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On the work function and the charging of small ($r \leq 5$ nm) nanoparticles in plasmas

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Abstract

The growth of nanoparticles (NPs) in plasmas is an attractive technique where improved theoretical understanding is needed for quantitative modeling. The variation of the work function W with size for small nanoparticles (NPs), $r_{NP} \leq 5$ nm, is a key quantity for modeling of three NP charging processes that become increasingly important at smaller size: electron field emission (EFE), thermionic electron emission (TIE), and electron impact detachment. Here we report theoretical values of the work function in this size range. Density functional theory (DFT) is used to calculate the work functions for a set of NP charge numbers, sizes and shapes, using copper for a case study. An analytical approximation is shown to give quite accurate work functions provided that $r_{NP} > 0.4$ nm, i.e., consisting of about > 20 atoms, and provided also that the NPs have relaxed to close to spherical shape. For smaller sizes W deviates from the approximation, and also depends on the charge number. Some consequences of these results for nanoparticle charging are outlined. In particular, a decrease in W for NP radius below about 1 nm has fundamental consequences for their charge in a plasma environment, and thereby on the important processes of NP nucleation, early growth, and agglomeration.

1. Introduction

Nanoparticles (NPs) in the size range r_{NP} below 5 nm are required for several important applications, for example where photonic properties are wanted or there are size constraints for other reasons, *e.g.* biosensors that need to be able to pass through human kidneys [1-3],

and catalysts with increased efficiency [4-6]. One attractive NP production technique is plasma processing which has many advantages [7-9] such as suppression of unwanted agglomeration by Coulomb repulsion and the possibility of fast growth through ion collection. Nanoparticles that are synthesized in a plasma are subject to charging processes. An understanding of the charging processes and the equilibrium

Fig. 1. Two cases of the potential seen by an electron as function of distance from negatively charged metal objects, a bulk metal in panel (a) and a nanoparticle in panel (b). Notice that the work functions W_{bulk} and W here are defined as the step in energy at the metal surface with the height it *would have* if mirror charge attraction did not round off the potential barriers, and lower them, as indicated by dashed lines.

floating potential that a NP can obtain is crucial for an understanding of nucleation and early-growth processes of nanoparticles in plasmas, to determine their final size and properties, and also for their transport to, and collection on, substrates. For nanoparticle sizes above $r_{\text{NP}} \approx 10$ nm the floating potential can be obtained from classical probe theory, with the condition of zero net ion and electron particle currents from the plasma. However three additional NP charging processes can become increasingly important at small size: thermionic electron emission (TIE) [10], electron field emission (EFE) [10], and electron impact detachment. These processes require knowledge of the height and shape of the potential barrier that the leaving electron has to cross.

Figure 1 illustrates three changes in the barrier, for a given electric field strength at the surface, when going from bulk metal to nanoparticles: the mirror charge attraction is reduced leading to a higher barrier amplitude, the width of the barrier increases due to the fact that the electric field strength decreases with distance from the NP, and the work function decreases with decreasing radius. The variation of the work function W with the radius r_{NP} and charge number N is the subject of the present work.

Fig. 2. The various energy measures used in this work, illustrated in a graph of the potential of a removed electron as function of distance r from the center of a negatively charged nanoparticle. The Coulomb potential $E_{\text{coul}}(r) = \frac{e^2}{4\pi\epsilon_0 r}$ is the potential between two point charges NP^{-} and e , and $E_{\text{F,bulk}}$ is the Fermi level of Cu bulk material. The rest of the variables are defined in the text. The numerical values in this example are $W_{\text{bulk}} = 4.6$ eV, $E_{\text{coul}}(r_{\text{NP}}) = 1.44$ eV, $\delta = 0.72$ eV, $E_{\text{remove}} = 3$ eV, and $W = 3.9$ eV.

