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Metal film growth on weakly-interacting substrates

Multiscale modeling

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Cover art: Illustration of the island growth stage of a vapor-deposited gold film on a weakly-interacting substrate. Designed with the help of Mr. Nahual Sobrino.

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"The pyramids are one of those things that live up to the hype."

Barack Obama

Abstract

Thin films are nanoscale layers of material used to functionalize surfaces or to serve as building blocks in more complex devices. In recent years, thin metal films have become vital for modern devices within, e.g., biosensing, catalysis, and nanoelectronics, whereby synthesis of metal layers with specific morphological features on two-dimensional (2D) crystals and oxides is required. However, this entails a great scientific challenge: in most of the afore-mentioned film/substrate combinations substrate and metal atoms interact weakly, causing the latter to self-assemble without control into three-dimensional (3D) clusters.

Nowadays, a significant fraction of thin films is synthesized via condensation from the vapor phase, a far-from-equilibrium process in which film morphology is governed by the kinetic rates of atomic-scale structure-forming processes. It is, therefore, evident that knowledge-based synthesis of metal layers in high-performance devices necessitates a comprehensive understanding of the dynamic competition among these processes at the nano- and mesoscale. Such understanding is today incomplete, since experimental materials science tools are often not capable of providing nanometer and sub-nanometer insights at time scales that are relevant for thin-film synthesis. Computational approaches offer the possibility to fill the afore-mentioned gap in knowledge by allowing to explore atomistic behaviors with picosecond resolution. Hence, in the present thesis, a combination of modern computer simulation techniques is used to investigate thin metal film growth on weakly-interacting substrates from a purely atomistic point of view and to elucidate the ways by which atomic diffusion mechanisms give rise to the final film morphologies.

In the first part of the thesis, an in-house kinetic Monte Carlo (KMC) simulation code and analytical modeling are used to investigate the early growth stages of Ag films supported on a generic weakly-interacting sub-

strate. The results show that the weak interaction strength between film atoms and substrates leads to the formation of strongly-faceted 3D Ag islands, whose vertical growth is mediated by the temperature-dependent upward adatom diffusion across the facets. Eventually, the 3D islands impinge on each other and coalesce via surface migration of facet layers. Migration can be promoted by an increase of the deposition flux, but it can also be hindered by material agglomeration if the flux exceeds a critical threshold. These findings provide the foundation for explaining several effects observed during thin film growth on weakly-interacting substrates, including the increase of film roughness with temperature, the transition from 3D to 2D film morphology upon suppression of coalescence, and the origin of changes in thin film roughness and grain boundary number densities when varying the magnitude of vapor flux arrival rate.

In the second part, *ab initio* and classical Molecular Dynamics simulations are used to investigate the diffusion dynamics of several transition metal adatoms (Ag, Au, Cu, Pd, Pt and Ru) and multi-atomic clusters (Ag, Au, Cu and Pd) on single layer graphene at room temperature (300K). The simulated diffusion trajectories reveal that diffusing adspecies experiencing a deep (hundreds of meV) potential energy landscape (PEL) on the substrate surface follow random walks; whilst those with a weak interaction with the substrate (PEL depth of a few meV) follow a superdiffusive motion pattern known as Lévy walk. This type of anomalous movement—also observed in other phenomena in physical, biological, and social systems—manifests itself as a continuous atomic motion with occasional flights over distances covering multiple adsorption sites. The fact that adspecies follow a distinctly different type of motion than what is observed in classical homoepitaxial growth theory implies that energy barriers readily available from static (0K) calculations may not be able to provide a physical accurate description of surface diffusion of metal adspecies on 2D crystals. As such, anomalous diffusion is a potentially important aspect to be considered when modeling growth of metal films and nanostructures on 2D materials.

The results and insights generated in the present thesis provide key knowledge for controlled synthesis of films and nanostructures with tailored properties. This, in turn, is relevant for developing high-performance energy-saving windows, improving the turnover frequency of catalytic reactions, and integrating 2D materials into novel nanoelectronic devices. Moreover, the techniques developed and employed herein contribute toward bringing modern computational tools closer to the field of thin film growth.

Populärvetenskap

sammanfattning

I antikens Egypten, för mer än 5000 år sedan, skapade skickliga hantverkare guldfilmer för att dekorera sina väggar, statyer och artefakter. Genom att gång på gång slå och forma, kunde hantverkarna förändra metallen i tunna blad som inte var tjockare än en tusendels millimeter. Mycket senare, på 1800-talet, upptäckte kemiker och fysiker hur förångnings- och kondensationsprocesser kunde användas för att syntetisera filmer med olika sammansättningar och ännu mindre tjocklekar, vilket tillät dem att bygga speglar och optiska beläggningar. Men det var inte förrän 1900-talet som genombrottet uppnåddes: vetenskapsmän lyckades att producera filmer som var så tunna som ett enda atomlager. Detta framsteg drev fram tunnfilmernas popularitet, tills de blev en av dem moderna teknologins hörnstenar. Till exempel, belägger vi filmer på ytor för att skydda verktyg mot slitage och för att spara information i hårddiskar, eller kombinerar dem med andra komponenter för att bygga lysdioder (LEDs), transistorer, och solceller. Eftersom de möjliga kombinationerna av film och substrat (dvs. materialen filmerna beläggs på) är praktiskt taget obegränsade, fortsätter forskare numera att undersöka potentiella designer för att ta itu med våra teknologiska behov.

En av de här nya film-substratkombinationerna består av en metallisk film belagd på material med högt syreinhåll (oxider), eller på material som naturligt förekommer i mycket små tjocklekar (2D-material), som den välkända grafen. Denna kombination skulle kunna tillämpas för att tillverka fönster med oöverträffade värmeisoleringssegenskaper, katalysera kemiska reaktioner för att minska förluster i industriella processer och, kanske den mest spännande tillämpningen, för att inkorporera 2D-material i integrerade kretsar. Detta skulle bidra till att möjliggöra en ny generation av nanoelektroniska komponenter och, tillsammans med dem, futuristisk teknologi som

kvantdatorer eller människa-maskin-gränssnitt. Men filmers prestanda beror starkt på deras kvalitet, och uppgiften att applicera ett platt och jämnt metalliskt lager på en oxid eller ett 2D-material är högst icke-triviellt. En gemensam egenskap som metalliska atomer delar är en svag interaktion med dessa substrat, medan de har en stark interaktion med liknande atomer, vilket orsakar att filmerna utan kontroll agglomererar till tre-dimensionella öar på bråkdelen av en sekund. För att undvika den här oönskade tendensen, måste vi titta på den intrikata filmsyntesprocessen, och sätta fingret på det fysikaliska ursprunget till de beteenden som observeras i labbet.

Vi påbörjar detta sökande med en analys av de olika steg som filmsyntes består i. Först förångas materialet från en källa och styrs mot ett substrat, där det kondenserar (eller beläggs). Då börjar materialet att forma öar i olika regioner på substratet, vilka växer i storlek tills de stöter på varandra, och formar så småningom en kontinuerlig film som täcker hela substratet. Den här processen kan också övervägas från ett atomistiskt perspektiv. Under beläggningen, separeras atomer från källan, landar på substratet och sprider sig då över substratets yta eller över atomistiska öar tills de hittar en stabil position de kan binda till. I moderna filmsyntestekniker, sker däremot beläggningen i sån hög takt att atomer inte hinner hitta stabila positioner innan de nya landar, vilket orsakar att de interagerar med varandra och samlas i instabila öar med många olika former. Detta säger oss att filmens slutliga utseende är mycket känsligt för atomernas beteende under de tidiga filmsyntesstegen, och därför, att det skulle kunna kontrolleras om vi kunde identifiera och rikta uppmärksamheten till de diffusionsmekanismer som sker på nanoskala.

För att genomföra den här typen av forskning, kan datormetoder ge ovärderlig hjälp. Med den stora ökning av moderna datorers beräkningskraft, har det blivit möjligt att simulera utveckling av stora atomensembler under långa tider. Detta tillåter observationer och studier av atomens rörelser i kontrollerade omgivningar, med en detaljnivå som är omöjlig att uppnå med konventionella experimentella tekniker som mikroskopi. Med den anskaffade kunskapen från simuleringar och labexperiment, kan vi på så sätt finjustera beläggningsbetingelserna (genom att tillsätta en liten mängd av ett annat material, tex) för att förstärka eller stävja specifika diffusionmekanismer, och manipulera filmens slutliga form som vi önskar.

I den här avhandlingen fokuserar jag mina ansträngningar på förståelsen av de tidiga tillväxtstegen hos tunnfilmer av ädelmetall på svagt interagerande substrat. Genom användning av simuleringsmetoder, baserade på kvant-

mekanik och probabilitet, utforskar jag diffusion av atomer på grafen och deras interaktioner med andra rörliga atomer, såväl som hur öar växer och förenas (dvs. när öar fusionerar till en enda efter att ha stött på varandra). Denna nya kunskap hjälper till att förklara förbryllande experimentella resultat från både min grupp och i litteraturen, och utgör den teoretiska grunden för att utveckla effektiva strategier för att kontrollera filmformer. Kanske ska den här arbetet inte bli ett tidlöst konstverk dolt inom en pyramid, men förhoppningsvis ska det bidra till ett grönare samhälle med energisparande material och industrier, samt till en förbättring av människors livskvalitet med en ny generation nanoelektroniska komponenter.

Popular science summary

Back in Ancient Egypt, more than 5000 years ago, skilled artisans crafted gold films to decorate their walls, statues and artifacts. By repeated beating and shaping, these artisans were able to turn this metal into foils not thicker than one thousand part of millimeter. Much later, in the 1800s, chemists and physicists discovered how to employ vaporization and condensation processes for synthesizing films of diverse compositions with even smaller thicknesses, which allowed them to build mirrors and optical coatings. But it was not until the 1900s when the key development was achieved: scientists succeeded to produce films as thin as one single atomic layer. This advance propelled the popularity of thin films, until they become one of the cornerstones of our modern technology. For instance, we deposit films on surfaces to protect tools from wear and to store information in hard disks, or to combine them with other components for building light emitting diodes (LEDs), transistors, and solar cells. Since the possible combinations of materials forming the film and the substrate—the material where the film is deposited—are virtually unlimited, researchers today continue investigating potential designs to address our technological needs.

One of these novel film and substrate combinations consists of a metal film supported on materials with high oxygen content (oxides), or on materials which naturally appear in very small thicknesses (2D materials), such as the acclaimed graphene. We could apply this to fabricate windows with unprecedented thermal insulation capabilities, catalyze chemical reactions to reduce energy losses in industrial processes, and, perhaps the most gripping application, to incorporate 2D materials into integrated circuits. This would contribute to unlock a new generation of nanoelectronic devices and, with them, futuristic technologies such as quantum computers or human-machine interfaces. But the performance of the films relies heavily on their quality, and the task of applying a flat and smooth metal layer on an oxide or on a 2D

material is far from trivial. One common property shared by metal atoms is a weak interaction with these substrates, while keeping a strong interaction with alike atoms, and this causes the films to self-assemble without control into three-dimensional (3D) islands in fractions of seconds. To avoid this unwanted tendency, we must peek into the intricate process of film synthesis, and spot the physical origin of the behaviors observed in the lab.

We begin this quest by analyzing the different stages involved during the film synthesis. First, material is vaporized from a source, and directed towards a substrate, where it condensates (or is deposited). The material then starts self-assembling into islands in different regions of the substrate, which grow in size until they come into contact with each other, and eventually form a continuous film covering the whole substrate. This process can also be considered from an atomistic point of view. During deposition, atoms separate from the source, land on the substrate, and then diffuse across the surface of the substrate or of atomic islands until finding a stable position where they can attach. However, in modern film synthesis techniques, deposition takes place at such high rates that atoms do not have time to find stable positions before the new ones land, and, as a result, they interact with each other and form unstable islands with many different shapes. This tells us that the final appearance of films is very sensitive to the atomic behavior during the early stages of film synthesis, and therefore, that it could be controlled if we could identify and target the main diffusion mechanisms taking place at the nanoscale.

For this type of research, computational approaches may provide invaluable help. With the steep increase of processing capabilities of modern computers, it has become possible to simulate the evolution of large ensembles of atoms over long times. This allows to observe and study atomic movements in controlled environments with a level of detail impossible to attain with conventional experimental techniques, such as microscopy. Thus, with the knowledge obtained from these simulations and from the lab, we can tune the deposition conditions—by, for example, adding a small amount of other material—to enhance or suppress specific diffusion mechanisms, and manipulate the final film shape at will.

In this thesis I direct my efforts to understanding the initial growth stages of noble-metal thin films on weakly-interacting substrates. Using simulation tools based on quantum mechanics and probability, I study the diffusion of single atoms on graphene and their interaction with other mobile atoms, as well as how islands grow and coalesce (that is, when islands merge into

a single one upon contact). This new knowledge helps to explain puzzling experimental data from both my group and the literature, and constitutes the theoretical foundation for devising efficient strategies for controlling film shapes. Perhaps this work will not become timeless art hidden inside a pyramid, but hopefully will contribute to a greener society with energy-saving materials and industries, and to improve human life quality with a new generation of nanoelectronic devices.

Resumen de ciencia popular

Hace más de 5000 años, los hábiles artesanos del Antiguo Egipto fabricaban láminas de oro para decorar sus paredes, estatuas, y artefactos. Utilizando técnicas de martilleo repetitivo y de moldeado, eran capaces de darle a este metal forma de láminas no más gruesas que una millonésima parte de metro. Más tarde, en el siglo XIX, físicos y químicos descubrieron cómo usar procesos basados en vaporización y condensación para sintetizar láminas de diversas composiciones con grosores aún más pequeños, lo que les permitió construir espejos y recubrimientos ópticos. Pero no fue hasta el siglo XX cuando se obtuvo el logro clave: los científicos consiguieron producir láminas que consistían en una única capa de átomos. Este avance impulsó la popularidad de las láminas delgadas hasta convertirlas en una de las piedras angulares de la tecnología moderna. Por ejemplo, depositamos láminas en superficies para proteger herramientas contra el desgaste y para almacenar información en discos duros, o las combinamos con otros componentes para construir diodos emisores de luz (LEDs), transistores y placas solares. Ya que las posibilidades de combinar distintos materiales en la lámina y el sustrato (i.e., el material sobre el que se deposita la lámina) son virtualmente ilimitadas, a día de hoy los investigadores siguen buscando diseños potenciales para abordar nuestras necesidades tecnológicas.

Una de las novedosas combinaciones de lámina y sustrato consiste en aplicar una lámina de metal sobre materiales con alto contenido en oxígeno (óxidos), o en materiales que tienen grosores extremadamente finos de forma natural (materiales 2D), como el célebre grafeno. Estos diseños podrían usarse para fabricar ventanas con una capacidad de aislamiento térmico sin precedentes, catalizar reacciones químicas para reducir pérdidas energéticas en procesos industriales y, quizás la aplicación más fascinante, incorporar materiales 2D en circuitos integrados. Esto contribuiría al desarrollo de una nueva generación de componentes nanoelectrónicos y, a su vez, a aplica-

ciones futuristas como ordenadores cuánticos o interfases entre máquinas y humanos. Pero el rendimiento de las láminas depende de su calidad, y la tarea de aplicar una capa de metal fina y uniforme sobre un óxido o un material 2D no tiene nada de trivial. Una propiedad común que comparten los átomos metálicos es su interacción débil con estos sustratos, al mismo tiempo que presentan una fuerte interacción con átomos del mismo tipo, lo que provoca que las láminas se agrupen sin control en montículos (o islas) en fracciones de segundo. Para evitar esta tendencia no deseada, uno debe asomarse al intrincado proceso de síntesis de láminas, y localizar el origen físico del comportamiento observado en el laboratorio.

Esta búsqueda comienza con el análisis de las diferentes etapas involucradas en la síntesis de láminas. En primer lugar, el material se vaporiza desde una fuente y se dirige hacia un sustrato donde se condensa (o se deposita). Entonces, el material comienza a aglomerarse en islas en diferentes regiones del sustrato, que crecen hasta que empiezan a hacer contacto unas con otras, y eventualmente forman una lámina continua que cubre todo el sustrato. Este proceso también se puede considerar desde un punto de vista atomístico. Durante la deposición, los átomos se separan de la fuente, aterrizan en el sustrato y se difunden sobre el sustrato o sobre las islas hasta encontrar una posición estable donde puedan permanecer fijos. Sin embargo, en las técnicas de síntesis modernas, el material se deposita a un ritmo tan elevado que los átomos no tienen tiempo de encontrar posiciones estables antes de la llegada de nuevos átomos y, en consecuencia, éstos interaccionan los unos con los otros y forman islas inestables con formas variadas. Este hecho indica que la apariencia final de las islas es muy sensible al comportamiento de los átomos durante las etapas iniciales de la síntesis y, por tanto, podría ser controlada si se pudieran identificar y manipular los mecanismos principales de difusión a escala nanoscópica.

Para este tipo de investigación, los métodos computacionales pueden proporcionar una ayuda inestimable. Con el rápido incremento de la capacidad de procesamiento de los ordenadores modernos, se ha vuelto posible la simulación de grandes conjuntos de átomos durante largos periodos de tiempo, lo que permite observar y estudiar movimientos atómicos en entornos controlados con un nivel de detalle imposible de obtener con técnicas tradicionales, como la microscopía. Así, con el conocimiento obtenido a través de las simulaciones y experimentos de laboratorio, las condiciones de deposición podrían ajustarse (por ejemplo, añadiendo una pequeña cantidad de un material diferente) para facilitar o suprimir procesos de difusión específicos y manipular la

apariciencia final de las láminas a voluntad.

