

Predicting nucleation and growth processes: Atomistic modeling of metal atoms on ionic substrates

J. H. Harding and A. M. Stoneham

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom

J. A. Venables*

School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton BN1 9QH, United Kingdom

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Classical simulation methods are used to predict the energies required by nucleation models to explain the growth behavior of silver and gold on ionic substrates. Adsorption E_a and diffusion E_d energies are found to be small, with $(E_a - E_d)$ systematically smaller than several experimental estimates. Dimers have a large binding energy E_b , but may have smaller diffusion energies than single adatoms. We show that surface point and line defects adsorb metal atoms, and discuss the implications of these results for analyses of nucleation data. [S0163-1829(98)05011-5]

I. GROWTH MODES OF FILMS ON IONIC SURFACES

There are three main modes of growth possible when a material is deposited on a surface: layer by layer (Frank-van der Merwe) growth, island (Volmer-Weber) growth, and layer then island (Stranski-Krastanov) growth. These modes have been discussed in detail by Venables and co-workers.^{1,2} Although growth modes are characterized by the thermodynamics of the system, growth away from equilibrium requires a detailed study of the kinetics.

In particular, the atomic processes responsible for the nucleation and growth of thin films on a substrate have been modeled by a number of authors. One of the simplest and most successful is the pair-binding model of Venables.² Here, the maximum value of the nucleation density N_x for two-dimensional (2D) growth in the complete condensation limit is given by an equation of the form

$$N_x \propto R^p \exp\{(E_i + iE_d)/(i+2)kT\}, \quad (1)$$

where R is the deposition rate (often denoted the flux F in the recent literature), T is the deposition temperature, and E_d the surface diffusion activation energy for the adatom. The quantity $p = i/(i+2)$, where i is the critical nucleus size, is calculated self-consistently within the model. The model uses the lateral binding energy of arbitrary 2D clusters, $E_j = b_j E_b$ (where b_j is the number of bonds and E_b is the binding energy of a pair of adatoms on adjacent sites). It evaluates i as that cluster size j (and configuration), which results in the lowest nucleation rate and density at the deposition temperature consistent with the constraints of the model. The model also allows for incomplete condensation, using a more complete expression than Eq. (1) and can deal with 3D islands, as well as 2D monolayer clusters.² The description of incomplete condensation requires knowledge of the adatom adsorption energy E_a . The value of N_x on a perfect, clean substrate is a sensitive test of E_d and E_b , and, at higher temperatures, also of E_a . Higher values of E_b prolong the lower critical sizes, and higher nucleation density, to higher temperatures. It is therefore of interest to attempt to

calculate these energies. In the following sections we discuss how to do this and compare results with experiment before finally turning to more general issues.

II. METHOD OF CALCULATION

We use here the classical model of interatomic interactions that has been widely successful in ionic solids. In practice, such methods usually assume that there is no electronic redistribution during the calculation—the rearrangement of the ions only affects the degree of interaction by varying the interatomic distance, not by changing the form of the interaction potential. The methods used here have been widely used to model many other systems involving planar interfaces,³ grain boundaries,⁴ and metal oxide interfaces.⁵ The ionic crystal surface is first calculated using the MIDAS program,³ which models ionic interfaces with two-dimensional periodicity. The program considers the crystal to be divided into two regions. The energy and energy derivatives of the inner region, the region next to the interface, are calculated and used to relax the atomic configuration to equilibrium. The outer region is relaxed as a rigid block. The Coulomb energy of the interface is calculated using a two-dimensional lattice sum technique. The short range interaction between the ions is calculated either empirically, by fitting to experimental properties, or by some kind of quantum calculation.

A related program, CHAOS,⁶ is used to calculate the energies of point defects near planar interfaces in ionic crystals. The point defects are introduced to the relaxed interfacial configuration and a spherical region around the defect is relaxed explicitly to equilibrium. The defect energy, the energy difference between the interface with the point defect and the undefective interface, is calculated by relaxing the ions in a spherical region around the defect to equilibrium. The displacements of the ions in the outer region are calculated by treating this region as a dielectric elastic continuum.

