

METALLIC CLUSTERS DEPOSITED ON SURFACES

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The quasi-classical theory of matter aggregation is briefly reviewed and the guiding principles of formation of the atomic clusters are discussed. The interaction potential of a metallic ion with a semi-infinite solid exhibiting a free plane surface is derived and atomic clusters deposited on surfaces are constructed. Binding energies, ground-states, magic geometries, isomers, inter-atomic distances, vibration spectra and monolayers are thus obtained, and further developments are outlined.

(Received December 22, 2007; accepted December 29, 2007)

Keywords: Metallic clusters, Surface deposition, Simulation, Computer calculations,
Magic geometries

1. Introduction

Solid atomic aggregates occur through delocalization of the electrons in the upper valence shells. The chemical bond originates in a superposition of atomic-like orbitals and extended orbitals that vary slowly in space. Such a picture is amenable to a quasi-classical description of the Hartree-Fock equations. An atomic aggregate looks like an ensemble of electrons spinning around and the ionic cores left behind.[1] The ionic cores have effective charges z_i^* , where i is the label of the ion. These charges are distributed radially-symmetric, as for s-orbitals, or directionally, as for p, d, f-orbitals; several electrons in d- and f-orbitals may approximately be viewed as radially-symmetric. In addition, such atomic-orbital charges may also be approximated for the beginning by point-like distributions. Most of the metallic ions fall in this class of s-, or d, f-orbitals. The effective charges may be estimated for atoms sufficiently heavy by making use of the atomic screening theory. For instance, $z_{Na} = 8.44$ for Na (sodium) and $z_{Fe} = 0.57$ for Fe (iron). Under the circumstances given above, within the quasi-classical description, the electrons in an atomic aggregate move in a self-consistent Hartree potential

$$\varphi(\mathbf{r}) = \sum_{i=1}^N \frac{z_i^*}{|\mathbf{r} - \mathbf{R}_i|} e^{-q|\mathbf{r} - \mathbf{R}_i|}, \quad (1)$$

where N is the number of ions, \mathbf{R}_i denote their positions and q is a screening wavevector to be determined variationally. The well-know atomic units are used, namely the Bohr radius $a_H = \hbar^2/mc^2 = 0.53 \text{ \AA}$ and twice the rydberg $e^2/a_H = 27.2 \text{ eV}$. Due to the self-consistency the electron

density n depends on the potential ϕ by $n = (q^2/4\pi)\phi$, so that we obtain the potential energy

$$E_{pot} = -\frac{3}{4}q \sum_{i=1}^N z_i^{*2} + \frac{1}{2} \sum_{i \neq j=1}^N \Phi(R_{ij}) \quad (2)$$

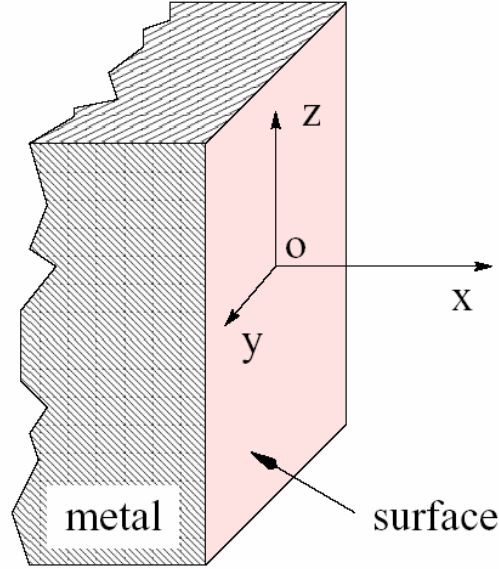


Figure 1 A free plane surface of a semi-infinite solid

of the interacting electrons and ions (electron-electron and ion-ion Coulomb repulsions included), where

$$\Phi(R_{ij}) = -\frac{1}{2}qz_i^*z_j^*\left(1 - \frac{2}{qR_{ij}}\right)e^{-qR_{ij}} \quad (3)$$

are effective interaction (pseudo-) potentials between ions separated by distance $R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$.