En esta tesis me centro en entender las etapas de crecimiento iniciales de láminas delgadas de metales nobles sobre sustratos de interacción débil. Usando herramientas de simulación basadas en mecánica cuántica y probabilidad, he estudiado la difusión de átomos en grafeno y sus interacciones con otros átomos móviles, además de estudiar la manera en la que las islas crecen y se fusionan. Este nuevo conocimiento ayuda a explicar datos experimentales confusos obtenidos por mi grupo y publicados en la literatura, y constituye el fundamento teórico para concebir estrategias eficientes para controlar las formas de las láminas. Es posible que este trabajo no se convierta en arte atemporal escondido dentro de una pirámide, pero con suerte contribuirá al desarrollo de una sociedad más verde con materiales e industrias eficientes energéticamente y a mejorar la calidad de vida humana con una nueva generación de componentes nanoelectrónicos.

Preface

This doctoral thesis concludes my Ph.D studies carried out between 2016 and 2020 in the Nanoscale Engineering Division at the Department of Physics, Chemistry and Biology, Linköping University, Sweden. The introductory chapters provide an overview of thin film growth theory and of computational tools for atomistic simulations, to provide the reader with an overview of the research field and the methods employed. Much of the contents of these chapters have been previously published in my Licenciate Thesis (No. 1830, Linköping Studies in Science and Technology).

My research have been financially supported by Linköping University (“LiU Career Contract, Dnr-LiU-2015-01510, 2015-2020”), the Swedish research council (contract VR-2015-04630), the ÅForsk foundation (contract ÅF 19-137) and the Olle Engkvist foundation (contract SOEB 190-312) for financial support. Simulations and data handling were enabled by resources provided by the Swedish National Infrastructure for Computing (SNIC) at the National Supercomputer Centre (NSC) partially funded by the Swedish Research Council through grant agreement no. VR-2015-04630.

Víctor Gervilla Palomar
Linköping, October 2020

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Here concludes the work-related block of acknowledgements. However, if somebody asked me how I survived during these intense years, I would probably start talking about the colorful international community that I have been part of. Yes, yes, here is where I will mention all of you!

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PS: I would like to use this last space of self-expression to confess that Laurent Souqui and I might have been responsible for the flying pig accident.

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Chapter 1

Introduction

1.1 Background and motivation

Thin films [1] are nanoscale layers of material used to functionalize surfaces or to serve as building blocks in devices. As the number of possible film/surface combinations is nearly unlimited, thin films are employed for applications within multiple technological areas, including information processing and storage, and energy conversion and saving. In addition, thin films play an important role in fundamental research of elusive physical phenomena, such as high-temperature superconductivity [2] or electrical conductance quantization [3, 4], which only manifest themselves at length scales that are comparable to the electron wavelength.

The properties of thin films are not only determined by their chemical composition, but also by their morphological features which are, in turn, a result of the film synthesis process. A significant fraction of thin films is today synthesized via vapor condensation [5]. Material from a solid or liquid source is vaporized using physical and/or chemical means (e.g., by heating or momentum transfer) and, subsequently, vapor is transported through the gas phase to condense on a surface (referred to as *substrate*). The deposited material then self-assembles into dispersed atomic islands, which grow in size until they impinge onto each other and coalesce (i.e., merge into a single island via mass transport), and eventually form a continuous layer that covers the entire substrate surface.

During the condensation process, the flux of atoms (and molecules) from the vapor to the solid substrate is typically multiple orders of magnitude

larger than the flux of material returning from the substrate surface to the vapor phase. This flux anisotropy (also known as *high supersaturation* at the vapor/solid interface) leads to excess of atoms on the substrate, so that atoms do not have sufficient time to self-assemble in minimum-energy configurations predicted by thermodynamics. It is then said the film formation proceeds *far from thermodynamic equilibrium* and the resulting film morphology is determined by the occurrence rates (i.e., *kinetics*) of atomic-scale structure-forming mechanisms. Hence, a fundamental understanding of the rules dictating the intricate process of far-from-equilibrium film growth is the basis for developing strategies for controlling film morphological evolution. By fine-tuning the deposition conditions, such strategies could then be used to fabricate functional layers and nanostructures with tailored physical properties.

1.1.1 Metals on weakly-interacting substrates

One potentially useful film/substrate combination is a metal supported on an oxide or a two-dimensional (2D) crystal [6, 7]. Such architectures allow to build energy-saving windows [8] and sensors useful in biomedicine [9], and to improve the turnover frequency on catalytic reactions [10]. Moreover, they may serve as metal contacts [11–13] for incorporating novel 2D materials [14–16] such as graphene [17], transition metal dichalcogenides [18], and MXenes [19], into integrated circuits, thus contributing to the development of a new generation of nanoelectronic devices.

The ability to leverage the unique features of functional oxides and 2D materials in key enabling devices necessitates growth of metal layers with controlled morphology. For instance, electrical metal contacts in low-emissivity windows and photovoltaic devices should exhibit a smooth surface, such that the layer conductivity is maximized [8]. Concurrently, sensors and catalytic devices rely on synthesizing nanostructures with well controlled size and shape distributions [9, 10]. Achieving such morphologies entails a great scientific challenge, since weak interaction among most metal atoms with oxide and 2D crystal substrates gives rise to an uncontrolled three-dimensional morphology. It is therefore essential to understand the mechanisms and processes that govern film morphological evolution on weakly-interacting substrates at multiple length scales, in order to synthesize layers and nanostructures with tailored morphologies and physical properties.

Current knowledge of metal growth on weakly-interacting substrates is

incomplete, as most established theories deal with *epitaxial* systems¹. This is most notably exemplified by the theoretical framework with regards to the origin of 3D morphology formation. In homoepitaxy, i.e., systems in which film and substrate are chemically and crystallographically identical, surface energy minimization arguments (i.e., thermodynamics) dictate that the film fully wets the substrates, i.e., growth proceeds in a 2D fashion. However, there is a large body of experimental data showing that 3D morphology is a common occurrence in homoepitaxy [20]. The explanation of this growth behavior lies in the kinetically-limited interlayer mass transport, which increases the probability for nucleation of new atomic layers before the substrate is fully covered by the film. In the case of weakly-interacting film/substrate systems—including Ag/SiO₂ [21, 22], Pd/TiO₂ [23], Cu/ZnO [24, 25], and Pb/graphene [26]—3D islands develop *before* the initially formed one-atom-high islands are large enough to efficiently capture vapor-phase deposition flux, such that limited interlayer transport becomes effective in determining film morphology. Hence, atomic-scale pathways that facilitate upward material transport from the base of the atomic islands to their upper layers need to be invoked for explaining experimental observations. By elucidating and establishing such mechanisms it is possible to design knowledge-based strategies for tailoring morphology of thin films and nanostructures to serve specific technological requirements [27–29].

1.1.2 Computational tools for growth studies

Experimental studies on thin film growth can benefit enormously from computational modeling tools. Such tools allow to create virtual copies of material systems and simulate their behavior in controlled environments with high precision and in great detail. Different computational techniques have been designed to explore materials features in depth for a wide range of length and time scales, often with atomic resolution, making these tools particularly convenient for investigating correlations between various observation levels. Moreover, given that sufficient computational resources are available, simulations may replace time-consuming and often costly experimental setups. It is, therefore, of little surprise that computer simulations have become a central element for understanding thin-film growth, which is governed by a

¹The term epitaxy refer to the scenario in which the substrate imposes crystallographic order on the film structure.

complex interplay among atomistic mechanisms operating at multiple time and length scales.

A wide gamut of material simulation tools is today available [30], and they are classified either as deterministic or stochastic. Deterministic tools implement physical laws to compute temporal evolution of atomic ensembles, which is unequivocally determined from their initial configuration. Molecular Dynamics (MD), undoubtedly the most popular method within this category, applies Newton's equations of motion to calculate the trajectories of each atom within an ensemble. Forces are obtained from classical interatomic potentials provided as a simulation input, although they can also be obtained by solving the Schrödinger equation corresponding to the particle configuration at each simulation step². In each of these approaches, MD simulations are denoted as classical (CMD) and first-principles or *ab initio* (AIMD), respectively. The latter approach is mostly founded on the Density Functional Theory (DFT), which is implemented in a multitude of softwares to calculate physical properties of materials based on their electronic structure. In the context of film growth, DFT is mainly used to estimate adsorption energies of atoms onto substrates via minimization procedures. Stochastic tools offer an alternative approach by computing temporal evolutions based on probabilistic laws, which implies that systems departing from identical configurations may evolve towards completely different ends. In kinetic Monte Carlo (KMC), all potential atomistic events and their associated transition rates are identified, and then these events are chosen to occur based on their rates using random numbers.

In order to study systems of a few tens of atoms, AIMD becomes the first choice due to its capacity to provide highly realistic representations and physically accurate descriptions. Yet the accuracy comes at the expense of a poor efficiency, hence simulations hosting a larger number of atoms or spanning longer times, both required to describe film growth, become exceedingly time-consuming. For the latter case, classical Molecular Dynamics CMD offers an adequate alternative, as the description of the material electronic structure is substituted by evaluating values of a potential energy function. However, lack of available interatomic potentials for most element combinations limits the applicability of this method to a few systems. In addition, despite its better efficiency compared to AIMD, CMD is still not capable of reaching

²Note that, in principle, it is also possible to obtain an interatomic potential from first-principles methods.

timescales that are relevant for film growth experiments ($\sim ms - s$). Within this framework, KMC offers an appealing compromise between simulation capacity and accuracy, as it restrains the atomic motion to single diffusive jumps between discrete lattice positions, i.e., the time during which atoms vibrate around their equilibrium positions is not explicitly modelled. Given that this approximation does not exclude concerted processes like exchange diffusion, and that there is an available catalog of transition rates for all relevant atomic jumps³, KMC allows to describe thin film growth dynamics in a purely atomistic fashion.

1.2 Research goal, strategy and impact

In the present thesis, I contribute to the fundamental understanding of the atomic-scale processes that govern early stages of metal-film formation on weakly-interacting substrates. This knowledge is crucial for explaining experimental data reported in the literature and generated by research work of my present and former colleagues at the Nanoscale Engineering division (NSE) [31–33]. My studies concern the growth of noble metal films on generic weakly-interacting substrates and graphene.

In the first part of the thesis, I use an in-house fully atomistic kinetic Monte Carlo (KMC) code [34] designed for simulating mesoscopic film dynamics ($\sim 10^4$ atoms). In Papers 1 and 2, KMC simulations supported by analytical models are employed to characterize the growth of isolated Ag 3D islands (i.e., clusters or nanostructures) on a generic weakly-interacting substrate with fcc symmetry, as well as to identify the atomistic mechanisms involved in island formation and vertical growth. Subsequently, in Paper 3, KMC and analytical models are used to study island coalescence, and to understand the way by which its dynamics are affected by island faceting and the presence of an active deposition flux. In the second part of the thesis, I use a combination of *ab initio* and classical Molecular Dynamics simulations to study the diffusion of noble metal adatoms (Ag, Au, Cu, Pd, Pt and Ru) on graphene at room temperature, with the goal to understand the effect of thermal vibrations on diffusion dynamics (Paper 4). In Paper 5, I extend the

³To generate a complete and accurate rate catalog able to capture the main physical properties is a highly non-trivial task, and often becomes the central discussion aspect on computational studies of bulk and surface dynamics. More information on this topic is provided in Sections 3.3.3 and 3.3.4.

studies of Paper 4 to the diffusion of noble-metal dimers and trimers.

The present thesis sheds light on the dynamics of atomic diffusion, key mechanisms and pathways leading to nucleation and growth of 3D islands, and on the way by which coalescence dynamics affects island shapes on weakly-interacting substrates. This understanding represents a decisive step toward extending growth theories and modeling methodologies beyond the well-established epitaxial framework, with relevance for directed synthesis of multifunctional metal contacts in a wide array of devices founded upon oxides and van der Waals materials. Alongside the contributions to the specific research area, my thesis brings computational techniques developed and tested mainly for bulk systems closer to the field of film growth.

1.3 Outline

The thesis is organized as follow. Chapter 2 provides a general introduction to the theory of thin-film growth, followed by detailed descriptions of the theoretical framework related to the early film formation stages of island nucleation, growth, and coalescence. Chapter 3 describes key aspects of the computational tools employed in the present work, including their accuracy, efficiency, and limitations when used for modeling film growth. Chapter 4 presents a summary of the appended papers, along with a discussion of possible future directions that my research opens up. The thesis also includes two appendices in which diffusion equations for the model described in Paper 2 are derived (Appendix A), and a parallel version of the in-house KMC algorithm is presented and documented (Appendix B).

Chapter 2

Thin film growth

Most modern film deposition techniques are far-from-equilibrium processes. Hence, film growth may follow numerous evolution paths through metastable configurations, in which every atomic-scale mechanism plays its own unique role for the final film morphology. Since the possible mechanisms are comprised by both individual and collective atomic transport processes, acting throughout several formation stages, film growth reveals itself as a process with inherent multiscale nature. The latter makes it exceptionally challenging to draw general conclusions regarding the origin of the overall film microstructure and morphology: accessing a certain formation stage allows to isolate and study thoroughly the laws governing growth at a specific observation length scale, but does not suffice to identify potential correlations between mechanisms belonging to different scales. Thus, a combined research approach aiming at both identifying atomistic mechanisms and understanding their interplay across multiple growth stages may provide key insights for manipulating thin film morphologies in a knowledge-based manner.

The present chapter serves as a general introduction to the early growth stages of metal films on weakly-interacting substrates, and it includes specialized brief reviews regarding limitations of current theory and possible implications of the main results of the appended papers¹. Section 2.1 describes the overall film growth process, then Section 2.2 addresses the fundamental mechanisms of atomic surface diffusion which is paramount for island nucleation (discussed in Section 2.3). Section 2.4 deals with the process of island growth, while island coalescence is discussed in Section 2.5.

¹For the sake of clarity, the growth stages are presented here in their natural order of appearance during a film synthesis process, although the corresponding appended papers do not strictly follow that order.

2.1 Thin-film growth stages

Growth commences with deposition of material (i.e., *deposit*) from the vapor phase on the substrate surface [20]. Once atoms are adsorbed on the substrate, they are said to be *adatoms*, and they diffuse until they meet other adatoms, or a low-energy site on the surface, to nucleate and form islands. For near-to-homoepitaxial systems, in which the chemical composition and crystalline structure of deposit and substrate are similar, islands are subjected to a thermodynamic driving force for wetting the substrate and initially adopting 2D shapes. In contrast, for atomic species interacting weakly with the substrate, the relatively strong self-affinity drives the formation of 3D islands from the very early growth stages. Once a certain number of islands covers the substrate, adatoms inevitably incorporate to already-existing islands, rather than nucleating new ones, which causes the film to reach a steady island saturation density

$$N_{sat} \sim \left(\frac{F}{D}\right)^\chi \quad (2.1)$$

which depends on the *deposition flux* F and the *adatom surface diffusivity* D . χ in Eq. (2.1) is an exponent that depends on the dimensionality of the islands.

Following density saturation, islands continue growing until they begin to impinge onto each other. When two or more islands come into contact, they form a *coalescing cluster*, and undergo an equilibration process known as *coalescence*, striving to merge into a single island in order to minimize the cluster surface energy. This process often entails the expulsion of grain boundaries—caused by possible differences in crystallographic orientation between the islands—via rotation or atomic rearrangement of both sides of the boundary between the original islands. For temperatures typical for metal growth experiments (300 - 500 K), the mass redistribution responsible for coalescence proceeds mainly by surface diffusion. For 3D islands, one consequence of coalescence is that the mass redistribution in clusters uncovers portions of the substrate previously covered by the islands. Thus, past island density saturation, the resulting decrease of the total surface coverage may permit new nucleation events and, in turn, give rise to a second generation of islands.

The rate at which islands come into contact eventually surpasses the speed of cluster shape equilibration, and new islands start impinging on the clus-

ters before they have completed coalescence. Consequently, clusters acquire increasingly elongated shapes, and soon collapse into a network spanning the entire substrate². From this point, deposited material contributes to increase the average thickness of the film, which becomes continuous after the substrate regions not covered by the percolated structure (i.e., holes) are filled with deposited material. It is worth pointing out that hole filling is a non-trivial process and may take considerable amounts of time, such that a rough growth front develops. This is particularly pronounced at low temperatures (e.g., room temperature for most metallic materials), due to the Zeno effect [35, 36].

Continuous films may present a variety of roughnesses and microstructures depending strongly on the way by which islands grow initially and the rate by which they coalesce, among other factors. In epitaxial systems islands tend to grow with the same orientation, which results in films exhibiting a single-crystalline structure with defects, including misfit dislocations, domain boundaries and twins. In contrast, for non-epitaxial systems, the random orientation of islands gives rise to polycrystalline films with grains separated by boundaries.