III. INTERACTIONS FOR METAL/IONIC INTERFACES

The interactions for the halides were taken from standard compilations (Sangster and Atwood⁷ for NaCl, NaF, and

TABLE I. Polarizabilities (α) and shell model parameters (Y, k_2, k_4) for the adatoms. Note that we use an extension to the shell model; where the polarization energy is given by $E(u) = k_2 u^2 + k_4 u^4$ where u is the core-shell displacement.

Atom	α (\AA^3)	$Y(e)$	k_2 (eV \AA^2)	k_4 (eV \AA^4)
Ag	9.0	1.0	1.6	250.0
Au	8.0	1.0	1.8	15.0

Catlow, Norgett, and Ross⁸ for CaF_2).

The interactions between the metal atom and the ions were calculated using the procedure discussed by Pyper and co-workers.⁹ There is one refinement necessary to the procedure discussed there because the metal atoms have an open shell. (We assume that silver has the configuration $4d^{10}5s^1$ and gold has the configuration $5d^{10}6s^1$). This was approximated by averaging the occupancy of the electrons in the open shell over all the open shell orbitals (the details are discussed in Ref. 10). This is not an entirely satisfactory procedure, but tests on the $\text{Ti}^{3+}-\text{F}^-$ interaction and on the cohesive energy of UO_2 show that it gives reasonable results (although significantly less accurate than for closed shell ions). The anion wave functions were calculated within a potential well comprising the Madelung term and a local potential describing the orthogonalization of the anion wave functions to those of the surrounding ions (for details see Ref. 11).

The interaction between the species was then calculated using RIP (Relativistic Integrals Program) (Ref. 9), which calculates the interaction within the Dirac-Fock approximation. Two terms were added: an estimate of the correlation energy obtained using electron-gas theory and the damped dispersion term. Details of the method are given in Ref. 11.

The calculation discussed so far does not permit the atoms to polarize. This effect is added using a shell model. The polarizabilities of the metal ions are taken from Ref. 12; these are also used in the shell model where it is assumed that the shell charge is given by the electron number for the metal atom. Values are given in Table I.

Combining this interaction with empirical interactions gives rise to one major problem; the status of the self-energy of the anion. This term is small, but not entirely negligible for the alkali halides. It has been shown¹³ that the anion self-energy in the crystal varies with local environment and further, that this effect is incorporated within empirical interactions. It is arguable, therefore, that such a contribution should be added to the metal/anion interaction. In this case it is more consistent not to. The empirical interaction was used for the pure surface and thus any approximation for the use of pair interactions at surfaces has already been made. Since the adatom calculations all refer to the perfect surface, any errors will tend to cancel out.

Some previous attempts have been made to derive interactions for these systems (e.g., Refs. 14 and 15). These used the Margenau formulas to estimate the dispersion term and a Lennard-Jones repulsion ($1/r^{12}$) fitted to the interatomic distance (assumed to be the sum of the covalent radii) to obtain the short-range term. The Margenau formulas are completely unreliable for estimating the dispersion energy, particularly for the higher-order terms.¹⁶ This can be seen in Table II

TABLE II. Comparison of the dispersion parameters C_6 and C_8 obtained by the Margenau formulae and by the methods used here.

Interaction	Margenau formula		This work	
	C_6 (eV \AA^6)	C_8 (eV \AA^8)	C_6 (eV \AA^6)	C_8 (eV \AA^8)
Ag^0-Na^+	20.4	169.8	9.87	205.5
Ag^0-Cl^-	234.9	4639.8	114.6	1627.2
Au^0-Na^+	27.9	37.7	4.1	35.7
Au^0-Cl^-	298.8	2030.6	73.5	674.0

where the results of the Margenau formulas are compared with the numbers calculated here. Still more important is the neglect of dispersion damping in the previous work. The standard expression for dispersion (an expansion in powers of r^{2n} for $n \geq 3$) is valid only in the limit of zero overlap of the wave functions of the atoms concerned. At close distances (for these purposes a typical interatomic distance is close) this seriously overestimates the dispersion contribution. At these distances a correction for the effect of wavefunction overlap must be made (the dispersion damping term). These are discussed by Pyper.¹¹ However, if the assumption of Refs. 14 and 15 that the sum of the covalent radii is reasonable, the derived repulsion term will tend to cancel out this error.