The potential energy given by (2) is minimized with respect to \mathbf{R}_i (actually $q\mathbf{R}_i$) in order to find the ionic equilibrium positions; this way, we determine the geometric forms of the atomic aggregates, both for their ground-states and isomers. Thereafter, the kinetic energy $E_{kin} = (27\pi^2/640)q^4 \sum_i z_i^*$ is added, and the quasi-classical energy $E_q = E_{kin} + E_{pot}$ is minimized with respect to the screening wave vector q ; finally the exchange energy $E_{ex} = -(9/32)q^2 \sum_i z_i^*$ is included to obtain the binding energy $E = E_q + E_{ex}$.

This theoretical approach has been applied to homo-atomic metallic clusters, where geometric magic numbers have been obtained, together with binding energies, inter-atomic distances and vibration spectra (up to $N \sim 160$) [2]. Leaving aside the small contribution of the interacting part in the potential energy at equilibrium, the screening wave vector reads approximately $q \sim 0.77z^{*1/3}$ in this case, and the average inter-atomic distance may be estimated as $a = \bar{R}_{ij} \sim 2.73/q$; all the same, the binding energy is given by $E = -N(0.43z^{*7/3} + 0.17z^{*5/3})$. Similarly, the theory has been used to estimate other, more complex structures, as, for instance, the equilibrium Fe-core structure of the iron-hydrocarbon $Fe_{13}(C_2H_2)_6$ -cluster [3].

The above theoretical description is to be developed along two directions at least. First, the directional character of the atomic-like orbitals (as well as their radial dependence) must be included in order to obtain, for instance, p- or sp-orbitals atomic aggregates. Secondly, the quantum corrections must be included to the quasi-classical treatment, in order to get a more accurate knowledge of the electronic single-particle properties, like energy levels (or bands), ionization potential, chemical affinity, optical properties, polarizability, magnetic properties, etc.

An error of cca 17 % is estimated without quantum corrections, while including them may lead to an accuracy of up to cca 3 %, at most. Various hetero-atomic aggregates could then be studied with more confidence.

Until then, the present theory can be employed to get a description of metallic surfaces or interfaces, or metallic clusters deposited on such surfaces, or atomic aggregates with various others geometric constraints.

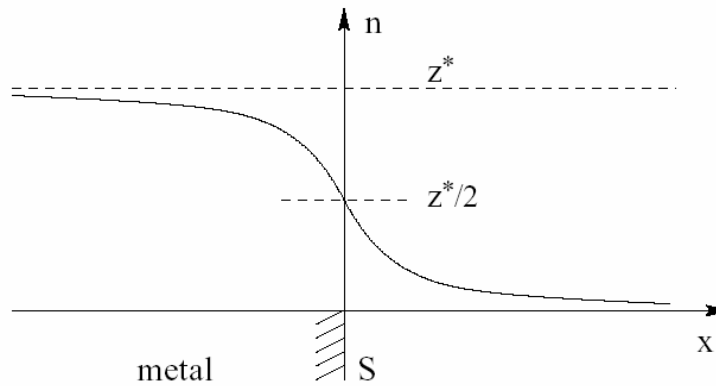


Figure 2 Electron density at the surface.

2. Metallic surface

The summation over ions in (1) can be restricted to a half-space, as for an semi-infinite solid with a free plane surface perpendicular to, say, the x-direction at $x = 0$. Such a surface is shown in Fig. 1. In the continuum approximation we obtain the self-consistent potential

$$\begin{aligned} \varphi(x) &= \frac{4\pi z^*}{q^2 a^3} \left(1 - \frac{1}{2} e^{qx}\right), \quad x < 0, \\ \varphi(x) &= \frac{2\pi z^*}{q^2 a^3} e^{-qx}, \quad x > 0, \end{aligned} \quad (4)$$