2.2 Surface diffusion

2.2.1 Potential energy landscape and energy barriers

Adatom diffusion is the most fundamental process taking place during crystal growth [37]. Any synthesis process, regardless dimensions or complexity, can be ultimately explained as the collective result of a multitude of atomic diffusion events. The most widespread framework to account for surface diffusion is based on the general random walk model, which regards atomic trajectories as discrete series of uncorrelated transitions or *jumps* between neighbouring adsorption sites. This description relies on the fact that the jump frequencies are at least two orders of magnitude smaller than the vibrational frequency of surface atoms, which allow the latter to loose memory of their previous position and configuration. At such conditions, atomic jumps can be considered *rare events* at the nanoscale. To perform each of these jumps, an

²This transition known as *percolation* is particularly easy to measure experimentally for metals on insulating substrates, since it gives rise to films that conduct electricity over macroscopic distances.

adatom is required to break the bonds with the substrate atoms underneath, and to move away from its initial position until subjected to the attraction of the substrate atoms defining the final position. As the potential energy experienced by a diffusing atom takes different values at each point of the surface, it is possible to define a function known as *potential energy landscape* (PEL), whose local minima associated to adsorption sites are called *basins* (or *wells*), and the local maxima, *ridges*. An adatom transitioning between two sites follows a trajectory in the PEL known as *minimum energy path* (MEP), and visits at least one *saddle point*, i.e., a maximum energy value of the MEP that is often located between two neighboring ridges (Fig. 2.1). Thus, in order to successfully transition between surface sites, the adatom must overcome an *energy barrier*³ E_a , i.e., the potential energy difference between an initial basin and the highest saddle point along the MEP.

Energy barriers E_a are always defined on specific atomic migration event, which do not necessarily correspond to the MEP. For any given surface, there are possibilities to find different transition paths with significant probabilities of occurrence, and the combination of these mechanisms and their associated transition rates ν defines the adatom diffusion dynamics on that surface.

2.2.2 Transition rates and diffusivities

The significance of the energy barrier concept lies in that it can be used to quantitatively estimate the diffusion dynamics of surface adatoms. The *diffusivity*⁴ D of an adatom transitioning between adsorption sites separated by a mean square distance l^2 is defined as

$$D = \frac{1}{4} l^2 \nu, \quad (2.2)$$

where ν is the mean transition rate between the sites, typically approximated to

$$\nu = \nu_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (2.3)$$

³This quantity is also referred as activation barrier or activation energy.

⁴Here, D refers to the so-called *tracer diffusivity*, measured for a single particle. It must be distinguished from the *collective diffusivity*, used in the framework of Fick's diffusion equations to measure the rate of expansion of an atomic ensemble. More on this topic can be found in Section 2.4.4.

Figure 2.1: Schematic representations of a (a) full 2D PEL corresponding to an adatom diffusing on an ideal square lattice, and of a (b) 1D PEL associated to the MEP of the adatom. E_a is the energy barrier corresponding to a diffusion jump between two adjacent sites in terraces at different heights.

according to (quasi-harmonic) transition state theories [38, 39]. In Eq. (2.3), known as the *Arrhenius equation*, ν_0 is the *attempt frequency*, or *prefac-*

tor, of the substrate, T is the substrate temperature and k_B is the Boltzmann constant.

The energy barrier E_a is usually regarded as a temperature-independent quantity, and can be determined directly by *ab initio* or classical computational methods, or indirectly through the Einstein's relation

$$\langle \mathbf{x}^2(t) \rangle = 4Dt, \quad (2.4)$$

where $\langle \mathbf{x}^2(t) \rangle$ is the adatom mean square displacement

$$\langle \mathbf{x}^2(t) \rangle = \frac{1}{N} \sum_{i=1}^N |\mathbf{x}_i(t) - \mathbf{x}_i(0)|^2. \quad (2.5)$$

of N trajectories after time t . In the latter case, $\langle \mathbf{x}^2(t) \rangle$ is measured experimentally or estimated via CMD simulations at different temperatures, and the respective diffusivities are plotted on a $\log(D)$ vs. $1/T$ curve, which has a slope equal to E_a .

Equations (2.2), (2.3), and (2.4) constitute the standard toolbox to treat atomic surface diffusion. This framework can, to a first approximation, describe both qualitatively and quantitatively the dynamics of diffusing atoms; for example, on an ideal surface with BCC symmetry, adatoms follow a unique migration path (MEP) while jumping between neighboring adsorption sites (Fig. 2.2 (a)), which implies that E_a alone is able to predict the adatom $\langle \mathbf{x}^2(t) \rangle$ as a function of time. However, the model is built on a series of assumptions that are fulfilled only in certain specific cases. For an ideal FCC surface, instead, adatoms may transition between *fcc* sites either directly, or passing through an unstable *hcp* site⁵ (Fig. 2.2 (b)), thus following different pathways through the PEL. If $\langle \mathbf{x}^2(t) \rangle$ is measured in this system, then the associated E_a would represent an effective value accounting for both fcc-fcc and fcc-hcp-fcc transitions, which would vary with temperature due to the non-linear dependence of rates ν on temperature (Eq. (2.3)). Thus, in this case, E_a serves as a black box that describes the overall diffusive behavior, but it does not contain any information about the specific mechanisms at the atomic level. Another possibility involves hopping diffusion combined with exchange diffusion, a process where an adatom penetrates into the surface while pushing out one of the atoms underneath, which becomes a new adatom replacing the former. In this case, the discrepancy between the rates

⁵Note that there are systems in which hcp sites can also be stable [40].

can be larger. For instance, the energy barrier for hopping diffusion of Au on Au(100) is 0.84 eV, while the barrier for exchange is 0.67 eV [41]. This difference induces an even more remarkable temperature dependence for the associated effective E_a , but still the trajectory can be approximated as a random walk from which D can be measured using Eq. (2.4).

As stated at the beginning of Section 2.2.1, the random walk model assumes that transition jumps are rare processes at the microscopic level. This is not always the case. Several experimental studies report unusually long diffusive jumps covering multiple adsorption sites, and recent computational models predict variations of the PEL morphology caused by temperature. In the next Section, the conventional framework based on random-walk-like trajectories is revisited, aiming for a more inclusive model able to account for anomalous effects.

Figure 2.2: Available transition paths for an adatom diffusing on a (a) bcc (001) and on a (b) fcc (111) surface.

2.2.3 Normal and anomalous diffusion

The simplicity of equations (2.2), (2.3), and (2.4) relies on the fundamental assumption that the adatom diffusion trajectory is a chain of uncorrelated rare event processes, which resembles a typical random walk. A classical theoretical result [42] predicts that by increasing the temperature, the frequency of transition jumps also increases, until the adatom diffusion path becomes continuous. This effect is expected to take place at any system at sufficiently high temperatures, due to the thermal energy $k_B T$ becoming comparable with the mean depth of the PEL, and has been confirmed by experiments

Table 2.1: Approximate energy barriers $E_a^{hom.(111)}$ and $E_{ads}^{graphene}$ for noble metals diffusing on their corresponding homoepitaxial substrates with fcc (111) symmetry and on graphene, respectively.

	$E_a^{hom.(111)}(eV)$	$E_{ads}^{graphene}(eV)$
Ag	0.100	0.004
Au	0.120	0.007
Cu	0.040	0.004
Pd	0.350	0.042

reporting long and correlated jumps on homoepitaxial systems [43–47]. This effect remains somewhat overlooked by experimentalists, as the error introduced in measurements is negligible for temperatures that are relevant for film growth.

Development of thin film applications based on novel materials may encounter certain weakly-interacting film/substrate combinations—or, equivalently, adatom/surface combinations with shallow PEL—that require further characterization and modeling. This category includes noble metals on 2D materials such as graphene, transition metal dichalcogenides and MXenes. Due to the in-plane screening of the electron charge, these materials interact via van der Waals forces and tend to not form bonds with foreign atoms, leading to low atomic adsorption energies on the surface. Several works report approximate energy barriers E_a [37, 48] calculated via static DFT minimizations and experiments, revealing that the PEL is on average one order of magnitude smaller than the PEL of metals in their corresponding homoepitaxial substrates (Table 2.1). E_a values of the order of tenths of meV compare with the thermal energy corresponding to room temperature growth experiments ($k_B T \approx 25$ meV), which indicates that these systems may not fulfill the rare-event assumption of the random walk model.

Moreover, besides the impact of small adsorption energy barriers at 0K, collective surface vibrations induced by temperature may affect the effective PEL and increase the atomic mobility, further compromising the rare event assumption. 2D materials are a good candidate for displaying the latter effect, since their reduced dimensionality and the smaller density of vibrational modes they host in their lattice, renders them less efficient in dissipating adatom energies less efficiently as compared to bulk crystals. In

Eq. (2.3), E_a is essentially the average potential energy change [37] $\langle \Delta E_a \rangle$ between the bottom and the saddle of the atomic migration path, as PEL at finite temperatures is a dynamic function. For instance, the oscillations of a vibrating graphene sheet may alter the average interatomic distance between adatom and the surface atoms forming adsorption sites. Thus, when considering temperature, all quantities must be averaged over sufficiently long times due to the dynamic nature of the surface. Temperature effects can be better understood by expanding the prefactor ν_0 in Eq. (2.3) as

$$\nu = \nu^* \exp\left(\frac{\langle \Delta S \rangle}{k_B}\right) \exp\left(-\frac{\langle \Delta E_a \rangle}{k_B T}\right), \quad (2.6)$$

where ν^* accounts for the vibrational frequencies of the system, and $\langle \Delta S \rangle$ is the vibrational entropy change during the migration event. As Eq. (2.6) reveals, the quantity in the exponential term that describes the PEL is the free energy change $\langle \Delta F \rangle = \langle \Delta E_a \rangle - T \langle \Delta S \rangle$. The latter is, in general, assumed to not depend strongly on temperature, since variations on the order of few tenths of meV are unlikely to affect the diffusion dynamics of adatoms for which $E_a^{0K} > 100$ meV. Hence, $\langle \Delta S \rangle$ is included in ν_0 for the sake of simplicity. In contrast, these variations may become critical if the PEL is shallow⁶.

The study of diffusion requires averaging $\langle \mathbf{x}^2(t) \rangle$ over a considerable number of trajectories $\mathbf{x}_i(t)$, since these may experience large statistical fluctuations. The latter poses a problem for studies with limited resources. A possible alternative, extensively tested and used for studying particle diffusion within biological systems, consists in performing internal averages over a single long trajectory $\mathbf{x}(t)$, in the following way:

$$\overline{\delta^2(\tau)} = \frac{1}{N} \sum_{n=0}^{N-1} |\mathbf{x}(n\Delta t + \tau) - \mathbf{x}(n\Delta t)|^2. \quad (2.7)$$

The quantity $\overline{\delta^2(\tau)}$ in Eq. (2.7) is known as *time averaged mean square displacement* [49, 50]. Δt is the sampling time step, τ is a variable representing a specific observation time scale, and N is the total number of sub-trajectories with a duration τ that can be defined over the total atomic trajectory (note that two different sub-trajectories defined in this way may

⁶In Paper 4 it is shown that Pd acquires an anomalous diffusion character due to temperature effects on $\langle \Delta E_a \rangle$.

partially overlap). For a total simulation time T and an observation scale τ consisting of N_T and N_τ time steps Δt , respectively, $N = N_T - N_\tau + 1$. In principle, $\overline{\delta^2(\tau)}$ and $\langle \mathbf{x}^2(t) \rangle$ are equivalent and can be used interchangeably when sufficient statistics are available, although they may differ for certain types of diffusion [51] or for studies with low sampling level (this issue is further discussed at the end of Paper 4).

In case of anomalous diffusion, the mean square displacement is assumed to follow a dependence

$$\overline{\delta^2(\tau)} \simeq 4D_\alpha \tau^\alpha. \quad (2.8)$$

In Eq. (2.8) [51], α is an exponent that accounts for the type and the degree of anomaly of diffusion relative to an ideal random walk, for which $\alpha = 1$: $0 < \alpha < 1$ corresponds to subdiffusion, and $1 < \alpha < 2$ corresponds to superdiffusion. The exponent $\alpha = 2$ represents the case of ballistic motion, in which a particle moves in one direction along a straight line⁷. D_α is a generalized diffusion coefficient with physical dimensions [$L^2 \cdot T^{-\alpha}$]. The α -dependence of the time units imply that the numerical value of a diffusivity changes at a different rate across observation scales for two particles with different anomalous character. For instance, a change from $\text{nm}^2 \cdot \text{ps}^{-\alpha}$ to $\text{cm}^2 \cdot \text{s}^{-\alpha}$ requires multiplication by a factor $10^{12(\alpha-1)}$. This non-intuitive dependence implies that a particle with $\alpha = 1.4$ has, at the cm/s timescale, a diffusivity value ~ 250 times larger than that of another particle with $\alpha = 1.2$ and the same diffusivity value at the nm/ps timescale.

Analysis in Paper 4 reveals that Ag, Au, Cu and Pd adatoms on graphene follow a superdiffusive pattern known as *Lévy walk* [52–56]. As the trajectories in Fig. 2.3 show, adatoms do not perform discrete jumps, but instead move continuously across the surface, in accordance to the prediction of Chen and Ying [42] for diffusion at high temperatures. The superdiffusive character may be inferred from the trajectories, since, due to the bias of the adatoms to maintain a specific movement direction, the covered area $\overline{\delta^2(\tau)}$ increases at a higher rate than if the adatom moves randomly after each transition jump. Besides continuous movement, Lévy walks feature a specific distribution of jump lengths⁸, consisting of a majority of relatively short

⁷It is important to point out that $\alpha = 2$ is not a limiting case for the atomic diffusion and that, in general, Eq. (2.8) does not cover all possible cases of anomalous motion patterns, specially for the case of subdiffusion.

⁸Since the movement is continuous and smooth, the jumps are here regarded as the trajectory sections in which the adatoms do not change significantly the diffusion direction.

Figure 2.3: *Ab initio* MD anomalous diffusion trajectories for Ag, Au, Cu and Pd (0.2 ns). The circles in the trajectories mark a short-range diffusion domain (figure reprinted from Paper 4 with the permission of the American Chemical Society).

jumps (which still cover several adsorption sites) and a few long jumps covering several nanometers. While performing the short jumps, adatoms are confined to certain areas or domains, and these are separated by the long jumps; thus, sufficiently long trajectories resemble a random walk, in which the domains correspond to the adsorption sites and the long jumps to the transitions between these sites. The former remarks indicate that adatoms exhibit a distinctive diffusive behavior depending on the observation time scale. This can be exemplified in Eqs. (2.7) and (2.8), which show that α

and D_α are defined on the context of the timescale τ employed for calculating $\overline{\delta^2}(\tau)$. Thus, for short time scales in which adatoms cover distances on the order of several nanometers, $1 < \alpha < 2$, while for longer times scales in which the trajectory exhibits qualitative resemblance to a random walk, α effectively becomes 1 and Eq. (2.4) is recovered from Eq. (2.8)) [57]. Moreover, Paper 4 reveals an inverse correlation between the value of α and the average depth of the PEL.

Although we do not perform explicit diffusivity measurements at higher temperatures, visual inspection of additional simulations (not published) show that the anomalous character of the adatoms increases for increasing temperatures, in agreement with the theoretical predictions of Chen and Yin [42]. We attribute this effect to a flattening of the PEL caused by surface vibrations.

Due to the qualitative changes in the effective nature of diffusion explained above, modeling film growth across several observation scales must be performed with care, since using a unique value for α and D_α may lead to unphysical results. For instance, an α measured at the nm/ps scale for a superdiffusive adatom cannot represent its movement at the cm/s scale, because then it is likely to be following a quasi random walk (as explained above), for which measurements would yield α values close to 1. Based on this information, it is advisable to model each growth stage with α and D_α values measured at a specific observation level.

In the broader context, adatom superdiffusion at the atomic level has an important two-sided implication for film growth modeling. The first is that the adatom tendency to keep memory of previous locations and move in a continuous path violates the fundamental assumption upon which Eqs. (2.3), (2.4), and the concept of energy barrier E_a are founded: that diffusion is a rare event and successive jumps are uncorrelated. Hence growth models should be revisited, incorporating Eq. (2.8). Such modifications are of significance in the modeling of nucleation and coalescence and they will be addressed later in the present chapter. The second implication is that E_a values extracted from diffusion experiments describe the effective random walk behavior of superdiffusive adatoms at large time scales, and thus they represent complex adatom dynamics at the nanoscale at specific temperatures, rather than the local shape of the PEL around a certain adsorption energy site.

The above-described picture holds for metals on graphene. However, based on the diffusion energy barriers presented in Table 2.1, anomalous

diffusion is expected to be found in other metal/2D material combinations, and in general, in any adatom/substrate combination for which $k_B T \approx E_a$. This applies, for instance, to metals on oxides [58], transition metal nitrides [46, 47], etc.

2.2.4 Cluster diffusion

Adatoms eventually come into contact with each other and form *clusters* (i.e., *dimers*, *trimers*, etc.). Although in many cases their mobility is small in comparison to that of adatoms, clusters of varied sizes are still able to diffuse across the substrate surface before reaching a *critical nucleus size* and become static⁹. Much of what is discussed in the previous section applies for cluster diffusion; however, cluster motion is the result of the collective behavior of its constituent atoms and may exhibit non-trivial dynamics without adatom counterpart, and therefore deserves a separate discussion. Here, the properties of atomic clusters as diffusive entities are reviewed, while in the next section clusters are regarded as the primitive form of mesoscopic islands.