The metal-metal potential is obtained by fitting spectroscopic data^{17,18} to a Morse potential. A full set of data is available for Ag_2 ; a combination of spectroscopic and thermodynamic data are used for Au_2 . Details are given in Table III.

The model contains two main sources of error. First, there is the approximation inherent in using classical potential models as discussed above. The second approximation comes when we compare the calculated values (which are internal energies in the static lattice limit) with experimental ones (which are enthalpies measured at finite temperature). The validity of this procedure has been discussed in the literature.^{19,20} It is not possible to give an exact measure of the error, but comparison with full calculations of the free energy for other ionic systems²⁰ suggests that ± 0.1 eV is a reasonable estimate.

IV. Ag AND Au ATOMS ON IONIC SURFACES: RESULTS FOR E_a AND E_d

Calculations of the adsorption and migration of single adatoms have been performed. These calculations assume that the processes take place on a simple (100) terrace for the rocksalt structure and a (111) terrace for fluorite. The results for the adsorption energy and diffusion energy are given in Table IV. This table also contains comparisons with previous calculations^{14,15} and with experimental estimates based on rate equation analyses of nucleation experiments with

TABLE III. Morse potentials for the adatom molecules M_2 where $V(r) = D\{1 - \exp(A[r_0 - r])\}^2$.

Molecule	D (eV)	A (\AA^{-1})	r_0 (\AA)
Ag_2	1.784	1.43511	2.5303
Au_2	2.33	1.682	2.4715

TABLE IV. Values for the rate theory parameters E_a and E_d . Experimental estimates in round brackets (Refs. 1, 21, and 28) and previous calculations (Refs. 14 and 15) in square brackets.

Parameter	Ag/NaCl	Au/NaCl	Ag/NaF	Au/NaF	Ag/CaF ₂
E_a (eV)	0.27, [0.27], (0.41)	0.15, [0.69], (0.49)	0.26	0.18, [0.59], (0.63)	0.36
E_d (eV)	0.15, [0.09], (0.19)	0.07, [0.22], (0.16)	0.24	0.14, [0.08], (0.08)	0.34 (0.4–0.5)
$E_a - E_d$ (eV)	0.12, [0.18] (0.22)	0.08, [0.47] (0.33±0.02)	0.02	0.04, [0.51]	0.02

$i = 1$.^{1,21} In this limit the results do not depend on the metal dimer binding energy E_b .

In Table IV, the calculated adsorption energies are significantly less than the experimental estimates in almost all cases. There is also a recent Hartree-Fock cluster calculation for Cu, Ag, and Au on a simulated NaCl(100) surface²² which gives very small values for E_a , all below 0.1 eV. Values for E_d obtained by this method would presumably be even smaller. Whether or not the correct values are really as low as this is debatable, but it indicates that presently available theory, for which we claim an accuracy of about ± 0.1 eV, does give very low values for both E_a and E_d . This is perhaps surprising in comparison with experimental measurements, where several workers in the field believe that the combination energy ($E_a - E_d$) is reasonably well determined from the condensation coefficient, the nucleation rate and the growth rate of islands for both Ag and Au/NaCl(100).^{1,21,28}

We could argue that ($E_a - E_d$) for Ag/NaCl, calculated as 0.12 eV, is within our expected error bar in comparison with the best experimental value of 0.22 eV. However, the calculated value for Au/NaCl, 0.08 eV, is definitely below the best experimental value, 0.33 ± 0.02 eV. In general, if ($E_a - E_d$) is too small, single atoms will reevaporate too readily and the initial condensation coefficient will be much too low, since this energy determines the mean-square displacement before desorption, which approaches atomic dimensions when E_d tends to E_a .²¹

These features suggest that there may be a missing component in the calculation, particularly of E_a .