where z^* is the average effective charge and a denotes the average inter-atomic distance. When compared to the bulk contribution $\varphi = 4\pi z^*/q^2 a^3$ one can see that a dipolar potential $\delta\varphi$ occurs at the surface, which gives rise to a spill over of the electrons and a surface charge double layer. The electron density $n = (q^2/4\pi)\varphi$ is shown in Fig.2, and the total charge density is plotted in Fig. 3 vs x . The work function of the solid as computed from (4) is φ , as expected. The interaction energy $-1/2 \int dx \cdot \delta\varphi \delta n$ associated with the electronic double layer (per unit area) is $-\pi z^{*2}/2q^3 a^6$, and it acts like an additional uncertainty in the quasi-particle energy giving rise to boundary (finite-size) lifetime; it also leads to a weak relaxation of the ionic positions at the surface. On the other hand, the potential energy can be estimated from (2) and (3) for a semi-infinite solid; in the continuum approximation we obtain

$$E_{pot} = -\frac{3}{4} q z^{*2} N + \frac{\pi z^{*2}}{2q^3 a^6} A, \quad (5)$$

where A is the area of the cross-section; therefore, the potential energy (5) includes a surface contribution $(\pi z^{*2}/2q^3 a^6)A$, beside the bulk contribution given by the first term (the interacting part

vanishes in the bulk continuum limit); the surface tension of the solid is $\sigma = (\pi z^{*2}/2q^3 a^6)$, and it agrees with the double layer energy given above.

Similarly, we can estimate the interaction potential between a semi-infinite solid and an ion with an effective charge z^*_0 placed at distance x from the surface; indeed, making use of (2) and (3),