Much experimental and theoretical work [60–62] has been devoted to study diffusion of metal clusters on graphite at room temperature, in particular Au clusters, hence we take the reported data as representative for the class of metals on weakly-interacting substrates¹⁰. Overall, these studies show that Au clusters up to ~ 100 atoms have a significant mobility on the substrate and, in particular, dimers diffuse at rates comparable to those of adatoms [64]. However, the diffusion of clusters and adatoms is different in nature; while adatoms are point objects bonding to the surface in a unique way for each point of a surface, clusters are ensembles that may adopt a myriad of different structures [65], and this allows a whole range of both individual and concerted atomic mechanisms [37] (Fig. 2.4). To name a few, a cluster may diffuse via peripheral, leapfrog movement, gliding or shearing. The activation energies associated to each diffusion mechanism can differ considerably, since each of the atomic structures bond to the surface in a particular way, and as a consequence temperature dictates which mechanisms govern diffusion [66–68]. For metal clusters on graphite at room temperature, diffusion proceeds in two distinct regimes [61]. During the *stick*

⁹For very weakly-interacting film/substrate systems, clusters may diffuse and coalesce before reaching the island stage, as it is the case for Ag clusters on graphite [59].

¹⁰Similar conclusions to the study of metal clusters on graphite are found, for instance, on Cu-on-Au systems [63].

Figure 2.4: Different mechanisms for cluster diffusion: (a) peripheral, (b) leapfrog, (c) gliding, and (d) shearing diffusion.

regime, cluster adatoms diffuse individually and cause net displacements of the cluster mass center, which oscillates confined in small areas. In contrast, during the *slip* or *ballistic regime*, clusters slide with little friction over the substrate aided by thermal surface vibrations, and cover arbitrary long distances [69]. The combination of the two regimes gives rise to a Lévy walk movement type which, in a similar way to adatoms, transitions to an effective random walk at long timescales [62].

Cluster diffusion does not only resemble that of adatoms in its superdiffusive character, but also in its dependence with temperature, as the level of correlation—i.e., the frequency and duration of slip diffusion—increases with temperature [63]. More energetic surface vibrations induce a transition from random walk to Lévy walk which, due to similarity with the transition of adatoms [42], can possibly be explained quantitatively by the flattening of the effective PEL of the cluster/substrate system. These transitions from correlated to uncorrelated motion are remarkable in the sense that, despite exhibiting qualitatively different diffusion mechanisms at the atomic level, the motion of both adatoms and clusters can be characterized by the same mathematical model (Eq. (2.8)).

Paper 5 confirms that above-explained notion also applies for the case of Ag, Au, and Cu dimers, as well as for Ag trimers on graphene at room temperature. This is a relevant result regarding metal film growth on weakly-interacting substrates, since a possible Lévy character of the dimers has not been considered explicitly in the models—multiple studies investigating cluster motion at high temperatures focus on tribological properties of Au-graphite interfaces, rather than on film growth. The main difference with the adatoms is the shift to lower α values observed for dimers, which is in agreement with the intuitive notion that diffusivities and anomalous character decrease as clusters grow larger in size [70, 71].

As a last remark, the discussion in the present section assumes diffusion over ideal surfaces. Real substrates are, however, likely to host point defects such as vacancies or impurities, boundaries between regions with different crystallographic orientations, cracks, etc. All of these factors affect diffusion and may indirectly play a significant role for later growth stages, and require specific modeling to be addressed.

2.3 Nucleation

2.3.1 Thermodynamics of nucleation

Nucleation is an universal process that triggers an ample variety of natural phenomena, including droplet formation in clouds [72], ice crystallization in water [73], or mineral growth under the Earth crust [74]. Within the field of film growth, nucleation plays an important role as it does not only determines the initial distribution of islands on the substrate, but also controls the

growth rate of individual islands (Section 2.4.4) and the type and speed of island coalescence (Section 2.5). The classical description of nucleation [75], which stems from thermodynamics, treats the nucleating body as a gaseous, liquid, or solid phase separated by an ambient phase by an enclosing 2D interface. Along with the nature of film synthesis, in this section we focus on a solid nucleating phase and a vapor phase, although the derivation below translates to any nucleating system.

From a thermodynamic perspective, nucleation results from a difference $\Delta\mu$ between the chemical potential of the vapor phase and the chemical potential of the substrate. $\Delta\mu$ drives the vapor/substrate system to incorporate atoms from the vapor-phase into the bulk of the substrate for minimizing the total energy. $\Delta\mu$ can be calculated from the Gibbs-Thomson equation

$$\Delta\mu = k_B T \ln \left(\frac{P}{P_0} \right), \quad (2.9)$$

where P is the pressure of the vapor-phase and P_0 is the *equilibrium vapor pressure*, the pressure at which mass transfer occurs at the same rate in both directions between the solid and the vapor phase. The ratio P/P_0 is referred as *supersaturation*, and is a quantitative representation of the departure of the solid/vapor interface from equilibrium.

For a vapor atom to become part of the bulk, once it has been deposited it needs to meet with other atoms to form a stable nucleus of p atoms. Since the nucleus holds a homoepitaxial relationship with the bulk surface, it is assumed here to adopt a 2D morphology. The formation requires the system to spend an energy $2\gamma_{line}\sqrt{\pi p}$ for building a 1D vapor/solid interface—the line around the nucleus perimeter—where γ_{line} is the line tension of the nucleus, but it simultaneously gains an energy $p\Delta\mu$ by incorporating the atoms from the vapor phase. Thus, the free energy change associated to the formation of the nucleus becomes

$$\Delta G(p) = 2\gamma_{line}\sqrt{\pi p} - p\Delta\mu. \quad (2.10)$$

This function reaches a maximum ΔG^* value at $p^* = \pi\gamma_{line}^2/\Delta\mu^2$, which constitutes the *critical size* of the nucleus (Fig. 2.5). Once the latter is formed, it tends to evolve according to the free-energy minimization principle; if $p < p^*$, the nucleus will tend to decrease in size and disappear, since this would lower the total energy of the system, while if $p > p^*$, whether the nucleus disappears or survives and grows depends on random thermal

fluctuations of its environment. Deposition conditions are usually adjusted to make p^* as small as possible.

Figure 2.5: Plot of the free energy variation $\Delta G(p) = 2\gamma_{line}\sqrt{\pi p} - p\Delta\mu$ of a surface after the formation of a nucleus of p atoms, as a function of p . This variation reaches a maximum value ΔG^* for a critical nucleus formed by p^* atoms.

2.3.2 Kinetics of nucleation

A more profound description of nucleation includes kinetic effects. This is achieved by regarding $\Delta\mu$ in Eq. (2.10) not as an energy difference between two equilibrium states, but as the energy gain resulting from an atom traversing through an specific path. For the case of nucleation on a clean substrate, this change of perspective rejects the picture of atoms incorporating to the growing nucleus directly from the vapor phase, and considers the entire process of deposition, surface diffusion, and bond formation with the 1D nucleus interface. It follows that the energy $\Delta\mu$ gained from incorporating an atom

to the nucleus becomes the sum of the energy increase $\Delta\mu_{dep} = \mu_{solid} - \mu_{vapor}$ due to deposition from the vapor phase to the solid surface, plus the increase $\Delta\mu_{diff} = \mu_{\mathbf{x}(T)} - \mu_{\mathbf{x}(0)}$ due to diffusion from the deposition point $\mathbf{x}(0)$ to a final position $\mathbf{x}(T)$, and the final $\Delta\mu_{bond}$ increase due to bond formation with the nucleus. Then, the form

$$\tau_{nuc} \propto \exp\left(\frac{\Delta G^*}{k_B T}\right) \quad (2.11)$$

can be used to estimate the mean formation time τ_{nuc} of a nucleus of p^* atoms¹¹.

By explicitly considering the physical path followed by atoms, the former description allows to indirectly account for morphological elements of a growing film/crystal. This serves to model not only the onset of island formation on a bare substrate, but also equilibration processes in which the source of mobile adatoms are in the islands themselves, instead of a vapor phase. In addition, Eqs. (2.9) and (2.10) may be used to account for the combined effect of two simultaneous atomic sources, i.e., islands and the vapor phase, and thus model later dynamic stages of film growth, such as coalescence, taking place under realistic deposition conditions (see Paper 3). Section 2.4.2 introduces the main morphological features of atomic islands, necessary to define more complex atomic paths across a film surface.

2.3.3 Atomistic nucleation theory

In order to advance toward the goal of understanding film growth, *atomistic nucleation theory* [20] merges the previous knowledge about isolated atomic nuclei into a broader framework capable to describe island ensembles. By introducing the concept of *capture numbers* σ_s , which account for the propensity of a cluster of size s to adsorb an adatom, this theory predicts the island density N to evolve according to

$$N \approx \frac{1}{\Omega} \eta(\Theta, i^*) \left(\frac{\Omega^2 F}{D} \right)^{\frac{i^*}{i^*+2}} e^{\Delta G_{i^*}/(i^*+2)k_B T}, \quad (2.12)$$

with $\eta = [(i^* + 2)\sigma_{i^*}\bar{\sigma}^{-(i^*+1)}\Theta]^{1/(i^*+2)}$. In Eq. (2.12), Ω denotes the area of an adsorption site, $\Theta = \Omega Ft$ the *coverage*—i.e., the amount of material

¹¹Despite that τ_{nuc} in Eq. (2.9) is a mere qualitative estimation, it is introduced in this section because time variables lie outside the realm of thermodynamic theories.

deposited onto the substrate—after a time t , i^* the critical island size¹², and ΔG_{i^*} the formation energy of an atomic island of size i^* . Note that the grouping of all variables in Eq. (2.12) except F and D into a multiplying factor, and the definition $\chi = i^*/(i^* + 2.5)$, which holds for 3D islands, can be used to obtain the simplified form Eq. (2.1). It is often assumed that atomic detachment is a relatively infrequent process relative to the rate of island formation, which implies that $i^* = 1$ and by extension that $\chi = 2/7$.

Eq. (2.12) constitutes one of the central results of thin film growth theory. Based solely on the deposition rate and the atomic diffusivity, it can predict the final density N_{sat} of islands present on a substrate prior to the coalescence stage. This is remarkable since, for growth conditions at which island coalescence is not active, N_{sat} sets the density of film grain boundaries or, in other words, the final film microstructure. In addition, it is useful to intuitively associate an elevated number of substrate islands with a low atomic mobility and a high atomic deposition rate, and viceversa.

The findings of Paper 4 concerning adatom superdiffusion indicate that predictions from the atomistic nucleation theory must be approached with care when modeling metal growth on weakly-interacting substrates, even at room temperature. Theoretical works [76, 77] reveal that the bias in diffusion direction characteristic of Lévy walks reduces the density of stable islands on the substrate, and modifies the scaling relation χ from Eq. (2.1). This implies that attempts to predict N_{sat} from atomistic arguments will result in overestimated values and, in a similar way, estimates of D will result in underestimated values. In case quantitative predictions are desired, the direction to follow is to revisit the derivation of the quantity N_{sat} , including the fractional time units defined in Eq. (2.8) and replacing D by the generalized diffusivity D_α .

In addition, Paper 5 shows that atomic dimers not only are mobile, but also execute Lévy walks¹³. This finding is supported by multiple works from the literature reporting high mobility of large clusters at high temperatures. The derivation of Eq. (2.12) assumes that all clusters, including dimers, are immobile. For the contrary case, the scaling relation takes a value

¹²The notation i^* refers to the particular case of critical *island* size, to distinguish it from the critical *nucleus* size p^* , which is a more general concept.

¹³It is important to remark that clusters may be mobile irrespectively of having reached their critical size.

$$\chi = \frac{i_{mob}^*}{2i_{mob}^* + 1}, \quad (2.13)$$

where i_{mob}^* is the largest size for which a cluster can be mobile. However, there is no current alternative also accounting for the superdiffusive character of the clusters. In fact, the previously mentioned errors in the estimations of N_{sat} and D are likely magnified to a certain extent by the cluster behavior. Further work in the field of atomistic nucleation is thus required in order to obtain more accurate forms for N_{sat} .

While the present description briefly discusses the origins of film microstructure based on island nucleation on the surface, the next section focuses on the growth dynamics and morphology of large individual islands, and the impact they have on the final film roughness.

2.4 Island growth

2.4.1 Equilibrium and far-from-equilibrium growth

Islands are a central concept in thin film growth research, as their shape evolution dynamics can be easily associated with film morphological and microstructural features, including grain size and orientation, crystallographic texture, and surface roughness. Hence islands serve as the bridge between the multitude of fast atomic-scale diffusion events and the mesoscopic film morphological evolution.

Although film growth proceeds far from equilibrium, thermodynamic arguments are instructive for predicting film morphologies on a qualitative level. Such arguments are summarized in the classical work of Bauer [78] in 1958, who classified island and film growth modes as a function of the energy balance between the surface free energy γ_S of the substrate, the surface free energy γ_D the deposit, and the interfacial free energy¹⁴ γ_{int} . For the case

$$\gamma_S < \gamma_D + \gamma_{int}, \quad (2.14)$$

the energy balance dictates that the substrate area covered by the deposit is minimized, i.e., deposit atoms agglomerate in dispersed 3D islands. This

¹⁴Thermodynamic minimization principles requires that the ratio between each of the areas of the system is such that the total free energy reaches its minimum possible value.

mode, known as *Volmer-Weber growth* (Fig. 2.6 (a)), corresponds to the behavior observed during, e.g., metal layer deposition on weakly-interacting substrates. On the contrary, if

$$\gamma_S \geq \gamma_D + \gamma_{int}, \quad (2.15)$$

the deposit fully wets the substrate to maximize the interface vs. the substrate area, leading to *Frank-van der Merwe* mode (Fig. 2.6 (b)). In this mode, thin films grow via consecutive formation of layers of one-atom thickness (i.e., monolayers), and it is mostly found in purely and approximately homoepitaxial systems¹⁵.

Figure 2.6: Classification of epitaxial growth modes according to Bauer, in which (a) corresponds to Volmer-Weber growth, (b) to Frank-van der Merwe growth and (c) to Stranski-Krastanov growth.

If Eq. (2.15) holds for a material with a significant lattice mismatch with the substrate, as layer-by-layer growth proceeds elastic energy caused by the lattice mismatch builds up increasing the magnitude of the right-hand side part of Eq. (2.15). After deposition of a certain amount of material, this progressive accumulation of elastic energy inevitably leads to a reverse of condition (2.15) to condition (2.14), and the deposit forms dispersed 3D islands in order to release excess strain energy. This growth scenario is referred to as *Stranski-Krastanov* mode or strain-induced roughening (Fig. 2.6 (c)). It

¹⁵In a purely homoepitaxial system, $\gamma_{int} = 0$ and $\gamma_D = \gamma_S$ by definition.

should also be noted that the transition from 2D to 3D morphology is not the only mechanism by which strain energy is released; generally, for low temperatures and low lattice-parameter mismatch, this can also be achieved by the generation of misfit dislocations while maintaining a 2D growth morphology [79]¹⁶.

The Bauer classification describes growth in near-to-equilibrium epitaxial systems. Concurrently, all thin-film deposition techniques are fundamentally far-from-equilibrium processes, in which kinetic effects dominate or are an important component of film growth, which evolves via metastable configurations associated with local minima in the film/substrate system free energy landscape¹⁷. A well-known analogy is the shape of snowflakes: while thermodynamics predict a unique equilibrium configuration of a given number of water molecules at given ambient pressure and temperature conditions, snowflakes are encountered in countless forms [80] (Fig. 2.7) as a result of the different kinetic conditions prevailing during their nucleation and growth in the atmosphere.

Thus, describing island shape evolution dynamics requires viewing growth as a far-from-equilibrium process, whose outcome is determined by the collective effect of individual atomic-scale events taking place on the film/substrate system.

2.4.2 Kinetics of island growth

Understanding kinetic aspects of island growth requires identification of key atomic diffusion processes. The first step of this task consists on defining the main morphological features of a crystalline substrate surface, which can be conveniently done by using the step-edge-kink model [82] (Fig. 2.8). Atoms are adsorbed on a flat empty surface called *terrace*, and form new layers, or *islands*, bounded by *edges*. When an edge is regarded as the boundary between terraces at different heights, it is instead called *step*. The intersection between two edges is called *corner*. Edges may be disrupted by *kinks*, which are single-atom-width displacements of an edge.

¹⁶It is important to point out that the 3D island growth observed for metals on weakly-interacting substrates does not correspond to the Stranski-Krastanov mechanism, since metal 3D growth begins well before complete deposit layers form. Besides, the weak interaction between metals and substrate only causes negligible amounts of strain energy.

¹⁷The energy landscape of the entire film/substrate system must not be confused with the atomic PEL, which refers exclusively to the energetic environment of a single atom.

Figure 2.7: Several metastable shapes for ice crystals grown at different ambient conditions (Figure extracted from Reference [81]).

The easiness by which atoms diffuse may be, to a first approximation, intuitively inferred from the local geometry based on the change in the coordination (i.e., bond number) that an atom undergoes when transitioning from its initial to the final adsorption site. Diffusion on a terrace is the most frequent process, as the atom only distances slightly from its neighbours at the initial adsorption site before feeling the attraction of those in the final position. Along the same lines, edge diffusion is also frequent, albeit not as frequent as terrace diffusion and only along ideal edges formed by straight lines of atoms; rounding a corner requires the atom to take a considerable distance from its initial neighbors in order to reach the saddle point, and thus it occurs at lower rates. It follows that detachment from edges and kinks, where bonds are broken but there is no attraction from other atoms in similar positions on the final adsorption site, become the most infrequent processes¹⁸.