We will here avoid the commonly used term affinity E_{EA} because there is some confusion in the literature regarding its definition for multiply charged nanoparticles. The electron affinity for a non-charged particle (atom, molecule, or cluster) is straightforward and defined by the energy difference before and after addition of an electron, *i.e.*, when an electron is added to form a singly charged negative ion. When the particle is charged, it must be specified if this

electron is moved from the vacuum just outside the particle or from infinity, *i.e.*, if the Coulomb energy shall be included or not. Here *e. g.* Gallagher [11] defines the affinity of nanoparticles as only the step at the surface ($E_{EA} = W$ in Fig. 2), while Martinez *et al.* [12] includes the Coulomb energy ($E_{EA} = E_{remove}$ in Fig. 2). A third use of the term affinity for nanoparticles is found in Picard and Girshick [13] who use the bulk material step at the surface, without subtracting the shift δ that appears for small nanoparticle sizes ($E_{EA} = W_{bulk}$ in Fig. 2).

The paper is organized as follows. In section 2 density functional theory (DFT) calculations are used to calculate the work function for a set of charge numbers, sizes, and NP shapes, using copper for a case study. These values are then used to verify an analytical approximation $W(W_{bulk}, r_{NP}, N)$, derived from a jellium model [14-17] of the NPs, which is shown to be quite accurate for all sizes $r_{NP} > 0.4$ nm, *i.e.*, consisting of about > 20 atoms, provided that the NPs have relaxed to close to spherical shape. Section 3 contains a brief discussion of the consequences of these results for the charging of small nanoparticles.

2. Theoretical calculations

We will discuss reactions of the type

$$NP^N \leftrightarrow NP^{(N-1)} + e. \quad (1)$$

We first need to define variables.

- The charge number N is the number of electrons on the nanoparticle to the left in Eq. (1), *i.e.*, including what we will call the “removed electron”. Positive charges are included by letting negative N account for missing electrons. This notation is used to match that of Perdew [14].
- The work function W is the step in the *unperturbed* potential (without the mirror charge effect) from the weakest bound state in the nanoparticle to the vacuum just outside its surface.

- The removal energy E_{remove} is the energy needed to take the removed electron from inside the nanoparticle and all the way to infinity.

The third definition is needed because we need a quantity that is generalized to include any charge number: negative, zero, or positive. For the special cases of $N=0$ and $N=1$, E_{remove} can be identified with the usual definitions (for zero charged atoms, molecules and clusters) of the ionization potential and of the electron affinity, respectively. Figure 2 exemplifies these definitions in a graph of the potential at a distance r from the center of a spherical Cu nanoparticle, with a radius $r_{NP}=1$ nm, and which is charged to $-e$, (*i.e.*, has our charge number $N=2$). The work function W is decreased from the work function of bulk material by an amount to be determined $\delta = W_{bulk} - W$. From Fig. 2 we can resolve W as

$$W = E_{remove} + E_{coul}(r_{NP}) = E_{remove} + \frac{(N-1)e^2}{4\pi\epsilon_0 r_{NP}}, \quad (2)$$

where the second term is the Coulomb potential at $r = r_{NP}$. From Eq. (2) follows that the task of determining W and δ is reduced to the task of determining E_{remove} .

2.1. E_{remove} estimated for metallic particles

Perdew among others [14-17] has calculated several properties for spherical metallic particles using the jellium model, in which the ion cores are treated as uniform background. The removal energy can then be described as

$$E_{remove}(N, r_{NP}) = W_{bulk} - \frac{e^2}{8\pi\epsilon_0} \frac{(2N-1)}{r_{NP}}. \quad (3)$$

(The radial centroid of excess charge on a metallic sphere of radius r_{NP} is given by Perdew as $(r_{NP}+a)$. It is here approximated by r_{NP} .) Perdew however limits the applicability of Eq (3) to $N \geq 2$, *i.e.*, NPs that are negatively charged also after removing one electron. In this case he identifies the second term on the right-hand side with the inter-electron repulsion energy.