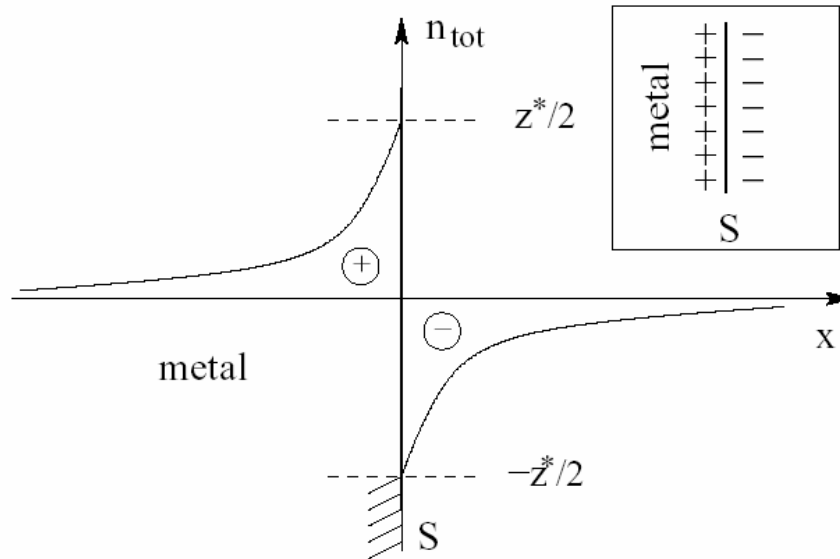


Figure 3 Charge distribution at the surface by-layer

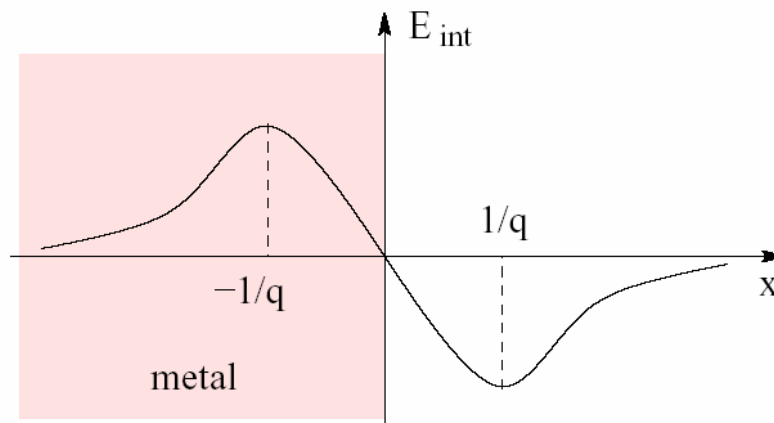


Figure 4 Interaction potential between an atom and a semi-infinite solid

we get

$$E_{pot} = E_s - \frac{3}{4}qz_0^{*2} - \frac{\pi z^* z_0^*}{qa^3} x e^{-q|x|} \quad (6)$$

where E_s is the potential energy of the solid as given by (5); the second term in (6) is the self-energy of the added atom and the third term represents the interaction potential of the atom with the semi-infinite solid; it is shown in Fig. 4. This interaction potential exhibits a potential barrier just beneath the surface, and has an attractive part above; the latter is responsible of adsorbing additional atoms on the surface, and of stabilizing deposited atomic clusters.

Now it is easy to write down the potential energy of an ensemble of N atoms of effective charges z^*_i deposited on the surface; it reads

$$E_{pot} = E_s - \frac{3}{4}q \sum_{i=1}^N z_i^{*2} + \frac{1}{2} \sum_{i \neq j=1}^N \Phi(R_{ij}) - \frac{\pi z^*}{qa^3} \sum_{i=1}^N z_i^* X_i e^{-q|X_i|} , \quad (7)$$

where the potentials $\Phi(R_{ij})$ are given by (3) and X_i is the x-coordinate of \mathbf{R}_i . It is worth noting that the screening wave vector q is the one corresponding to the solid, as the latter prevails upon the deposited cluster in the thermodynamic limit. In this respect the deposited clusters differ from the

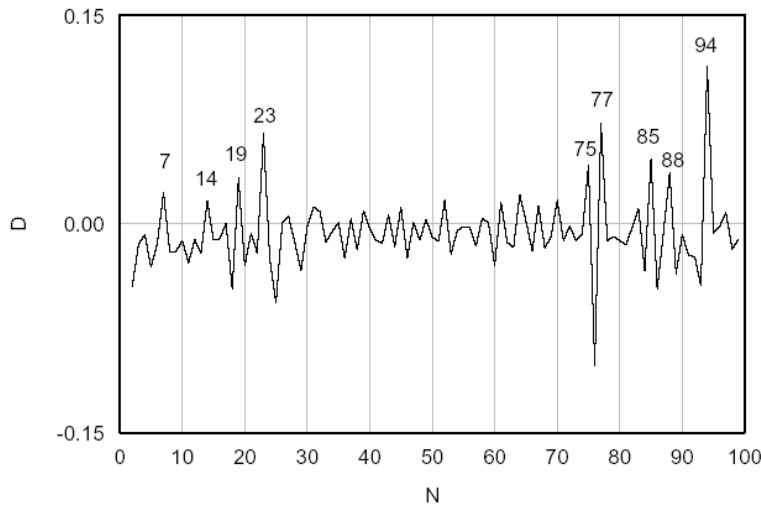


Figure 5 Ground-state abundance spectrum and magic clusters deposited on surfaces

isolated clusters, which have their own screening wave vector as it results from the minimization of their quasi-classical energy. The binding energy of a deposited cluster is given by $E = E_q + E_{ex}$, where the quasi-classical energy is $E_q = (27\pi^2/640)q^4 \sum_i z_i^* + E_{pot} - E_s$, and the exchange energy is given by $E_{ex} = -(9/32)q^2 \sum_i z_i^*$; the potential energy given by (7) is minimized with respect to the ionic positions \mathbf{R}_i . It is worth noting that an interaction energy

$$E_{int} = -\frac{\pi z^*}{qa^3} \sum_{i=1}^N z_i^* X_i e^{-q|X_i|} \quad (8)$$

can be defined from (7), between the deposited cluster and the solid, which may serve as a measure of the energy needed to separate the cluster from the surface (the difference in the cluster energy must be added, arising from its own screening wave vector corresponding to the cluster relaxation).