The hierarchy of the transition rates associated with each atomistic event

¹⁸Extense lists of energy barriers for surface diffusion processes have been calculated for metal-on-metal homoepitaxial systems [83, 84], e.g., Cu/Cu(100) and Ag/Ag(111), based on the coordination numbers of initial and final positions (see Section 3.3.3).

Figure 2.8: Schematic representation of a crystalline surface and its morphological features according to the step-edge-kink model.

can be quantitatively established with Eq. (2.3). Unlike the case of superdiffusion on the substrate, island adatoms experience local homoepitaxial environments which impose rare-event diffusion, and therefore the Arrhenius equation suffices to provide good rate estimates. One of the key implications of Eq. (2.3) is the exponential dependence of rates on temperature. This implies that differences between rates become more or less pronounced when varying growth temperatures, and it may have a drastic impact on the final island and film morphology. A good example is the growth of monolayer islands with different morphologies on homoepitaxial systems, such as Ag/Ag(111) [85] or Pt/Pt(111) [86], where their shapes transition from dendritic to compact upon a growth temperature increase. While these dendritic shapes are the result of low diffusion rates along the island edges with respect to deposition and surface diffusion rates at low temperatures, edge diffusion may be enhanced by a temperature increase, which causes edge adatoms to fill the gaps between the dendrite branches and, in turn, to make the islands compact. Along the same reasoning, Section 2.4.3 discusses island heights at different temperatures, based in the rate of interlayer transport.

2.4.3 Step barrier and 3D growth

The atomistic pathway to follow for crossing a step downward, from a terrace to the edge position below, is considerably longer than for other processes and therefore its corresponding energy barrier is larger and is difficult to estimate by mere bond counting. The additional energy arising from the extra length of the diffusion jump is known as *Ehrlich-Schwobel barrier* or *step barrier*. This barrier is associated with atomic descent and limits the interlayer mass transport between the top of flat islands and the substrate,

and, in the same way, in a percolated film limits the transport between the most exposed regions and the bottom of the holes of the film (Zeno effect) [35, 36]. The reverse process, i.e., adatoms crossing the step barrier while diffusing toward a layer above, is negligible in homoepitaxial systems.

Atomic diffusion across steps regulates island heights, and is therefore a key element in the discussion of island growth dynamics. Upon deposition of material on a substrate, small single-layer islands start forming with their perimeters being bounded by a step with an associated step barrier. This implies that any atom directly deposited on top of an island must overcome this barrier in order to diffuse down to the substrate, a process which, according to the Arrhenius equation (Eq. (2.3)), will occur more often with increasing temperature. From this it follows that for a deposition experiment, if temperature is sufficiently large for atoms to overcome step barriers and escape the island tops, layer-by-layer growth occurs. Otherwise, atoms are confined within island tops, where they eventually nucleate new layers and the islands evolve to 3D stepped structures or *mounds*. The process of gradual switch between flat 2D islands and 3D mounds is known as *kinetic roughening*, and it is a characteristic feature of the non-equilibrium character of film growth.

Figure 2.9: Schematic illustrations of possible upward atomic transport mechanisms during 3D island formation on weakly-interacting substrates. (a) A small barrier $E_{S \rightarrow 1}$ facilitates transport from the substrate onto the first atomic layer, but the homoepitaxial conditions from the first layer causes a larger barrier $E_{1 \rightarrow 2}$, which impedes further upward diffusion. (b) The formation of sidewall facets provides a facile diffusion pathway for upward diffusion with a barrier E_S (figure reprinted from Paper 1 with the permission of the American Physical Society).

Interestingly, for weakly-interacting substrates, islands tend to adopt pronounced 3D morphologies. It is known that they form already at the very initial stages of film growth, as measurements of surface coverage after deposition of small amounts of material [87] reveal that only a fraction of the deposit is in contact with the surface, and the fact that these islands are still too small to efficiently capture atoms from the vapor phase indicates that an upward transport mechanism is involved in their formation. The most intuitive explanation is that the atomic bond between a film and a substrate atom is much weaker than the bond between two film atoms, edge atoms are allowed to cross the step barrier in the opposite direction and ascend to the island top from the substrate—this is a very unlikely process in homoepitaxy—and in this case a high temperature favors 3D growth [88], in contrast to homoepitaxial growth. However, the concept of step barrier can only explain partially the formation of 3D islands on weakly-interacting substrates, which in addition exhibit a morphological evolution radically different than that observed in near-to-homoepitaxial film/substrate systems; this picture does consider that, once atoms are on top of the second layer of an island, they are bounded to atoms of their same type below and therefore a further ascent becomes, at best, improbable (Fig. 2.9 (a)). Thus, although the step crossing mechanism suffices to explain roughness changes in near-to-homoepitaxy systems [89], it cannot account for the pronounced 3D island morphologies observed on weakly-interacting substrates [48], which might be explained by a complementary atomistic process. A hint that could shed some light on this question is the difference between the surface features of 3D islands grown in homoepitaxial and weakly-interacting substrates: while in the former case the island sides are formed by stepped surfaces [90], in the latter case the sides might be smooth facets [91, 92], which, for a diffusing atom, mimic the environment experienced when crossing a flat terrace (Fig. 2.9 (b)). This is a viable explanation to the origin of the 3D island, but yet there is no agreement on whether it indeed occurs in this way or not. In addition, the concept of step-edge barrier constitutes a kinetic limitation which alone determines the final morphology of islands grown in homoepitaxial systems depending on temperature, but there is no known equivalent process responsible of the 3D island morphologies.

Paper 1 provides evidence supporting the hypothesis above. Small nuclei comprised of tenths of atoms adopt 3D morphologies, first via jumps to the second layer across the steps, and then via upward rapid diffusion across flat sidewalls facets. This explanation alone is however not sufficient to explain

the island size dependence from a kinetic perspective, since the initial nuclei display facets for both high and low temperatures. Instead, results also show that the energy barrier associated to the crossing between the facets and the island top acts as a rate-limiting step—i.e., the process regulating morphological changes as a function of temperature—for the island heights, in the same fashion that step crossing does for homoepitaxial islands. In addition, Paper 1 reveals that 3D islands grow in a self-similar manner, maintaining the faceted pyramid structure for increasing coverage levels.

2.4.4 Top-layer nucleation

Identification of the main atomistic processes involved in 3D island growth allows to understand the dependence between synthesis conditions and island shape evolution. Multilayer growth of mounds at homoepitaxial conditions has been previously investigated through the concept of critical radius [93–95] R_c , defined as the average radius of the top layer of an island which is required for the nucleation of a new layer to take place.

Obtaining an expression for R_c requires following a series of steps. First, the relevant timescales involved in the top-layer nucleation process must be identified; these are the mean time interval

$$\Delta t = \frac{1}{F\pi R^2} \quad (2.16)$$

between subsequent arrivals of atoms on the island, which is approximated to a circle, the *diffusion time*

$$\tau_D \sim R^2/D_c \quad (2.17)$$

required for an atom to diffuse across the island, and the mean *residence time*

$$\tau = \bar{u}/F \quad (2.18)$$

that an adatom spends on the island, if no nucleation occurs¹⁹. The quantity $\bar{u}$ in Eq. (2.18) represents the mean adatom density on the island top. $\bar{u}$ is obtained from the stationary diffusion equation

¹⁹The variables Δt and τ defined here are not to be confused with the sampling time step and the timescale of $\delta^2(\tau)$ introduced in Section 2.2.3.

$$D_c \nabla^2 u(\mathbf{x}) + \sigma = 0, \quad (2.19)$$

or Fick's second law of diffusion, which implicitly assumes that the local atomic density $u(\mathbf{x}, t)$ does not change with time, i.e., it has reached a *steady-state* regime. The collective diffusion coefficient D_c corresponds to the average diffusivity of an atomic ensemble in a certain region of space. In the present study, where adatom-adatom interactions are neglected, D_c coincides with the tracer diffusivity D of single adatoms defined in Sec. 2.2.2—a derivation of Eq. (2.19) and a discussion of the assumptions concerning the steady state approximation is presented in the Appendix A.

For homoepitaxial islands, the rate ν' of downward step crossing is much lower than that of terrace diffusion, and adatoms spend a considerable amount of time on the island top ($\tau \gg \tau_D$). Concurrently, the mean time interval between subsequent depositions is much larger than the residence time ($\tau \ll \Delta t$), although both τ and Δt have broad statistical distributions and are thus subject to fluctuations. The latter implies that nucleation does not occur only when the island radius reaches large enough values for $\tau \sim \Delta t$, but also much earlier due to the fluctuations. This is in fact the main top-layer nucleation mechanism. Under these premises, second layer nucleation theory predicts a nucleation rate

$$\omega_{nuc} = \frac{\tau}{(\Delta t)^2} = \frac{\pi^2 F^2 R^5}{2a\nu'}, \quad (2.20)$$

as well as a critical radius for nucleation

$$R_c = \left(\frac{7}{\pi^3} \frac{a\Omega\nu'}{FN} \right)^{1/7}, \quad (2.21)$$

in which a is the substrate lattice parameter. Eq. (2.21) succeeds on explaining experimental observations of 2D islands at high temperature growing to large sizes before the onset of second layer nucleation, as R_c increases when ν' does.

This model is, however, only applicable to islands for which the interlayer diffusion is constrained to only one direction—the energy barrier for step crossing from the island edge to the top layer is prohibitively large, and virtually no atoms undergo this process—and nucleation depends on atoms deposited directly on the island top (Fig. 2.10 (a)).

Figure 2.10: Possible pathways for adatom arrival from the vapor phase to the top layer of an island growing on a (a) homoepitaxial and a (b) weakly-interacting substrate.

For the case of 3D islands on weakly-interacting substrates the situation is qualitatively different, as the weak bonding between substrate and deposit atoms results in a lower barrier for upward diffusion which leads to an ascending mass flux (Fig. 2.10 (b)) that is not accounted in the previous derivation. In addition, the edges of the layers above may expand and reach the edges of the layers below, forming low-index facets which facilitate even further the transport of mobile atoms from the island bottom to its top.

Paper 2 shows the way by which an upward mass flux between the substrate and island top modifies the growth dynamics of 3D faceted islands with respect to that of mounds. To this purpose, the top-layer nucleation model presented above is adapted to include the key microscopic diffusion mechanisms identified in Paper 1, i.e., detachment from the substrate toward the island facets, attachment to growing layers and kinks on the facets, and crossing between the facets and the top layer. The calculation of the density of mobile atoms on the substrate, and on the facets and top of a single 3D island, allows to estimate ω_{nuc} and R_c , and thus capture the general growth trends of metal islands on weakly-interacting substrates with a simple analytical description (note that the goal is not to develop an accurate modeling tool to compute quantitative predictions). Results show that increasing temperatures lead to a decrease in R_c , which is in agreement with the experimental observation of 3D growth enhanced by increases of synthesis temperature. In addition, the updated model recovers the characteristic R_c vs. T trend of homoepitaxial 2D islands by manually inhibiting upward diffusion.

The Lévy walk character of adatoms found in Paper 4 also has an indirect impact on top layer nucleation models. The decrease of N_{sat} due to superdiffusion is accompanied by an increase of the island capture areas, which causes a net increase in the atomic flux arriving to the island. Thus, since diffusion on the substrate is treated as a random walk in both analytical and computational models, all R_c values reported in Paper 2 are overestimated.

2.5 Coalescence

2.5.1 Thermodynamics of shape equilibration

Island coalescence may completely erase morphological features attained during island nucleation and growth [96–99]. For deposition conditions favouring high coalescence rates, all islands covering relatively large substrate areas will eventually impinge on each other²⁰ and become single crystalline structures—expulsing possible boundaries due to lattice mismatch—resulting in a substrate with a small density of large islands capturing any small island nucleating nearby. This growth mode, commonly referred as *droplet-growth*, is in high contrast with the evolution undergone by a film in the absence of coalescence. In the latter case, the deposit percolates while the islands are still small, because surface diffusion is slow and clusters do not manage to equilibrate before other islands come into contact. This results in films which host dense networks of grain boundaries, and are smoother compared to those grown at conditions of large coalescence rates. From the discussion above, it is easily inferred that an understanding of the coalescence process, as well as of the process parameters that it depends on, is required in order to make possible the prediction and control of nanostructure and film growth.

The problem of two solids redistributing their mass to become a single one was first undertaken while developing the sintering theory in the 1950's. The range of temperatures treated by these studies spans up to values close to the melting point of materials, and several mechanisms of mass transport are considered, such as viscous flow or bulk diffusion, although for deposition experiments material is assumed to be redistributed mostly by surface diffu-

²⁰Coalescence may also occur without island contact via mass diffusion directed from small to large islands, a process known as Ostwald ripening [100], which we do not consider in this thesis as we focus on evolution and coalescence of single islands, rather than ensembles.

sion. Specific research of the latter case by Herring [101] revealed that the time τ_{eq} required for solid bodies to equilibrate towards their lowest-energy configuration is proportional to the fourth power of their length scale R as

$$\tau \propto R^4 \quad (2.22)$$

and, later, Nichols [102] and Brailsford and Gjostein [103] showed that, for coalescing spheres, the proportionality constant in Eq. (2.22) is

$$B = \frac{D_S \gamma \Omega^2 \rho}{k_B T} \quad (2.23)$$

where D_S is the self-diffusion coefficient, γ the surface energy, Ω the atomic volume and ρ the atomic density per unit area. Eq. (2.23) indicates clearly that, alongside deposition rate F , T is the main parameter that may be adjusted to influence the coalescence rate on growth experiments for a given material system. However, equilibrating solids must fulfill two fundamental conditions for Eq. (2.22) and Eq. (2.23) to be applicable. These equations are derived by calculating variations of the local chemical potential μ , which is the driving force for atomic redistribution, with flux $\mathbf{J}$ given as

$$\mathbf{J} = \frac{D_S \Omega \rho}{k_B T} \nabla \mu. \quad (2.24)$$

μ in turn depends on the curvature K of the solid, as shown in the generalized Gibbs-Thomson equation [104]

$$\mu \approx \mu_\infty + \Omega \left[\left(\gamma + \frac{\partial^2 \gamma}{\partial \theta_1^2} \right) K_1 + \left(\gamma + \frac{\partial^2 \gamma}{\partial \theta_2^2} \right) K_2 \right]. \quad (2.25)$$

It follows that, in order to compute $\mathbf{J}$ and arrive to Eq. (2.23), μ must be defined over the entire surface of the solid (Eq. (2.25)), and this surface must have a certain curvature K (Fig. 2.11 (a)). Thus, this framework cannot account for solids either too small or exhibiting flat surfaces or facets, as the curvature cannot be obtained, or becomes a singularity, respectively.

2.5.2 3D island coalescence

For many deposition experiments, coalescence dynamics cannot be predicted by means of near-to-equilibrium thermodynamic arguments (Eq. (2.22)), since below a certain temperature T_R characteristic of each material—i.e.,

Figure 2.11: (a) Coalescence under annealing conditions of a pair of 3D islands with rough morphologies. (b) Equilibration of a faceted solid cluster via 2D layer nucleation. (c) Coalescence of a pair of faceted 3D islands under the influence of an active deposition flux.

the *roughening transition temperature*—smooth facets start appearing on the surfaces [105]. The absence of kinks on the facets implies that shape evolution cannot be derived by assuming a continuous system where atoms can detach, diffuse, and re-attach from- and to any point of the surface. Atoms can only become stable if they find another diffusing atom in the facets and nucleate a new layer (Fig. 2.11 (b)), and thus any treatment of coalescence under such conditions must include the kinetics of nucleation [106]. In addition, all models available in the literature approach the problem exclusively during *annealing conditions*, i.e., the fact that in deposition experiments condensation of the vapor phase brings extra mobile atoms to the surface of the nanostructures is not taken into account (Fig. 2.11 (c)).

This situation is identical to that of nucleation from the vapor phase described in Sections 2.3.1 and 2.3.2. According to the thermodynamic and kinetic framework presented therein, the nucleation rate depends exponentially on the Gibbs energy barrier ΔG^* associated with the formation of a critical nucleus of size p^* (Eq. (2.11)). The only difference in this case is that the cluster kinks become the primary source of adatoms, as well as the unique source for annealing processes, and this must be reflected in the chemical potential variation $\Delta\mu$. In realistic film growth experiments, both deposition and kink detachment are non-negligible processes and should be taken into account for accurate descriptions.

Paper 3 deals with the morphological evolution and dynamics during coalescence of 3D faceted islands, emphasizing on the potential effects of a deposition flux, which has not been considered in current growth models.

Results show that, at annealing conditions, coalescence manifests itself by one of the islands absorbing the other via sidewall facet migration, which in turn is mediated by the nucleation and growth of two-dimensional (2D) layers on the island facets. This is in agreement with the theoretical works accounting for faceting in the descriptions of solid equilibration. Results also reveal that the supply of mobile atoms increases the nucleation probability and shortens the time required for coalescence completion, but for fluxes above 1 ML/s, coalescence is predominantly governed by deposition from the vapor phase and the island pair reaches a compact shape via agglomeration. In the latter case, the facet nucleation problem becomes identical to that of nucleus formation on the substrate, described in Section 2.4. These findings explain experimental results which show that two-dimensional film growth morphology on weakly-interacting substrates is promoted when the rate of island coalescence is suppressed. In addition, they show that deviations of experimentally reported film morphological evolutions in weakly-interacting film/substrate systems from predictions based on the sintering and particle growth theories [29, 88, 96, 101–103, 107–110] may be understood in light of the effect of deposition flux atoms on the energetics and kinetics of facet-layer nucleation during coalescence.

