

Supporting Information

Contact potentials, Fermi level equilibration and surface charging

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BASIC CONCEPTS: FERMI LEVEL AND WORK FUNCTION OF A METAL

The electrochemical convention assigns the zero energy to an electron at rest in a field-free vacuum. Then, the electronic energies in a metal have negative values. The Fermi-Dirac distribution describes the probability of occupation of electronic states. At any temperature, the probability of occupation of a state with energy equal to the chemical potential μ_{e^-} of the electrons is 1/2. The number density of electrons in the conduction band of a metal determines the difference between μ_{e^-} and the lowest energy level in this band. At absolute zero, the Fermi-Dirac distribution becomes a step function and μ_{e^-} is the energy of the highest occupied electron level. Rather often temperature dependence of μ_{e^-} (at fixed number density of electrons) is neglected, and μ_{e^-} in the Fermi-Dirac distribution is replaced by a constant value denoted as the Fermi energy. Unfortunately, there is considerable ambiguity in the use of this term.

Under isothermal conditions, electrons tend to move to locations where their electrochemical potential $\tilde{\mu}_{e^-}$ is lower. The electrochemical potential of the electrons is determined by their interactions with the other particles within the phase as well as by the interaction with the electrostatic field. That is, $\tilde{\mu}_{e^-}$ is affected by the charge state of the phase. The relation between the electrochemical potential and the chemical potential of the electrons is

$$\tilde{\mu}_{e^-} = \mu_{e^-} - e\phi \quad (\text{S1})$$

where e is the elementary charge and ϕ is the electrostatic potential. That is, $-e\phi$ is the electrostatic potential energy of the electron at its location. When two phases equilibrate with respect to the redistribution of electrons, $\tilde{\mu}_{e^-}$ takes the same value in both phases.

The electronic energies mentioned above, and μ_{e^-} , are intrinsic, bulk properties of uncharged metals and do not contain interfacial effects. That is, these energies include kinetic and potential contributions from electron-electron and electron-ion interactions but they do not include the potential energy of the electrons in any electrostatic field. In the metal-vacuum interfacial region, the spreading of the electronic charge into the vacuum creates a surface potential χ which raises the work function of the material,^{S1-S4} The state of the electrons inside metals with interfaces is described by the real potential (also called real chemical potential)^{S1}

$$\alpha_{e^-} \equiv \mu_{e^-} - e\chi. \quad (\text{S2})$$

The potential drop χ is the potential in the bulk of the metal minus the potential in the vacuum “just outside” it; where “just outside” refers to a position just out of the range of the image forces.^{S5}

The local work function $\Phi = -\alpha_{e^-}$ of a metal surface is the minimum work required to remove one electron from the bulk of a large piece of uncharged metal across a surface to a position at rest in vacuum just outside the metal surface; the distance from the surface should be so large that the image force is negligible but small compared with the distance from another face. From eq S2, the local work function $\Phi = -\alpha_{e^-}$ has a chemical contribution $-\mu_{e^-}$ that can be calculated from the bulk band structure and a surface or electrostatic $e\chi$ contribution that can be calculated from the surface electronic structure.^{S6}

The difference between $\tilde{\mu}_{e^-}$ and α_{e^-} is the electrostatic potential energy $-e\psi$ of the electron just outside the metal

$$\tilde{\mu}_{e^-} = \alpha_{e^-} - e\psi \quad (\text{S3})$$

where ψ is the outer or Volta potential of the phase, or vacuum level. The surface charge density σ on the phase and the outer potential ψ have the same sign and are linked together by the capacitance that depends on the geometry of the phase. According to its IUPAC definition,^{S6–S8} the electrochemical potential $\tilde{\mu}_{e^-}$ in a conducting phase is the work of bringing one electron from a reference point in vacuum (outside the range of the charge of the phase) to the bulk phase. The work to bring this electron from the reference point to just outside the metal is $-e\psi$.^{S1} The work function $\Phi = -e\psi - \tilde{\mu}_{e^-}$ is the difference in the energies of the electron just outside the metal ($-e\psi$) and inside the metal ($\tilde{\mu}_{e^-}$). From eqs S1–S3, the inner or Galvani potential of a phase is the sum of the surface potential and the outer potential, $\phi = \chi + \psi$. By definition, the inner potential is constant within the phase at equilibrium.^{S1}