One can also notice that the interaction energy (8) for the halves of a solid compensates exactly the surface energies of the two faces, as given by (5). If two distinct solids are put in contact there is a diffusion of one into another across the interface, according to the tunneling through the interaction potentials given by (8). Finally, we note that the continuum approximation is not necessary, and we can treat the cluster deposition by preserving the discrete summations over fixed ionic positions in solid; we have adopted the continuum approximation here for the sake of the simplicity; the errors introduced on this occasion refer to the few atomic layers in the vicinity of the surface, and of course to the matching problem of the lattice constants.

3. Clusters deposited on surface

The main problem of depositing atomic clusters on a surface is the minimization of the potential energy (7) with respect to the ionic positions \mathbf{R}_i (in fact with respect to $q\mathbf{R}_i$). Initially, we give positions \mathbf{R}_i randomly distributed in space and let the ions move step by step along the forces until a local equilibrium is reached (corresponding to forces less than 10^{-4} eV/Å); this equilibrium is checked by computing the corresponding vibration spectra. For each number N of atoms the

procedure is repeated for a few hundreds times, in order to get the ground-state and the isomers; the latter are clusters higher in energy with slightly different ionic positions. This procedure has been applied to Fe-clusters ($z^*_i = 0.57$) deposited on Na-surface ($z^* = 0.44$) up to $N = 100$.

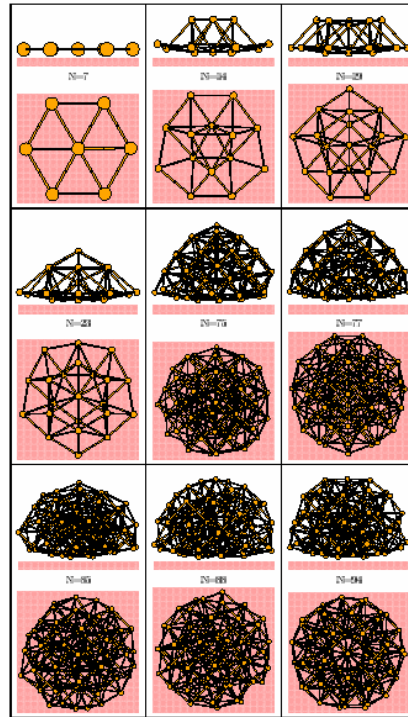


Figure 6 Magic clusters deposited on a surface

The original ionic positions are randomly distributed in space both below and above the surface of the solid; we find that equilibrium positions are reached mostly above the surface, as for deposited clusters. The binding energies $E(N)$ have been computed for the ground-state of these clusters as indicated before, and abundance spectra $D = \ln(I_N^2/I_{N+1}I_{N-1}) = E(N+1) + E(N-1) - 2E(N)$ have been obtained, where I_N is Boltzmann's statistical weight.

Such an abundance spectrum D is shown in Fig. 5; these spectra depend weakly on the nature of the clusters and of the substrate. Magic clusters deposited on surface are to be noted in Fig. 5, as, for instance, those corresponding to $N = 7, 14, 19, 23, 75, 77, 85, 88, 94, \dots$; they acquire highly symmetric forms, as shown in Fig. 6. The rather structureless island between $N = 23$ and $N = 75$ is intriguing in Fig. 5. As a general rule, for small values of N atoms are adsorbed on the surface in a monolayer, forming up more-or-less regular polygons. On increasing the number of atoms, they distribute themselves both horizontally and vertically, giving rise to multilayer structures, with various, intricate geometries, and sometimes beautiful symmetries, as those corresponding for instance to $N = 23, 77, 94$. It is worth noting that their binding energies are higher in comparison with their monolayer (two-dimensional) versions (which are isomers), i.e. growing up vertically helps stabilizing the clusters; such a comparison is shown in Fig. 7. In general, there is a competition between the two directions of growth, horizontal and vertical, and it is difficult to predict which would prevail for a given number of atoms.