As explained at the end of Section 2.4.4, superdiffusion induces larger capture zones with respect to those estimated with the random walk model. It follows that simulations in Paper 3 do not provide the coalescing cluster with enough atoms, hence the measured threshold for agglomeration may be smaller than the estimated value of 1ML/s.

Chapter 3

Multiscale modeling

Recent advances in computation have shaped the way we conduct science. Physical systems can now be faithfully recreated and manipulated in virtual environments, replacing costly, cumbersome, and sometimes unviable experiments by series of calculations performed in powerful computers. As these silicon labs are built by humans, it is possible to design experiments to suppress noise and selectively study phenomena, and to monitor the system from almost any angle. Thus, while computational tools themselves encompass a whole world of complexities and nuances, they have the advantages of convenience and versatility, and this is no exception for material science research. A notable number of tested algorithms are able to describe behavior of materials at different length scales using atoms as a fundamental system unit. This is well-suited to our goal of understanding the dynamics of early growth stages of thin films, since an appropriate selection of computational tools may bring detailed information of the main atomic-scale mechanisms across several length scales, making possible to identify correlations between these processes and, in turn, to draw general conclusions about the origin of film morphological features.

The present chapter describes the multiscale approach employed in this thesis. Each section includes a discussion of the strategy followed for the modeling of each observation scale, as well as a brief introduction to the corresponding computational methods. According to this scheme, Section 3.1 focuses on the computation of PELs with density functional theory, Section 3.2 on the simulation and monitoring of atomic diffusion behavior with molecular dynamics, and Section 3.3 on the simulation and characterization of nucleation, island growth, and coalescence with an in-house kinetic Monte Carlo code.

3.1 Atomistic potential energy landscapes

3.1.1 *Ab initio* models

The potential energy landscape [30] is a powerful theoretical concept. In the context of thin film growth, it associates the chemical composition and the spatial arrangement of an adatom and the substrate atoms below with the propensity of the adatom to perform diffusive jumps. This information can be supplied to algorithms able to determine the occurrence rate of such jumps or, alternatively, the forces acting on the adatom, and therefore constitutes the foundation for developing comprehensive multiscale models¹. The downside of this approach is that it is complicated to measure a PEL experimentally [111], and the most feasible way to obtain it is through first principles (or *ab initio*) methods [112], i.e., computing the PEL based on the laws of quantum mechanics. Given that it is obtained by a thorough procedure, *ab initio* information becomes an alternative for experiments and is deemed axiomatic for the purpose of material modeling. In fact, recent models reach such fidelity with reality that are used as a reference point to guide experimental procedures.

Basic *ab initio* schemes are able to reproduce the physical properties—e.g., elastic constants, thermal expansion or conductivity—of simple material systems by processing and computing the electronic structure alone, but advanced implementations include explicit corrections to account for a multitude of quantum effects. For the study of metals on weakly-interacting substrates, and more specifically, noble metals on graphene, we found that spin and van der Waals corrections had significant effects on the calculated energies and had to be included.

In general, PEL calculations are performed at 0K, i.e., *static*, since including temperature effects requires implementation of complex procedures such as *thermodynamic integration*—this term refers to a family of methods designed around the idea of measuring and then integrating free energy derivatives—to estimate free energies, rather than potential energies. A fundamental part of the calculation of a static PEL is the structural relaxation. Each possible configuration of an atomic ensemble has its own associated energy, due to differences in interatomic distances (and, in case of molecules,

¹This type of approach is known as *bottom-up*, while the departure from established macroscopic information and investigate progressively smaller length scales is referred as *top-down*.

orientation), but only the lowest energy is searched, as in real systems structures tend to adopt the most stable configuration available in the phase space. However, the atomic positions given as input to *ab initio* codes are always, at best, slightly displaced from those of the ideal configuration, and therefore numerical minimization algorithms [113] are employed to scan the configurational phase space and optimize the atomic positions throughout successive iterations. It is important to mention that the configurations are updated according to purely mathematical schemes, which implies that supervision is essential to uncover potential nonphysical situations in these minimizations. One good example was found during the calculation of adsorption energies of adatoms on a graphene sheet, as the adatom-graphene distance, and by extension the system energy, would be different depending on the initial position assigned to the adatom. This was caused due to the existence of several adjoining local energy minima, which meet the criteria of stable configuration and lead the algorithm to stop the iterative search.

For growth modeling, PEL calculations are generally used to estimate the energy barriers E_{ads}^{0K} associated with adatom diffusion processes. This requires to identify the main adsorption sites of the substrate—i.e., to find the basins of the PEL—which usually coincide with high-symmetry points of the substrate lattice structure. Then, *ab initio* methods are used to compute the adatom adsorption energies along a certain path between two PEL basins, and the maximum energy difference, i.e., that between the PEL saddle point and the initial site, corresponds to E_{ads}^{0K} . One popular way to do this is to apply *nudged elastic band* (NEB) method [114], since, by relaxing a chain formed by atoms linked by springs whose ends are located at the initial and final adsorption sites, the output E_{ads}^{0K} coincides with that of the minimum energy path. A more sophisticated technique consists on using a group of algorithms called open-end searches [115], that explore the PEL around initial adsorption sites aiming to find saddle points associated with unknown diffusion paths.

The methods described above are very accurate in determining 0K PEL, but this information must be handled with care. Any real system has a certain amount of thermal energy, which is negligible in some cases, but may provoke unexpected effects which are far away from the behavior predicted in static conditions. Some examples are the Lévy walk movement observed for metal adatoms on graphene, which breaks with the notion of rare-event jumps and energy barriers (see Section 2.2.3), or the exchange diffusion, that involves several atoms in the process preventing the depiction of PEL as an

uni-valued function between energy and adatom location. It is thus advisable to first identify the atomic-scale dynamics of any new film/substrate in order to establish its qualitative behavior, before the construction of models based on 0K energy barriers of the intuitive diffusion mechanisms. A deterministic method for calculating energy barriers and rates including thermal vibrations is introduced in Section 3.2.1.

3.1.2 Density Functional Theory

The basis for any quantum mechanical calculation of the electronic structure of a material system is the Schrödinger equation

$$\hat{H}\Psi = E\Psi, \quad (3.1)$$

which describes the energy E of a quantum system described by a Hamiltonian operator $\hat{H}$ and a wave function Ψ . For the case of an atomic ensemble, $\hat{H}$ may be written as

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 \\ & + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} + \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}, \end{aligned} \quad (3.2)$$

where the first and second terms are respectively the kinetic and self-interaction potential energies of the electrons, the third and fourth terms are respectively the kinetic and self-interaction potential energies of the ion cores, and the last term is the cross-interaction between electrons and ion cores. In Eq. (3.2), $\hbar$ is the Planck constant, e and Z_I the charge of the electron and the I th ion core, respectively, m_e and M_I the electron and ion core masses, respectively, and $\mathbf{r}$ and $\mathbf{R}$ the positions of electron and ion cores, respectively. Electrons interact with the positively charged atomic nuclei through an electrostatic potential.

Solving the electronic structure problem is formally straightforward, but there are no known approaches able to handle the exceedingly complex differential equation defined with Eqs. (3.1) and (3.2). For this reason, a series of approximations are applied in order to obtain a more practical model from which solutions can be extracted. The most important one is the *Born-Oppenheimer* (or *adiabatic*) approximation, based on the fact the motion of

electrons is orders of magnitude faster than that of the ion cores. Thus, it is reasonable to state that the complete electronic system reaches an equilibrium configuration during each infinitesimal time interval along the movement of the ions, in similarity with the steady state approximation applied for the atomic densities on the top layer of atomic islands (see Section A.2). This is equivalent to consider, for each time instant, an electronic system in motion interacting with itself and with a static distribution of positive charges, i.e.,

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext}. \quad (3.3)$$

In Eq. (3.3), $\hat{T}$ accounts for the kinetic energy of the electrons, $\hat{V}_{ee}$ for their self-interaction, and $\hat{V}_{ext}$ for their interaction with the ion distribution. Hence *ab initio* routines for dealing with atomic systems are composed of two main steps; first, the solution of the electronic structure problem defined by the Schrödinger equation (Eq. (3.1)) and the Born-Oppenheimer hamiltonian (Eq. 3.3) for each time step, and second, updating the ionic configuration by means of numerical optimization procedures (Section 3.1.1), or by deterministic computations based on physical laws (see *ab initio* molecular dynamics in Section 3.2.2).

Whole classes of methods have been devised for solving the electronic structure problem. However, most of them have been replaced by an approach based on a *density functional theory* (DFT) formulation of quantum mechanics [112]. DFT techniques have proved very effective for determining the electronic density of materials and for reproducing physical properties such as structural configurations from a purely theoretical basis, and for this reason DFT has dominated the computational material science field during the last decades. Thus, all references to *ab initio* methods throughout this manuscript refer implicitly to DFT methods.

The electron or charge density of a material system containing N electrons [116] is defined as

$$n(\mathbf{r}) = N \int |\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N. \quad (3.4)$$

From this quantity, Hohenberg and Kohn derived two seminal theorems which set the grounds for all DFT formulations. The first one states that the ground state electron density $n_0(\mathbf{r})$ determines uniquely the potential V_{ext} for the electron-ion interaction (up to an additive constant). The second,

shows that, for any and each external potential, there exists a functional of the electron density $E[n]$ whose absolute minimum is the system ground state energy E_0 , and the density at this minimum is the ground state density $n_0(\mathbf{r})$. It is possible to write a general expression

$$E[n] = T[n] + V_{ee}[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d(\mathbf{r}), \quad (3.5)$$

which separates $E[n]$ in three independent functionals, the first two describing the kinetic and self-interaction energies of the electron cloud, respectively, and the last one describing the potential energy of the ion cores. The Hohenberg and Kohn theorems demonstrate the existence of the functional $E[n]$ (Eq. (3.5)), but they do not tell what is the form of that functional, or how to find it.

Within the DFT formulations, the most popular branch is in turn the Kohn-Sham method. In the latter, the intricate problem of solving the Schrödinger equation for a multiparticle system composed of N electrons is separated into solving N single-particle Schrödinger-like equations

$$\left(-\frac{1}{2}\nabla_i^2 + V_{KS}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) \quad (3.6)$$

describing independent electrons i with energies ϵ_i and wavefunctions ψ_i , moving within a potential $V_{KS}(r)$ describing the effective interaction with the rest of the electrons and ions. Thus, the associated energy functional of the Kohn-Sham system is given as

$$\tilde{E}[n] = T_S[n] + \int V_{KS}(\mathbf{r})n(\mathbf{r})d\mathbf{r}, \quad (3.7)$$

where $T_S[n]$ is the non-interacting kinetic energy functional. The functional form of the energy of the fully interacting N -electron system (Eq. (3.7)) can be further expanded into

$$E[n] = T[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_H[n] + E_{XC}[n], \quad (3.8)$$

where $E_H[n]$ is the interaction energy of a classical system with density $n(\mathbf{r})$ (or *Hartree energy*),

$$E_H[n] = \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \quad (3.9)$$

and $E_{XC}[n]$ the *exchange-correlation energy*, an unknown functional defined to make Eq. (3.8) exact. By imposing to the functionals defined in Eqs. (3.7) and (3.8) to take the same value for $n_0(\mathbf{r})$, an expression for the Kohn-Sham potential in Eq. (3.6) is obtained:

$$V_{KS}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}). \quad (3.10)$$

In Eq. (3.10), the *Hartree potential* is defined as

$$V_H(\mathbf{r}) = \frac{\delta E_H[n]}{\delta n} = \int \frac{n(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}, \quad (3.11)$$

and the *exchange-correlation potential*,

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[n]}{\delta n}. \quad (3.12)$$

Following the above formalism, the entire effective potential $V_{KS}(\mathbf{r})$ can be computed in a systematic way, with the exception of the exchange correlation potential $V_{XC}(\mathbf{r})$, where all the complexity of the N -body problem is concentrated. Due to the amount of information this function encompasses, it adopts extremely complicated forms and constitutes the main object of study of KS-based DFT research. Although the discussion of specific exchange-correlation potentials is beyond the scope of this work, it is worth mentioning the two main functionals used in the field.

The most basic form for these energies is given by the *local density approximation* (LDA)

$$E_{XC}^{LDA}[n] = \int n(\mathbf{r})\epsilon_{XC}^{hom}(n(\mathbf{r}))d\mathbf{r}, \quad (3.13)$$

in which $\epsilon_{XC}^{hom}(n(\mathbf{r}))$ is the local exchange-correlation energy per particle of a surrounding homogeneous electron gas, and the next form in complexity is given by the *generalized gradient approximation* (GGA)

$$E_{XC}^{GGA}[n] = \int n(\mathbf{r})\epsilon_{XC}^{GGA}(n(\mathbf{r}), \nabla n(\mathbf{r}))d\mathbf{r} \quad (3.14)$$

which also includes the energy gradient $\nabla n(\mathbf{r})$. In general, LDA and GGA functionals provide reasonable estimates for the physical properties of diverse material systems, but a great amount of effort is devoted in the community for developing more elaborate and accurate versions.

All *ab initio* computations in the present study are performed with the Vienna ab initio simulation package [117] (VASP) [117], using GGA in the Perdew-Burke-Ernzenhof approximation and projector-augmented wave (PAW) pseudopotentials².

3.2 Atomic-scale diffusion behavior

3.2.1 Deterministic simulations

Direct monitoring of atomic-scale mechanisms is not a simple task. Experimental techniques such as *scanning electron microscopy* (SEM) and *scanning tunneling electron microscopy* (STEM) are accurate for surface analysis with nanometer resolution, and even to directly observe surface atoms. However, the latter must be performed post-growth, because the atomic movements take place at very small time scales. Moreover, even if real-time monitoring of atomic motion was possible, the energies of the electrons used in the microscopy reach thousands of electronvolts, which is enough to disturb the atomic movement and corrupt the measurements. For this reason, the approach of monitoring atomic-scale mechanisms from deterministic simulations rather than from direct experimental observation constitutes a valuable alternative.

The molecular dynamics method might be the most used tool within computational material science [118]. The idea behind this technique is very simple; given a potential energy U of an ensemble as a function of the position of the particles, the force $\mathbf{F}_i$ acting on each of the particles can be obtained as

$$\mathbf{F}_i = -\nabla_i U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = -\nabla_i U(\mathbf{r}^N), \quad (3.15)$$

and then the positions as a function of time are computed by numerical integration—using, e.g., the *Verlet algorithm*—of the Newton’s equations

$$\frac{d^2 \mathbf{r}_i}{dt^2} = \frac{1}{m_i} \mathbf{F}_i, \quad (3.16)$$

in which m_i are the atomic masses.

²These approaches replace the tightly-bound inner shell of electrons around the ion cores by an effective potential, and only take into account explicitly the atomic valence electrons. This is known as *frozen core* approximation.

MD simulations are performed with certain constraints, to reproduce the thermodynamic conditions in which the study system evolves. To model, for instance, a *micro-canonical* ensemble, the number of particles N on the ensemble, the system volume V and the total energy must be kept constant. The goal of the present study is to investigate atomic-scale mechanisms taking place in the course of film growth processes, which are performed at constant temperature T in a finite environment, hence V and T must be kept constant. Although growth proceeds under deposition conditions, the time scales of diffusion mechanisms are much shorter than the average time interval between successive deposition events. But more importantly, the focus are local events taking place in reduced volumes of the system, hence N can be assumed to be a fixed parameter. Thus, the diffusion processes and their local environments are modelled as *canonical* ensembles, or NVT , for which the energy equipartition theorem

$$\langle E_{kin} \rangle = \frac{3}{2} N k_B T \quad (3.17)$$

is derived. The instantaneous kinetic energy E_{kin} of the particle ensemble experience fluctuations, but the average over long times should converge toward a steady value. This value usually drifts due to progressive accumulation of errors during the numerical integration of Eq. (3.16). To solve this issue, the *Nosé-Hoover* thermostat [119] is applied; this algorithm keeps the total temperature of the system constant and ensures that the kinetic energy is conserved (Eq. (3.17)) for long time scales. One relevant aspect to take into account for ensemble simulations is the ergodicity. This intrinsic property states whether an system is able to access all points of the configurational space for any initial condition, which implies that all the statistical properties of the system may be deduced after a sufficiently long time of a single simulation. It follows from this the definition that the average of any system property after a long simulation must coincide with the average of the same property measured in an ensemble of identical systems departing from different initial conditions. If this is the case, then the system is said to fulfill the *ergodic hypothesis*. This is important because time and ensemble averages cannot be employed interchangeably in later analysis in case the hypothesis is not fulfilled. One example of a non-ergodic process is an adatom Lévy walk (see Paper 4).

Thus, all the afore-mentioned aspects considered, the qualitative behavior of metal surface atoms may be determined by a first simulation, and then the

found mechanisms may be induced in prepared simulation environments to extract their quantitative properties. One common procedure is to calculate the average occurrence rate ν_i of the process i , and then estimate its energy barrier E_{ads} through the Arrhenius equation (Eq. (2.6)), although this energy may take different values due to vibrational entropy effects.