In order to extend this result to any charge number including opposite charges (where the “inter-electron repulsion” E_{rep} is negative, *i.e.*, becomes an attraction), we assume the

nanoparticles to behave according to the jellium model presented by Perdew [14], *i.e.*, to have a spherical shape, and be ideal conductors with zero electric field inside and the field strength $E_r = Q/(4\pi\epsilon_0 r^2)$ outside. The electrostatic energy for charge $Q = -N|e|$ can then be calculated from the field energy,

$$E_{field}(N, r_{NP}) = \frac{1}{2} \int_{r_{NP}}^{\infty} E_r D_r 4\pi r^2 dr = \frac{1}{2} \int_{r_{NP}}^{\infty} \frac{(-N|e|)^2}{4\pi\epsilon_0 r^2} dr = \frac{N^2 e^2}{8\pi\epsilon_0 r_{NP}}. \quad (4)$$

The change in electrostatic energy when an electron is removed can be calculated as the energy of the final state minus that of the initial state:

$$\Delta E_{field}(N, r_{NP}) = E_{field}((N-1), r_{NP}) - E_{field}(N, r_{NP}) = -\frac{e^2}{8\pi\epsilon_0} \frac{(2N-1)}{r_{NP}}. \quad (5)$$

This is identical to the second term on the right in Eq. (3), including the sign. Since this derivation is general for all charge numbers N , positive and negative, it extends the applicability of Eq. (3) beyond the limitation $N \geq 2$ that was given by Perdew.

Combining Eq. (2) and Eq (3) we obtain the desired approximation for the work function,

$$W \approx W_{bulk} - \frac{e^2}{8\pi\epsilon_0 r_{NP}}, \quad (6)$$

where the second term to the right quantifies the decrease of the energy barrier that was denoted by δ in Fig 2. In physical terms, W_{bulk} can now be interpreted as the “internal” binding energy the electron would have in an infinitely large lattice (which gives zero external field), while the second term is the “external” electrostatic field energy around a charged perfectly conducting particle of finite size. As far as this description holds δ should therefore be independent of the material of the nanoparticle. In units of eV, and with r_{NP} in nm, we have an approximate value of the shift

$$\delta \approx \frac{e^2}{8\pi\epsilon_0 r_{NP}} = \frac{0.72}{r_{NP}}. \quad (7)$$

Notice that this expression of δ is independent of the charge number N . As both experimental data [18] and our DFT calculations show, a dependence on N appears below about $r_{NP} = 0.5$ nm (see Fig. 3). In this range the error in the approximate work function of Eq. (6) increases with reduced NP size.

2.2. E_{remove} calculated by density functional theory

The DFT calculations were performed by modeling small Cu nanoparticles [19] in the range of 1 to 38 atoms with different charges ranging from +1 to -2 (to avoid mixed nomenclature we use the term nanoparticles for all sizes, even down to single atoms). These were geometry optimized using the Berny algorithm [20] to find the local energy-minima structures (see figures in Appendix), thus obtaining the relaxed energy. Then one electron was removed and a single point calculation was performed. The energy for this new structure was extracted and a new geometry optimization carried out to calculate the relaxation energy for this new structure. As can be seen in Fig. 3 the energy change due to relaxation can safely be neglected in this context, i.e., compare the energies for single point calculations (cross) and relaxed structures (dots). All calculations were done with the B3LYP functional [21, 22] and the 6-311G++(3df,3pd) basis set [23] using the quantum chemical software Gaussian09. [24] Some additional calculations were performed using the M062X functional [25] and the extensive aug-cc-pVQZ basis set [26, 27] to investigate the functional dependency. The results are presented in the Appendix and show good agreement with those of the B3LYP functional.

