sergey Stolbov, Phys. Rev. B **73**, 115426 (2006).

6. "Sensitivity of Trio Interactions to Relaxation of Adatoms: Calculations and Implications," Rajesh Sathiyanarayanan, T.J. Stasevich, and T. L. Einstein, readable draft (citing DOE-CMSN support).

7. "Evolution of Terrace-width Distributions on Vicinal Surfaces: Fokker-Planck Derivation of the Generalized Wigner Surmise," Alberto Pimpinelli, Hailu Gebremariam, and T. L. Einstein, Phys. Rev. Lett. 95, 246101 [4pp.] (2005).

8. "Fokker-Planck Approach to Relaxation of Terrace-width Distributions on Vicinals: Physical Information in the Time Constant," Ajmi Bhadj-Hamouda, Alberto Pimpinelli, and T. L. Einstein, submitted to PRB.

9. "Capture-Zone Scaling in Island Nucleation: Phenomenological Theory Linking to Random-Matrix Theory," Alberto Pimpinelli, and T. L. Einstein, [cond-mat/0612471] (citing DOE-CMSN support), submitted for publication.

10. "Interactions Mediated by Surface States: From Pairs and Trios to Adchains and Ordered Overlayers," Per Hyldgaard and T. L. Einstein, J. Crystal Growth 275, e1637-42 (2005) and references therein.

11. “Distinctive Fluctuations in a Confined Geometry,” M. Degawa, T.J. Stasevich, W.G. Cullen, Alberto Pimpinelli, T. L. Einstein, and E. D. Williams, Phys. Rev. Lett. 97, 080601 [4 pp.] (2006), selected for the Sept. 4, 2006 issue of Virtual J. Nanoscale Sci. & Tech. doi: 10.1103/PhysRevLett.97.080601.

12. “Using the Wigner-Ibach Surmise to Analyze Terrace-Width Distributions: History, User's Guide, and Advances,” T. L. Einstein, Appl. Phys. A, online as doi: 10.1007/s00339-007-3908-x [cond-mat/0612311].