V. Ag AND Au ATOMS ON ALKALI HALIDES: DIMERS AND DEFECTS

The nucleation process for metals on ionic crystals may well be more complex than adsorption of a single atom onto a terrace followed by diffusion and coalescence into clusters. The most obvious points to consider are small cluster structure and mobility, and the effects of defects in the substrate such as steps and point defects. A measure of complexity is

TABLE V. Calculated dimer binding E_b , adsorption E_{a_2} , and migration E_{d_2} energies.

Parameter	Ag/NaCl	Au/NaCl	Ag/NaF	Au/NaF	Ag/CaF ₂
E_b (eV)	1.76	2.34	1.64	2.24	1.46
E_{a_2} (eV)	0.50	0.32	0.32	0.14	0.42
E_{d_2} (eV)	0.06	0.05	0.27	0.13	

indeed suggested by the detailed experimental studies of Robins and co-workers, particularly on the system Au/NaCl.^{23–29} The effects of cluster mobility and coalescence as a function of temperature have been modeled by several authors including Velfe, Stenzl, and Krohn³⁰ and Vicanek and Ghoniem.³¹ Few calculations of cluster structure and mobility have been performed. Gates and Robins³² calculated the adhesion and mobility of a variety of clusters using a simple potential model but ignored all cluster relaxation (although the cluster was allowed to move rigidly with respect to the rigid substrate). They found that cluster migration energies can be very small, but the neglect of relaxation in their calculation makes this result questionable. We have therefore performed a number of exploratory calculations on the three issues of cluster motion, the effect of surface steps and the effect of surface vacancies.

First, we have considered the binding, adsorption and migration energies of a number of dimers for the alkali halide systems discussed above. The results are shown in Table V. The binding energies of the metal dimers on the surface, E_b , are only somewhat reduced from their free space values. The binding energies of pairs of atoms in free space, E_{b_0} , are known for Ag (1.65 ± 0.06 eV) and Au (2.29 ± 0.02 eV), respectively.¹⁸ Adsorption on the surface reduces this interaction, but not nearly as much as, for example, the same metal atoms adsorbed onto metal surfaces. These high E_b values are consistent with the (experimental) finding that $i = 1$ over a large temperature range.^{1,21}

Adsorption energies E_{a_2} are given with respect to the free dimer molecules. The adsorption energies (for the adsorbed dimers) are all roughly twice that for the single atoms; only for the case of Au₂ on NaF, where there is a very poor match

TABLE VI. Binding energy of a metal atom at a surface step, relative to the atom on the terrace, and diffusion energy along the step. A negative value implies that the terrace site is more stable. (In the first two rows, the ion is the ion label in the column refers to the closest ion to the metal atom at the base of the step. In the last two rows, the energy E_s is the most stable position, and E_{ds} is the difference between the two ion positions).

Ion	Ag/NaCl	Au/NaCl	Ag/NaF	Au/NaF
Cation (eV)	0.02	0.0	-0.01	-0.01
Anion (eV)	0.21	0.12	0.23	0.18
E_s (eV)	0.21	0.12	0.23	0.18
E_{ds} (eV)	0.19	0.12	0.23	0.18

TABLE VII. Effect of surface point defects on metal adsorption; trapping energy E_t (eV) with respect to the free metal atom on the terrace of the crystal surface and height of the metal atom above the mean surface plane (in brackets; units of Å).

Defect	Ag/NaCl	Au/NaCl	Ag/NaF	Au/NaF
Terrace	−(2.61)	−(2.87)	−(2.20)	−(2.36)
Cation vacancy	0.69 (0.05)	0.27 (0.43)	0.35 (0.74)	−0.07 (1.12)
Anion vacancy	−0.21 (1.92)	0.09 (1.86)	0.05 (3.21)	0.06 (2.75)
Ca ²⁺ /vacancy pair	0.67 (0.09)	0.28 (0.85)	0.29 (0.18)	0.43 (1.28)

to the substrate, is the energy significantly less than this. What is of most interest, however, is the diffusion energy. This is very small, as observed by previous authors. The reason is that, with two metal atoms strongly bound together, it is necessary to find reasonably favorable sites for both of them. Whereas for a single atom it is possible to relax the system to maximize the attraction for the one ion, thus producing significant differences for different sites, it is not possible to do this for the pair. Similar considerations should apply for larger clusters, as suggested in previous work particularly for trimers.³²