The ionization energy IE is defined as the work to remove one electron from a particle (with a size that can range from the single atom to the bulk metal). The particle can be charged before the electron extraction or become charged due to the electron removal; the latter case is usually considered when reporting experimental or calculated values.^{S9} For a nanoparticle of radius r and charge ze the energy required to remove one electron in vacuum can be estimated as^{S10}

$$\text{IE}_{\text{NP}, ze}^V = \Phi_{\text{bulk}} + \int_{ze}^{(z+1)e} \frac{q}{4\pi\epsilon_0 r} dq = \Phi_{\text{bulk}} + \frac{(2z+1)e^2}{8\pi\epsilon_0 r} \quad (\text{S4})$$

In the case of bulk phases (*i.e.*, large radius), the second term in the rhs of eq S4 is negligible because there is no significant difference (in the state of charge) when one electron is added or removed. In this work, we consider that the ionization energy is

$$\text{IE} = -\tilde{\mu}_{e^-} = \Phi + e\psi \quad (\text{S5})$$

When two phases A and B are placed in contact, electrons flow until an equilibrium is reached in which the electrochemical potential of the electrons is equal in phases A and B, $\tilde{\mu}_{\text{e}}^{\text{A}} = \tilde{\mu}_{\text{e}}^{\text{B}}$.^{S1}

The condition $\tilde{\mu}_{\text{e}}^{\text{A}} = \tilde{\mu}_{\text{e}}^{\text{B}}$ and eq S5 imply that the outer potentials of two conductors in equilibrium differ in a quantity proportional to the difference of their work functions

$$\Delta_{\text{A}}^{\text{B}}\psi_{\text{eq}} \equiv (\psi^{\text{B}} - \psi^{\text{A}})_{\text{eq}} = -(\Phi^{\text{B}} - \Phi^{\text{A}})/e \equiv -\Delta_{\text{A}}^{\text{B}}\Phi/e. \quad (\text{S6})$$

This is known as the equilibrium Volta potential difference. Under equilibrium, the ionization energies, eq S5, of the conductors also become equal as the conductor with lower work function becomes positively charged with respect to that with higher work function,^{S3} and this makes equally difficult to extract one electron from one or another.

Different surfaces of a crystal may have different local work functions; however, if the electron were extracted to a final position at an infinitely large distance from the surface it would not be possible to discriminate between the work functions of different faces.²⁵ The differences in Φ originate from the differences in χ . The surfaces must then have different outer electric potentials because eq S6 also applies to two faces A and B of the same metal.^{S6} As the electrochemical potential for electrons has to be the same, independent of the surface through which the test charge is brought into the phase, this difference in the surface potentials is balanced by redistribution of charge on the surfaces, and hence different outer potentials. This is also the origin of observed differences in the potential of zero charges for different crystal facets. In physics, this is often described by saying that “the vacuum level changes”, simply meaning that different surfaces have different surface charge and hence different electric field.

MODEL DESCRIPTION

The potential distribution around a spherical particle with a radius of 12.6 Å with different ratios of Au and Ag was investigated both in vacuum and in an electrolyte solution containing 10 mM KCl. The separation distance between the two metals was set to 0.36 Å as described earlier.^{S11} The electrostatics of the system were described by the Poisson equation

$$\varepsilon_0 \varepsilon_r \nabla^2 \phi = -\rho_v \quad (\text{S7})$$

where ϕ is the electrostatic potential, ε_0 and ε_r are permittivity of vacuum and the relative permittivity, and ρ_v is the space charge density. The geometry is shown in Figure S1. The sharp corners were rounded with a radius of 0.2 Å. In the aqueous electrolyte solution the particle was surrounded by a Stern layer with a radius of 3.3 Å, where the space charge density is nil.