Independently of the molecular dynamics implementation used, the crucial factor determining the accuracy of simulations is the input interatomic potential. The two main types are briefly introduced in the following subsections.

3.2.2 *Ab initio* Molecular Dynamics

Ab initio molecular dynamics are a robust tool for studying diffusion including the effects of thermal vibrations, more complete than direct PEL scanning as it may reveal unknown mechanisms. For every time interval, AIMD calculates the ensemble PEL via DFT methods and then the forces for Eq. (3.16) are computed via Eq. (3.15). AIMD is in fact the most accurate computational tool available for the simulation of atomic ensembles, able to provide the most faithful representation of a real particle system given that a good enough *ab initio* model is provided. However, it has the inconvenient of a bad efficiency, as the required computation time increases rapidly with the number of atoms of the ensemble. AIMD are performed with VASP in the present study.

3.2.3 Classical Molecular Dynamics

Compared to AIMD, CMD has a limited accuracy, since the force field is determined from empirical models instead from *ab initio* models. However, despite of being less precise, it is immensely superior regarding performance; a single CMD simulation may host even millions of atoms, and compute the way by which these evolve during considerable long times. Thus, they constitute a powerful alternative to AIMD.

Since there is not an unique procedure for calculating forces, the choice of the interatomic potential is fundamental. These are often designed to modeling materials with specific properties, and may not translate well to other systems with a different physical nature, e.g., with atoms forming covalent bonds instead of ionic. Empirical potentials are parameter-dependent mathematical functions, and thus the issue of finding a good model reduces to

solving a constrained minimization problem. The concept is straightforward, but is often cumbersome in practice as the parametrization requires considering numerous parameters simultaneously, hence most research projects resort to already made and tested potentials.

The most basic potential is the *Lennard-Jones*

$$V_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (3.18)$$

where ε is the depth of a PEL basin, and σ is the finite distance at which the inter-particle potential is zero. The Ag-C and C-C interactions in the metal/graphene systems modeled in the present thesis are described using Lennard-Jones [120] and AIREBO [121] potentials, respectively. The AIREBO potential is well established in the literature for simulating carbon-based materials [122–125] and, together with Lennard-Jones, has been used to study the diffusion of noble metals (including Ag) clusters on graphite surfaces [126].

All CMD simulations of the present study are performed with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [127].

3.3 Mesoscale film growth dynamics

3.3.1 Stochastic simulations

Once the local atomic-scale mechanisms are identified, they are used as a reference for devising mesoscale stochastic models. At present, stochastic simulations are a fundamental tool in the study of diverse dynamic systems in material science, due to both their efficiency compared with other methods, e.g., molecular dynamics, and their stochastic nature, which allows to perform statistically independent simulations of identical systems.

The present work takes advantage of these properties to describe in an accurate way the deposition and growth dynamics of a thin film with a crystalline structure onto the surface of a solid substrate, by performing *kinetic Monte Carlo* (KMC) simulations [128, 129] of island growth. This tool, once fed with detailed information about the intrinsic properties of the diffusing atoms, serves to study the collective behavior of large ensembles in far-from-equilibrium conditions. It follows that the KMC output and its physical

correctness depends entirely on the input parameters, and that simulations do not reveal any fundamental behavior by themselves.

The speed of KMC simulations relies on the way rare events are treated. Since even mobile atoms vibrate around static lattice points during prolonged times before escaping from the local energy minima and diffuse toward other sites, KMC may circumvent the explicit calculation of surface vibrations. Thus, by avoiding the use of simulation time steps on the order of femtoseconds, the computation can focus exclusively on the rare-events inducing changes in the atomic configuration³.

Many available codes [27, 97–99] used to simulate growth beyond sub-monolayer regime on weakly-interacting substrates rely on important simplifications such as the approximation of 3D islands by hemispheres. They are, thus, incapable of modeling island shape and morphology evolution, e.g., when the temperature falls below the roughening transition temperature and facets start forming. As mentioned in Chapter 2, the formation stages of island growth and coalescence play a key role in determining the final roughness and microstructure of films. Hence, a kMC code is developed, which allows to study specifically the dynamic processes governing these stages in a fully atomistic fashion.

For the sake of computational efficiency, atoms are forced to occupy fixed positions on an hexagonal lattice with integer coordinates⁴ (*on-lattice* implementation), and calculate energy barriers using a Bond Counting Scheme (see Section 3.3.3), which is validated against literature values [83–85, 89] and NEB calculations for Ag diffusion on Ag(111) (homoeopitaxy). Substrate diffusion is modelled as a rare-event process.

The size of the simulation box is chosen to approximately match the areas of the island capture zones for the range of deposition rates used in the studies. According to results of Paper 4, the KMC rates based on static barriers do not provide an accurate physical description of the surface diffusion dynamics, but this does not have an effect on the conclusions since only one island is considered. However, attempts to model the nucleation and growth of an island ensemble would require specific corrections in the code in order to account for the Lévy walk nature of the adatoms and in turn obtain

³While this strategy succeeds for low and intermediate temperatures, if diffusion rates approach the femtosecond timescales due to high temperatures then the KMC efficiency becomes comparable to that of MD.

⁴It is also possible to assign the atoms to any point of the real space in the so-called off-lattice implementations [130, 131], for more accurate, though costly, representations.

realistic N_{sat} values and avoid overestimation (see Section 2.3.3).

This KMC code overlooks a few physical processes taking place in real experiments, in order to keep a light computational load. First, that overhanging and unsupported positions are not considered stable, and the code excludes diffusion mechanisms involving these positions. This could be problematic for environments with very low metal/substrate interactions in which clusters do not adopt pyramidal but rather more spherical shapes, such as gold on graphite at high temperatures [62]. Besides, all deposition effects are neglected. This includes athermal and biased diffusion [132], substrate encapsulation, desorption, etc.

Papers 1, 2 and 3 demonstrate the physical accuracy of the KMC code by replicating 3D island morphology and shape evolution dynamics, as well as providing a picture of coalescence consistent with established experimental knowledge. These results can be seen as a comprehensive benchmark of simulation code, and it legitimizes its use in more ambitious computational projects for modeling later film growth stages, such as the study of percolation and hole filling with atomic-scale resolution. The limitation in this case is the enormous computational load required to process simulation boxes hosting perhaps millions of atoms. The next section reviews briefly the KMC algorithm in the context of film growth—more details can be found in Refs. [128, 129]—and the Appendix B discusses a more sophisticated KMC implementation based on parallel CPU processing, that was attempted in this work aiming to improve the low efficiency of large-scale film growth simulations.

3.3.2 The Kinetic Monte Carlo Algorithm

The diffusion of an atom over the surface can—excluding special processes as concerted motion [133] or exchange diffusion [41]—be thought as a chain of discrete jumps between neighbouring lattice sites, well separated by extensive periods in which the atom vibrates around its new position. During those time intervals, the entire film/substrate system remains in a metastable configuration, and thus it can be regarded to be in a state i with average energy $\langle E_i \rangle$. This consideration implies that each individual atomic jump modifies the system configuration bringing it to a new and independent state j with average energy $\langle E_j \rangle$, and, by extension, that the surface evolves by a discrete series of transitions between states occurring randomly at mean

rates⁵ $\nu^{i \rightarrow j}$. As all memory of previously visited configurations vanishes in the vibrations between consecutive transitions, the states are uncorrelated and the system is said to follow *Markovian dynamics*.

This essential property is sufficient to define, in the framework of the theory of stochastic processes [134, 135], the following set of master equations

$$\frac{dP(i, t)}{dt} = \sum_j (\nu^{i \rightarrow j} P(j, t) - \nu^{j \rightarrow i} P(i, t)), \quad (3.19)$$

which determines the evolution of the probability $P(i, t)$ of finding the system in the state i at a given time t . If there is knowledge that the system is certainly in i at t , then $P(j, t) = 0$, and it will remain in i without transitioning during a time interval Δt . It is possible to integrate Eq. (3.19) over time to obtain

$$P(i, t + \Delta t) = \exp \left(- \int_t^{t+\Delta t} dt' \sum_j \nu^{i \rightarrow j} \right) = \exp(-K_{total}^i \Delta t), \quad (3.20)$$

where $K_{total}^i = \sum_j \nu^{i \rightarrow j}$. In this way, given any initial state i , there is a probability

$$P(i \rightarrow j) = \frac{\nu^{i \rightarrow j}}{K_{total}^i} \quad (3.21)$$

that a transition occurs to the state j in a time

$$\Delta t = - \frac{\ln [P(i, t + \Delta t)]}{K_{total}^i}. \quad (3.22)$$

Note that Δt is not specifically dependent on the particular process $i \rightarrow j$, but on all possible processes.

Initially, the KMC algorithm (i) sets time $t = 0$ and (ii) chooses an initial state i , which can be either a flat surface or an already-existing atomic configuration (Fig. 3.1). In the next step (iii) it identifies N diffusion jumps

⁵When implementing the system computationally, the fact that atomic vibrations between diffusion jumps do not bring the system out of its current state i makes possible to neglect these vibrations, and define a unique spatial arrangement for this state with static atomic positions.

Figure 3.1: Flowchart of the basic KMC algorithm.

between adjacent coordinated sites that may bring the system to a new state $j \in \{1, \dots, N\}$ and assigns a transition rate

$$\nu^{i \rightarrow j} = \nu_0 e^{\left(-\frac{E_a^{i \rightarrow j}}{k_B T}\right)} \quad (3.23)$$

to each of them. In Eq. (3.23), $E_a^{i \rightarrow j}$ represents the energy barrier between i and j that must be overcome for the transition $i \rightarrow j$ to occur. If deposition is activated in the simulation, the arrival rate F of atoms to the surface is

assumed constant and given as a simulation parameter, and the arrival of an adatom to the surface is regarded as another process with rate $\nu^{i \rightarrow j}$. Then, the algorithm (iv) constructs a cumulative set⁶ $\{K_1^i, \dots, K_j^i, \dots, K_N^i, K_{N+1}^i\}$ of elements $K_j^i = \sum_{k=1}^j \nu^{i \rightarrow k}$ associated with each process $\nu^{i \rightarrow j}$. By generating a random number $z_1 \in [0, K_{N+1}^i]$, it selects the process $\nu^{i \rightarrow j'}$. In order to increase the simulation time t , (vi) it generates a second random number $z_2 \in (0, 1)$, equates to the probability $P(i, t + \Delta t)$, and using Eq. (3.22) t is increased an amount

$$\Delta t = -\frac{\ln(z_2)}{K_{total}^i}. \quad (3.24)$$

The method described above constitutes an unprecedented advance in the simulation of systems with atomic detail, but has a main drawback that may affect considerably its efficiency. Since the processes are chosen depending on their probability to occur, the fastest processes will always be more likely to happen. Thus, if the system is in a low-energy region of the configurational space from which is difficult to escape, but is connected to other energy states within this region—e.g., an adatom trapped on the top of an island with a large barrier for downward stepping—a KMC algorithm will simulate a large number of transitions between these states before it moves away from this low-energy region. This issue is called the superbasis problem. For certain types of systems, the portion of the overall computational time spent simulating transitions within the superbasis might be very large, so several solutions have been proposed, as documented in the literature [136, 137].

3.3.3 Bond Counting Scheme

The most fundamental part in the construction of a realistic KMC model is the creation of a complete and correct rate list, which entails the identification of the possible processes that may occur in the system in question, and the assignment of an appropriate occurrence rate to each of them, since the algorithm makes the system evolve based on a priori provided processes. Hence, failing to create this list, would inevitably lead to corrupted results. It is interesting to note that, given a correct process list, in case the rates are not correct but the hierarchy between their relative values remains approximately unchanged, time progression would not be calculated correctly but

⁶ $K_{N+1}^i = \sum_{k=1}^N \nu^{i \rightarrow j} + F$.

the macroscopic evolution of the system would remain intact in a qualitative sense.

In order to identify possible processes, for every atom with sufficient mobility (i.e., with a low enough coordination) for the system in state i , the algorithm scans its atomic environment and finds all neighboring sites to which it can diffuse. Previous knowledge of the system is convenient since relevant processes as interlayer [89, 93, 95, 138, 139] diffusion might not be identified by the algorithm and require a specific implementation for the model to reproduce a realistic version of the object of study. Once the possible atomic diffusion pathways $i \rightarrow j$ bringing the system to states j have been identified, a rate $\nu^{i \rightarrow j}$ is assigned to each of them by using Eq. (3.23), based on the energy barrier $E_a^{i \rightarrow j}$ that the atom needs to overcome in order to diffuse from the initial to the final sites. For the simplest models, these energies are obtained externally by experimental measurements [85, 89] or theoretical calculations [83, 84], and provided *a priori* to the simulations, so that the algorithm only needs to retrieve these values from a fixed list. This strategy is often limited to simple systems with a reduced number of possible processes, since this number grows drastically as the complexity of the system increases, and the process-identification becomes a colossal task. To solve this problem, using diverse computational techniques [30], energy barriers are calculated or constructed⁷ *ad hoc* as their corresponding processes are identified. If the new barriers are stored permanently in a growing list for subsequent retrieval, so that its calculation is performed only once, the algorithm is referred to as self-learning [115, 140]. Many of these modern methods are based in molecular dynamics or first principles calculations, approaches that, although highly accurate, require long times to compute the energy barriers as well as high computational power, and thus are able to simulate physical systems at restricted time scales. As we are interested in modeling thin film growth beyond the nucleation stage, i.e., during relatively long timescales, we implement a *Bond Counting Scheme* (BCS) [141], a method in which the energy barriers are constructed as a function of the number of atomic neighbours at the initial and final positions of the corresponding diffusion jump. The BCS is conceptually similar to an interatomic MD potential, providing barriers instead of energies, and therefore must be

⁷Note: to *calculate* a barrier implies to reproduce its associated process within a model implementing physical variables such as forces or electronic structure, whereas the barrier is *constructed* if a general and simple scheme applied for any process encountered is used.

parametrized in a similar way. Here, it is tailored for modeling Ag/Ag(111), benchmarked with classical NEB calculations. This approach, while not being as accurate as an *ab initio* barrier list, is not as time-consuming, and is also capable of replicating the whole barrier list of other systems with different chemical compositions by merely changing a few parameters. Since this BCS is of a purely arithmetic character, we are able to account not only nearest-neighbour (NN) atomic interactions, but also next-nearest-neighbour (NNN) and both fcc and hcp sites in our model, without compromising the efficiency of the simulations. The weakly-interacting substrate is implemented by lowering the pairwise adatom/substrate atom bond strength relative to the corresponding adatom/adatom value, thus resulting in a reduced energy barrier for adatom ascent onto the island second layer and sidewall facets. In our scheme, we construct the barrier $E_a^{i \rightarrow j}$ by an arithmetic sum of three elements,

$$E_a^{i \rightarrow j} = E_k^{i \rightarrow j} + \Delta E_b^{ij} + C_S, \quad (3.25)$$

where $E_k^{i \rightarrow j}$ is the kinetic barrier of the jump, ΔE_b^{ij} the potential energy difference between initial and final sites, and C_S a parameter which has a value when the diffusion jump is longer than usually, such an atom descending to a layer below by step crossing. For the sake of a clearer representation, $E_k^{i \rightarrow j}$ can be associated to the potential energy difference between the saddle point of the jump and the site, either initial or final, with higher potential energy, and C_S with the Ehrlich-Schwobel barrier. Additional details concerning the physical model and algorithm implementation are found in Paper 1.

3.3.4 Detailed balance and code validation

Regardless of the method employed for updating the rate list, when constructing a KMC model it must be ensured that the set of transitions between states of the system defines a consistent energy landscape, in order for the master equations (Eq. (3.19)) to reproduce correctly the dynamics along the configurational space. This can be achieved by applying the *principle of detailed balance*, which states that, at equilibrium, each process should be equilibrated by its reverse process, expressed mathematically as

$$\nu^{i \rightarrow j} P(j, t) = \nu^{j \rightarrow i} P(i, t). \quad (3.26)$$

Letting our film/substrate system relaxate during a sufficiently long time to reach equilibrium, we can define a partition function

$$Z = \sum_i e^{-\frac{E_i}{k_B T}} \quad (3.27)$$

which accounts for all the accesible states of the system, and allows to derive the probabilities

$$P(i, t) = \frac{e^{-\frac{E_i}{k_B T}}}{z}. \quad (3.28)$$

Hence, by inserting Eq. (3.23) and Eq. (3.28) into Eq. (3.26), we obtain

$$E_i - E_j = E_a^{i \rightarrow j} - E_a^{j \rightarrow i}. \quad (3.29)$$

The important feature of Eq. (3.29) is that all its constituent terms are fixed values which remain unchanged even if the system is not in equilibrium—note that Eq. (3.29) does not imply Eq. (3.26) if we cannot define a partition function (Eq. (3.27))—and therefore to impose this condition when calculating energy barriers suffices to not only fulfill detailed balance, but also for ensuring a consistent energy landscape. Since the energies E_i and E_j are constant values, if the equality did not hold, the energy value of the saddle point would be dependent of the direction in which it is crossed.