Bound states can also be obtained for clusters deposited on surfaces with parts pervading beneath the surface, as shown in Fig. 8. Indeed, the first two pictures in Fig. 8 show a 50-atoms cluster diffusing into solid, while the last picture in Fig. 8 exhibits a 100-atoms cluster developing an interface with the solid. These states are isomeric, and, in some cases, atoms may escape into the solid where they acquire free positions, i.e. they are no more bound to the cluster. Similar formations can be obtained for a large variety of situations, including both geometric constraints,

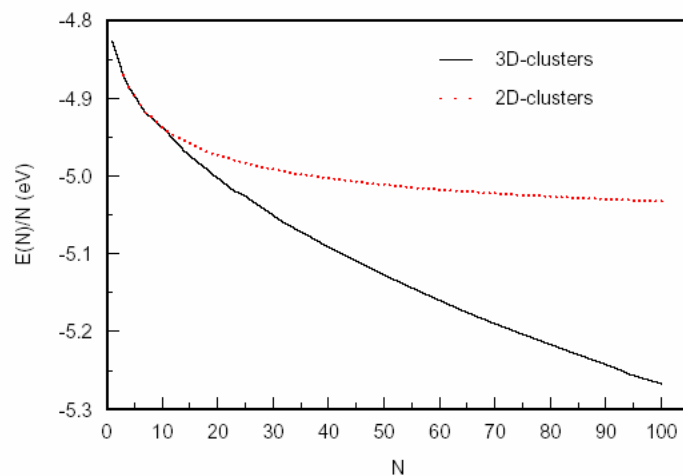


Figure 7 Ground-state energy per atom for Fe-clusters (3D, solid line) deposited on Na-surface vs number of atoms, as compared with monolayer cluster energy (2D, dashed line).

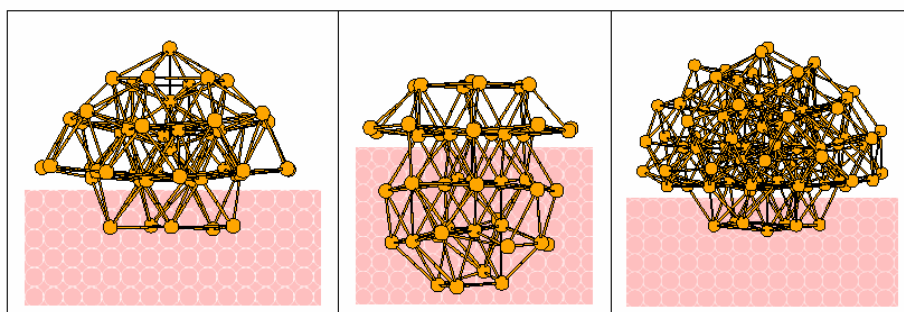


Figure 8 A 50-atoms cluster diffusing into solid (first two pictures), a 100-atoms one developing an interface with the solid (last picture).

like a deposition surface, and dynamic constraints, like applying external forces.

4. Concluding remarks

In conclusion, we may say that interaction potentials can be identified in the quasi-classical description of atomic aggregation, between atoms and semi-infinite solids, which allow to analyze the deposition of the atomic clusters on surfaces. At the present level of computations the geometric forms of deposited metallic clusters are obtained, as well as binding energies, inter-atomic distances and vibration spectra. Magic clusters are identified, deposited on surfaces, exhibiting, in general, high symmetries, both horizontally and vertically. Increasing the number of atoms they may intrude beneath the surface, giving thus the possibility of building up interfaces, and contacts, between two solids. Further investigations are pursued into extending the theory to directional chemical bonds and electronic single-particle properties.

Acknowledgments

This work has been partially supported by the Swiss National Science Foundation SCOPES Programme, Grant #7BUPJ062407.00/1-FCST, and by Romanian Government CERES Research Programme #65/2001.

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