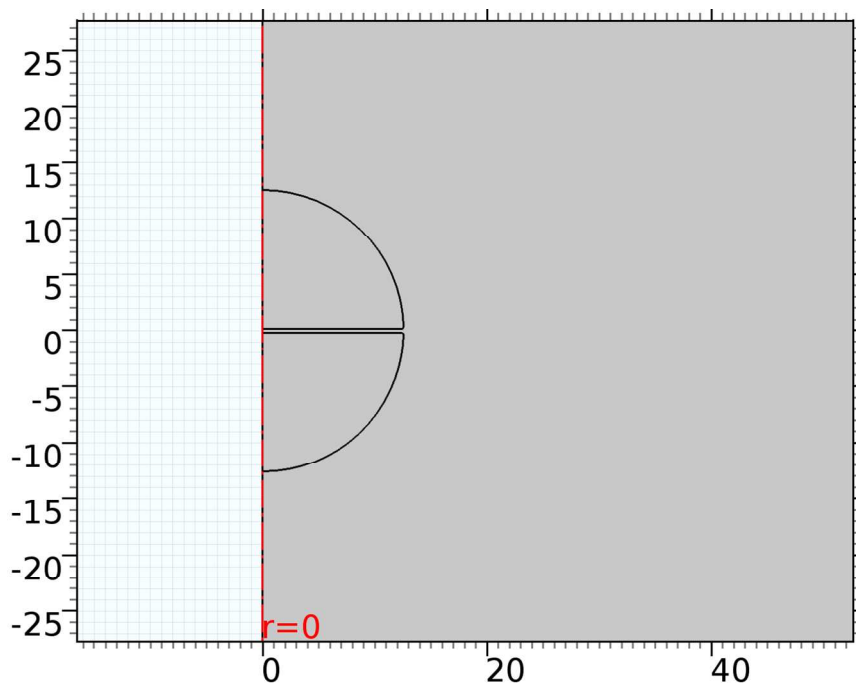


Figure S1. The simulation geometry.

The model was solved in 2D axial symmetry ($r = 0$ as the axis of symmetry). The electric potential difference between the Ag and Au was set to 0.86 V (the computational work function

difference between the two pure metallic particles of this size) and the outer boundary of the surrounding medium (10 000 Å away) was set to be insulating. The actual potential values were calculated from [eq 21](#) in the main text, considering that silver surface area weighted ratio of the potential difference is on the silver metal (e.g. with Janus particle 50% of the potential difference is on the silver side, and with the 5 % Ag covered particle 5% of the potential difference is on the silver side). Silver is positive because of the electron transfer to the gold to equilibrate the Fermi levels. The mesh density was increased until the results did not significantly change. The validity of [eq 21](#) was confirmed by checking that charge conservation was maintained within the particle.

ANALYTICAL SOLUTION AND VALIDATION OF THE SIMULATION RESULTS

In the case of an ideal Janus particle made of two hemispheres of equal size and radius a , the solution of the Laplace equation of electrostatics (in polar coordinates) is

$$\phi(r, \theta) = \frac{\Delta\psi}{4\sqrt{\pi}} \sum_{m=0}^{\infty} (-1)^m (4m+3) \frac{\Gamma(m+1/2)}{\Gamma(m+2)} \left(\frac{a}{r}\right)^{2(m+1)} P_{2m+1}(\cos\theta) \quad (\text{S8})$$

which satisfies the boundary conditions $\phi(r=a, \pi/2 < \theta \leq \pi) = -\Delta\psi/2$ and $\phi(r=a, 0 \leq \theta < \pi/2) = \Delta\psi/2$. Here no gap between the two hemispheres is considered. This analytical solution was compared with the results from the numerical simulations, as shown in [Figure S2](#), showing very good match.

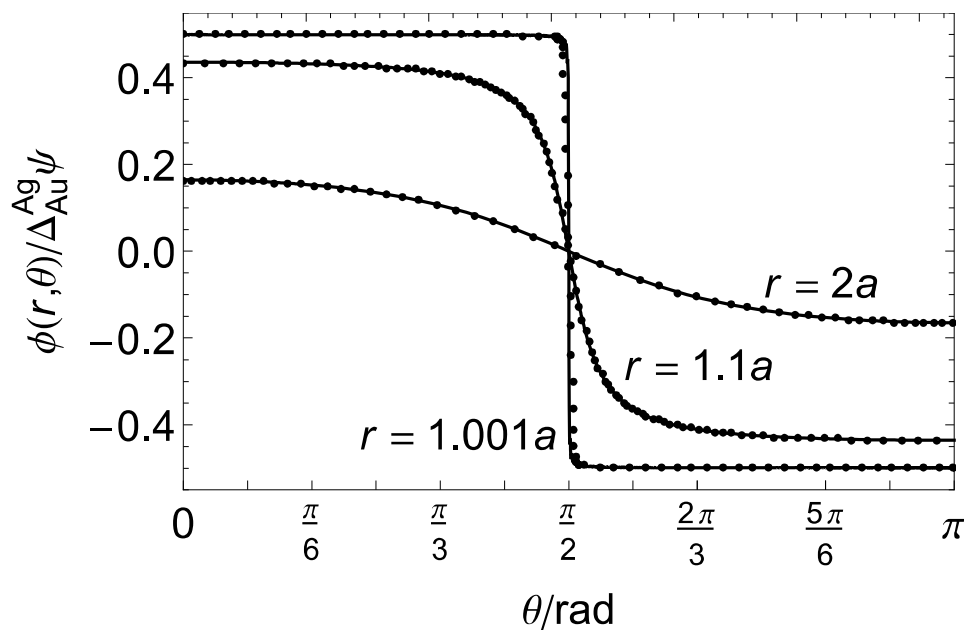


Figure S2. Comparison of the numerical (points) and analytical (solid lines) potentials at different distances around the Janus sphere in vacuum.

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