For KMC codes implementing simple methods for obtaining energy barriers on film/substrate systems, e.g., a bond counting scheme based on nearest-neighbour interactions on a cubic lattice [142], to track the processes and their reverse counterparts in order to ensure that detailed balance is fulfilled is a straight-forward task, whereas verifying this principle at more elaborated representations becomes easily unfeasible. Good examples of such representations are off-lattice implementations [130, 131], multiple atom species on the film and substrate [143, 144], and more detailed descriptions of the local environment of each atom [145]. The consequence of the inherent complexity of the previous representations is that detailed balance cannot be rigorously ensured, and can be only assumed to be virtually correct if simulation results are consistent with established knowledge. For instance, the physical correctness of our bond counting scheme is validated by replicating characteristic homoepitaxial growth modes for single islands, shape evolution of 3D islands upon annealing (Paper 1) and coalescence scaling laws (Paper 3).

Chapter 4

Contribution to the field and outlook

The present chapter summarizes the conclusions that I draw from this theoretical study of thin metal film growth on weakly-interacting substrates, as well as my contributions to the current state of international research. The chapter concludes with a discussion about possible directions toward which this research could expand in the future.

Metal films and nanostructures are an important element in modern devices based on weakly-interacting oxides and 2D crystals, but their morphology cannot be easily manipulated, due to an uncontrolled tendency of metals to form 3D islands from the very early growth stages. Papers 1 and 2 investigate the kinetic origin of 3D island and morphology formation, aiming to identify the atomic-scale processes that must be targeted in order to control film growth. Results reveal that islands grow 3D by facile upward ascend across the island steps, and then form smooth sidewall facets, which further facilitates upward mass transport. In addition, atomic diffusion between facets and the island top is found to be the rate-limiting step that controls the island vertical growth rate, which increases with increasing temperature. The latter finding suggests that 3D morphology, which may be undesired in specific applications, can be initially suppressed by lowering synthesis temperatures, while island shapes can be fine-tuned by directly intervening on the upward mass transport mechanisms.

Suppressing formation of individual 3D islands may, however, not be sufficient for controlling roughness built up at the growth front in case coalescence takes place upon island impingement, since reshaping of 3D coalescing clus-

ters contributes to out-of-plane island growth. The importance of coalescence lies also on the fact that subsequent growth stages are unlikely to substantially influence the final film morphology. Paper 3 reveals that coalescence of faceted 3D islands proceeds by absorption of one island by the other via migration of 2D layers. This effect is found to be enhanced by the steady supply of mobile atoms from the vapor phase, although it can also be halted if the deposition rate is too fast, and in this case the cluster equilibrates via material agglomeration. Thus, careful control of the vapor flux temporal profile during the coalescence stage of film growth [28], as well as direct inhibition of 2D layer migration by deploying minority species at the growth front [146–148], are potentially promising strategies for promoting 2D growth morphology. Moreover, the analytical model developed in Paper 3 may serve as the basis for expanding film growth theories by incorporating descriptions of the equilibration dynamics of faceted 3D islands, while it helps to explain inconsistencies between theoretical and experimental reports with regards to film growth dynamics.

The results in Papers 1 through 3 are of general character as metal growth is simulated on a generic fcc(111) weakly-interacting substrate. In contrast, the second part of the thesis deals with a specific film/substrate combination by investigating the diffusion dynamics of noble metal adatoms and clusters on graphene. Paper 4 reveals that Ag, Au, Cu and Pd adatoms follow a superdiffusive movement pattern known as Lévy walk, which is different in nature from the random walk behavior established in classical epitaxial thin film growth theory. This result shows that the concept of surface diffusion barrier, which is widely used to account for the migration dynamics of adatoms performing random walks between adjacent surface adsorption sites, may not be relevant for describing diffusion on weakly-interacting substrates. Paper 5 shows that Au and Cu dimers, and Ag dimers and trimers also follow Lévy walks, indicating that cluster motion is another potential aspect to consider during film growth modelling.

The knowledge generated in this thesis provides guidelines for the experimental synthesis of metal layers on weakly-interacting substrates with controlled morphologies, and it casts the scientific foundation to further develop the thin film growth theory. Naturally, many questions remain unanswered and new ones emerge, which opens up new paths for this research to be continued, as explained in the following.

The in-house KMC code, which has been the workhorse in the present thesis, can be used to gain deeper understanding of film growth dynamics by

investigating mechanisms for island reshaping and growth, including Ostwald ripening and coalescence of islands with different sizes. Along the same lines, established knowledge of key atomistic processes could be used to design and theoretically test deposition protocols for creating new film structures, by e.g. controlled annealing and pulsed vapor deposition. Another possibility would be to leverage knowledge from the field of crystal growth, to continue the research about dynamics of faceted 3D islands at far-from-equilibrium conditions.

The main future research direction I propose is modeling of binary metal alloy film growth, which is not possible with the current KMC algorithm, due to the vast list of energy barriers and interactions that cannot be modeled using the BCS approach. A code capable of modeling two interacting species on a foreign substrate would open new and interesting pathways for the study of growth manipulation, as a plethora of additional micro- and macroscopic phenomena, such as controlled nucleation and material segregation, respectively, would come into play. In addition, it could be used to design multicomponent thin film materials with controlled nanoscale atomic arrangement [149, 150].

I also believe that it is of great interest to study adatom and cluster diffusion on other 2D materials [14–16, 18, 19], since whole new classes of 2D crystals beyond graphene have been synthesized in the recent years. Their discovery is accompanied by potential applications that are likely to require the growth of metal films and nanostructures at some stage of development and, while adatom and cluster diffusion on these substrates may resemble those on graphene, it may also be affected by physical phenomena such as magnetism or encapsulation, and as a result exhibit different behaviors.

With regards to the technical aspects of this thesis, several computational strategies could be implemented in order to realize one of the tasks for which the KMC code was originally conceived, namely to simulate and characterize a complete film growth experiment from nucleation to continuous film formation in a fully atomistic fashion. One possibility would be to solve the superbasin problem, which would shorten significantly the simulation times, allowing to directly compare computational results of percolation, hole filling and continuous growth with experimental data. Another possibility is to develop an efficient algorithm for performing parallel KMC simulations, for increasing arbitrarily the size of the simulated surface. But the greatest potential, in my opinion, for development of new strategies is in the field of machine learning (ML) [151, 152]. The capacity of ML algorithms to predict

the behavior of a system, given that sufficient training on relevant scenarios is performed, would allow to skip incountable computational operations when simulating long diffusion trajectories with AIMD, or when calculating energy barriers for a multispecie KMC, to name a few.

Appendix A

Derivation of diffusion equations

A.1 Fick's second law of diffusion

For a surface with diffusing atoms, the local atomic density $u(\mathbf{x}, t)$ and the rate σ of generation of atoms per unit surface and unit time¹ can be related with the mass flux $\vec{j}(\mathbf{x}, t)$ through the well-known continuity equation in its differential form

$$\frac{\partial u(\mathbf{x}, t)}{\partial t} + \nabla \cdot \vec{j}(\mathbf{x}, t) = \sigma. \quad (\text{A.1})$$

In order to exclude the explicit term $\vec{j}$ from the model, Eq. (A.1) can be trivially combined with Fick's first law of diffusion

$$\vec{j} = -D_c(u, \mathbf{x}) \nabla u(\mathbf{x}, t), \quad (\text{A.2})$$

where the collective diffusivity $D_c(u, \mathbf{x})$ is a proportionality constant between $\vec{j}$ and the gradient of the atomic concentration $\nabla u(\mathbf{x}, t)$, to obtain the general *diffusion equation*

$$\frac{\partial u(\mathbf{x}, t)}{\partial t} = \nabla \cdot [D_c(u, \mathbf{x}) \nabla u(\mathbf{x}, t)] + \sigma. \quad (\text{A.3})$$

¹Positive generation is referred as a source (e.g., deposition from vapor-phase) while negative generation is referred as a sink (e.g., surface desorption). σ is written as a sum of source and sink terms.

This partial differential equation describes the collective behavior of the atoms on the surface resulting from the random movement of each atom, and once solved it returns the local density of mobile atoms $u(\mathbf{x}, t)$. Assuming that the surface is a continuous, homogeneous medium without defects, it is possible to define a constant diffusivity D_c where the adsorption site structure and energetics are implicit. This allows to write Eq. (A.3) as

$$\frac{\partial u(\mathbf{x}, t)}{\partial t} = D_c \nabla^2 u(\mathbf{x}, t) + \sigma, \quad (\text{A.4})$$

which corresponds to Fick's second law of diffusion and is mathematically analogous to the heat equation. For the case of diffusion on a 3D island, the adatom density is sufficiently low that adatom-adatom interactions can be neglected, and D_c can be approximated to the tracer diffusivity D . As a remark, it is worth noting that the a small density of diffusing atoms is associated to a continuous variable u . Evidently, assigning a real number to a discrete quantity as the number of atoms implies that the results must be understood in probabilistic terms, i.e., measuring $u(r, t)$ in an ensemble of identically prepared systems will yield an average atom density $\langle u(r, t) \rangle$.

A.2 Steady-state approximation

Most of partial differential equations require numerical solutions. In particular, for equations describing temporal evolution of physical quantities such as radiation, waves, probability functions or diffusion (Eq. (A.4)), space and time are discretized and system evolution is computed iteratively. All techniques implementing this general strategy are called finite difference methods [153]. However, although highly effective in providing accurate numerical solutions, they are not the optimal tool for analyzing qualitative trends.

In order to simplify Eq. (A.4) and to obtain an analytical solution, the adatom population of the island/substrate system is assumed to reach an equilibrium configuration after each small change in the island shape, remaining constant at mesoscopic time intervals. This *steady-state approximation* is justified by the fact that time scales between atomic motion and macroscopic changes on island morphologies differ by various orders of magnitude. In this way, considering a certain point of the growth of the island, the time dependence vanishes and we can calculate the atomic densities for island top and facets easily from the simple differential equation

$$D_c \nabla^2 u(\mathbf{x}) + \sigma = 0, \quad (\text{A.5})$$

referred as the stationary diffusion equation. By suppressing the time dependence, the model is restricted to the stage of growth in which the shape of the island remains constant over time. That is, extracting information about nucleation probability from densities calculated with this model for islands with different sizes also requires islands to conserve their shape, since morphological changes are not be accounted in Eq. (A.5). Paper 1 sheds some light on this question, by revealing that once islands have reached a certain size, they keep growing in a self-similar manner maintaining their characteristic facet structure (Fig. (A.1)). This enables to apply the steady-state approximation to describe single island growth.

Figure A.1: Faceted 3D island obtained from KMC simulations. The figure was generated with the visualization freeware Ovito [154].

Assuming a constant adatom density requires a further consideration, related with the generation σ of atoms: the latter must indeed be time-independent. This implies that the rate of adatoms arriving to the system is constant and equals the rate of adatoms leaving the system, since otherwise the difference in the incoming and outcoming fluxes would result in adatom accumulation and, in turn, in density fluctuations over time. The adatom

APPENDIX A. DERIVATION OF DIFFUSION EQUATIONS

sources and sinks are deposition and attachment to the island facets, respectively, but desorption from the substrate is neglected. Adatoms attach to the growing facets at the same rate they arrive, but still they must arrive at a constant rate, which only occurs if the island density on the substrate has saturated to a constant value (i.e., $N \rightarrow N_{sat}$). In this situation, the capture area² of the island does not change over time and all the atoms deposited in this part of the substrate will diffuse to the island, thus maintaining a constant arrival rate. In contrast, if a new nucleation event would take place close to an island, the capture area of the latter would automatically be reduced, with the subsequent change on its incoming adatom flux.

²The capture area [155, 156] of an island refers to the region of the substrate for which deposited atoms will migrate towards that island, instead to any other.

Appendix B

Parallel KMC

As mentioned in Section 3.1, one of the purposes of writing a fully atomistic code is to open the possibility of modeling film growth beyond the island coalescence stage, up to a continuous film. This task does not require any further development of the physical model, but has a fundamental issue concerning computational capabilities; in order to study collective phenomena such as elongation and percolation transition, it is necessary to simulate a surface able to host a large number of islands. Since the KMC algorithm is of serial nature, all the processes occurring in this vast surface from the deposition of the first atom until the completion of a continuous film would have to be evaluated one-by-one, which would require extremely long simulation times, leaving a conventional approach unfeasible. Besides using strategies that accelerate the serial algorithm [136] there exists the possibility of exploiting the parallel architecture of modern supercomputers in order to perform simultaneously several tasks of a common simulation, using different interconnected computer processing units (CPU). For this work, we upgrade our code to a parallel version following the method devised by Shim and Amar [157]. In the following lines we provide a concise description of the functioning of the new code. A more complete explanation about parallel KMC algorithms can be found in Ref. [158]. The main idea consist on, at the beginning of the simulation, dividing the substrate surface (global) into N adjoining stripes (local) (Fig. B.1), and assign each of them to a CPU that will apply the serial KMC algorithm to make them evolve. After each of the CPU have simulated a certain time t_{synch} of its correspondent local surface, it stops and remains halted until all the others have stopped too, and then sends and receives information of the processes that took place in the boundaries to

its neighbouring CPUs, so that all the local surfaces together constitute a global evolving surface. This step is called synchronization, and t_{synch} , synchronization time, which is the inverse of the rate ν_{fast} of the fastest process identified in the global surface,

$$t_{synch} = 1/\nu_{fast}. \quad (\text{B.1})$$

Figure B.1: Schematic visualization of the parallelization strategy, in which the global surface is decomposed in several local surfaces, each of them associated to an independent CPU.

The time t_O spent by the CPUs transferring information is called overhead time, and it depends on the volume of data transferred. The main drawback of this implementation is that, once an atom diffuses through the boundary to another lattice, it remains immobile until its new position is sent to the corresponding boundary at the next synchronization. Although this effect is strictly unphysical, if the time the atom is inactive is kept under certain threshold it does not corrupt the evolution of the system. Contrarily, many inactive atoms may lead to undesired corrupted results, such as preferred island nucleation along the boundaries (Fig. B.2).

Figure B.2: Snapshot of a parallel film growth simulation, in which long synchronization times between CPU corrupt a realistic physical system evolution, by causing preferential nucleation at the boundaries between surfaces. These boundaries can be localized from the parallel diagonal lines formed by rows of islands, marked with dashed lines.

We implemented the parallel algorithm successfully, but this particular strategy turned out to be incompatible with our purpose and the project remains currently on hold. The main issue arised from the wide range of timescales in the simulation process list; the presence of very fast diffusion processes—in general between hcp and fcc sites—requires short synchronization times (Eq. (B.1)), which implies that the number n of synchronizations necessary for evolving the film/substrate system a certain time t_{sim} is very high compared with more simple surface descriptions. In this way, the total time t_{total} spent by the machines (the time we have to wait for the results) to simulate t_{sim} ,

$$t_{total}(t_{sim}) = t_{sim} + n(t_{synch})t_O, \quad (\text{B.2})$$

increases considerably. In our implementation, the efficiency gain attained with the parallel computing algorithm is overshadowed by the lost due to very frequent synchronizations.

A possible solution would be to remove the hcp sites from the surface model, which would reduce considerably $n(t_{synch})$: on a homoepitaxial substrate, at 300 K, the jump frequency of an Ag atom from an hcp to a fcc site is 20 times larger than the frequency between two fcc sites, and it follows that by suppressing the former process only one out of twenty synchroniza-

tions for simulating t_{sim} . However, the strong feature of our code is precisely the implementation of hcp sites, from which the morphology asymmetries in nanostructures origin (e.g., truncated triangular shapes of islands grown in homoepitaxial substrates [85]). Without them, only a crude reproduction of the film growth process is possible, so we are still looking for a solution or an alternative strategy for approaching this research project.

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Appended papers

1. **"Formation and morphological evolution of self-similar 3D nanostructures on weakly-interacting substrates"**
B. Lü, G.A. Almyras, V. Gervilla, J.E. Greene and K. Sarakinos.
Phys. Rev. M **2** 063401 (2018)
<https://doi.org/10.1103/PhysRevMaterials.2.063401>
2. **"Dynamics of 3D-island growth on weakly-interacting substrates"**
V. Gervilla, G.A. Almyras, F. Thunström, L.E. Greene and K. Sarakinos.
Appl. Surf. Sci. **488** 383 (2019)
<https://doi.org/10.1016/j.apsusc.2019.05.208>
3. **"Coalescence dynamics of 3D islands on weakly-interacting substrates"**
V. Gervilla, G.A. Almyras, B. Lü and K. Sarakinos.
Sci. Rep. **10** 2031 (2020)
<https://doi.org/10.1038/s41598-020-58712-1>
4. **"Anomalous versus normal room-temperature diffusion of metal adatoms on graphene"**
V. Gervilla, M. Zarshenas, D.G. Sangiovanni and K. Sarakinos.
J. Phys. Chem. Lett. **11** 8930 (2020)
<https://doi.org/10.1021/acs.jpcllett.0c02375>
5. **"Room-temperature superdiffusion of metal clusters on graphene"**
M. Zarshenas, V. Gervilla, D.G. Sangiovanni and K. Sarakinos.
In manuscript

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1. I contributed to the upgrading and validation of the simulation code, performed the simulations and analyzed the data.
2. I contributed to the design of, I conceived and developed the analytical model proposed in the article. I designed the simulation method and discussed the simulation results. I wrote the manuscript.
3. I contributed to the design of, I performed the simulations, analyzed the data, and formulated the analytical model presented in the manuscript. I wrote the manuscript.
4. I led the design of, performed the AIMD simulations, and analyzed all data. I wrote the manuscript.
5. I developed the analysis methodology and participated in the analysis and discussion of the results. I wrote parts of the manuscript.

Papers

The papers associated with this thesis have been removed for copyright reasons. For more details about these see:

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