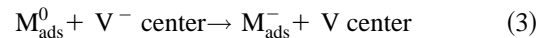
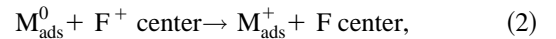
Second, we consider the effect of steps. Here we confine attention to the rocksalt structure where some data are available. A step was produced by choosing a surface vicinal to the (001). A few trial calculations showed that the (107) surface produces an array of steps far enough apart not to interact significantly. The results are shown in Table VI. The attraction of the metal atom to the step is clearly seen in all cases. Also, we can use the data to estimate the diffusion energy along the step. This is also shown in the table. The results are somewhat smaller than the experimental analysis of Gates and Robins,²⁶ who give 0.23 ± 0.025 eV for the threshold energy of diffusion along the steps, but agree within the likely accuracy of the calculation.

Third, we consider the effect of surface point defects. Here the obvious defects to consider are vacancies. We consider three cases; the simple isolated cation and anion vacancies and a vacancy bound to a calcium ion. The calculations of the trap energies, E_t , of isolated defects (see Table VII) show that the metal ions are usually bound to the cation vacancies but not to the anion vacancies. We note that the cation vacancies (caused by removing a positive ion) are *negatively* charged regions of the crystal, corresponding to a surface V^- center. Similar considerations apply to anion vacancies; these are *positively* charged regions corresponding to surface F^+ centers. As a general rule, the height of the metal atom above the nominal surface plane is greater the smaller the binding energy. This is to be expected since the polarization of the metal atom is reduced as it is further way from the charged defect. The defects comprising a vacancy bound to calcium are not charged (although they still have a dipole moment) and so the correlation is less reliable here.

The formation energy of Schottky pairs is fairly high (of the order of 2–2.5 eV) for most alkali halides. This is high enough to ensure that thermally produced surface vacancies do not affect the measured adsorption energy at typical deposition temperatures. However, it is well known that divalent cation impurities cause constitutional cation vacancies, and that such defects can have a dramatic effect on nucleation

densities when present at the ppm level.^{28,30,33} In our calculation, we consider the Ca²⁺ ion to be a K⁺ ion, but with two units of charge rather than one. The errors resulting from the different ion sizes should be small. The calculations show that the effect of the nearby doping ion is negligible except for the case of Au/NaF. In almost all cases, the metal atom is strongly bound to the cation vacancy and is (slightly) repelled by the anion defect.

One interesting possibility that should be considered in future work is the ionization of the metal atom on the terrace, with the resulting electron trapped in a vacancy to form a surface F center. Simple Born-Haber cycles suggest that the reactions



are close to exothermic. The possibility of partially charged metal adatoms (and their interaction with electric fields) is worth consideration. The reactivity of surface centers with metal atoms has been considered by Ferrari and Pacchioni³⁴ for (100) surfaces in MgO.

VI. CONCLUSIONS

Much has been achieved in understanding the nucleation and growth of metal clusters on substrates using simple models containing only three parameters, E_a , E_b , and E_d . However, as previous experimental and theoretical work has already suggested, nucleation and growth of metal clusters on ionic substrates is a complex process both involving the trapping effects of line steps E_s and surface point defects E_t , as well as the participation of other mobile species, E_{d_2} , etc. Thus the simple comparison of calculations of the adsorption and diffusion of single metal atoms with experimental parameters can be misleading, and will tend to overestimate the energy values. The calculations presented here, which illustrate a range of possibilities, show that the adsorption and diffusion energies are remarkably low, and that these extra processes cannot in general be ignored. A more complex analysis of the experimental data is therefore likely to be required in several specific cases; in particular, the possibility of a significant dimer term should always be examined. The possibility that partially charged adatoms might affect the calculated value of the adsorption energy should be investigated.

- * Also at Department of Physics and Astronomy, Arizona State University, Tempe, AZ 85287.
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