Fig. 3. Test of accuracy of the approximate Eq. (3) for E_{remove} , for the case of Cu nanoparticles. The curves for charge numbers 0, 1 and 2 are compared to DFT calculations for the “closest to spherical” relaxed and unrelaxed nanoparticles with up to 38 Cu atoms. The curves represent the analytical expressions (for $N = 0, 1$ and 2) of the jellium model in Eq. (3), while the filled circles and the crosses represent the results from the DFT calculations.

Figure 3 shows the result of the DFT theory calculations of E_{remove} (not to be confused with the work function) for Cu nanoparticles up to Cu_{38} where the nanoparticles closest to spherical shape were used. It is assumed that the electron leaves the nanoparticle at such a speed that the geometry of the nanoparticle is not changed, *i.e.*, the Born-Oppenheimer approximation is used. Nanoparticles composed of a few atoms are not truly spherical but as a guidance a typical radius based on the density of copper metal is used. The nanoparticle radius as a function of the number of Cu atoms N_{Cu} is approximately given by:

$$r_{NP} = \left(\frac{3}{4\pi} \frac{M_{Cu}}{\rho_{Cu} N_A} \right)^{1/3} N_{Cu}^{1/3} = r_{Cu} N_{Cu}^{1/3} = 0.1411 N_{Cu}^{1/3}, \quad (8)$$

where the radius r_{NP} of the nanoparticle is given in nm, M_{Cu} is the molar mass for copper, ρ_{Cu} is the density for copper and N_A is the Avogadro constant. This gives a radius of 0.141 nm for

a “cluster” consisting of one atom which could be compared to the real atomic radius of 0.128 nm for copper. A separate scale in Fig. 3 shows the approximate relation between r_{NP} and the number of Cu atoms N_{Cu} in the nanoparticles.

The solid, short dashed and dot-dashed lines in Fig. 3 shows E_{remove} from Eq. (3). The dashed and dot-dot-dashed line shows the ionization and electron affinity curves obtained using the analytical curves and empirical parameters by Svanqvist and Hansen [18]. They analyzed previously published experimental data of ionization energies and electron affinities for metal clusters of 14 different metals, and derived analytical empirical scaling formulas, valid for their data set, for the parameters of the expansion of the energies in the reciprocal radius. We observe a good agreement with our results. For the bulk material work function we here adopt an average value of 4.6 eV but note that this is uncertain by about 0.3 eV and depends on the crystallographic orientation [1]. Let us first look at the case $N = 1$, *i.e.*, the reaction $NP^- \leftrightarrow NP + e$. In this case the Coulomb energy (see Fig. 1) is $E_{coul} = 0$, and we can directly identify E_{remove} with the work function W (and with the electron affinity E_{EA}). The shift down from W_{bulk} (which is drawn as a horizontal dashed line) is thus equal to δ . The DFT calculations agree with the jellium model both concerning the average and the trend with r_{NP} , but are scattered by typically 1 eV around the curve. We interpret this scatter as due to the unavoidable deviations from spherical shapes that are shown in the Appendix and the quantization of the motion of electrons.

For charge number $N = 2$ there is below $r_{NP} = 0.4$ nm a systematic discrepancy between DFT and Eq. (3) with up to 5 eV: the electron is in this size range stronger bound (has a higher work function) according to the DFT calculations than the jellium model predicts. This might be expected since the small particles are very non-spherical with high non-symmetrical electric fields. The trend of the residuals, however, indicates that this discrepancy disappears with increasing size and that Eq (3) agrees with the DFT values within about 1 eV for sizes $r_{NP} > 0.5$ nm.

3. Summary and Discussion

Two comments on our nomenclature are necessary for negatively charged nanoparticles, such that naturally arise in a plasma. (1) The term of electron affinity was avoided and we defined instead a general electron removal energy E_{remove} , which can be identified with the usual electron affinity for charge number $N=1$ and the usual ionization energy for $N=0$. (2) The common definition of the work function W of a metal is the “step in potential energy of an electron when it is taken from inside the metal to the vacuum just outside it”. For a particle that is negative also after this electron is removed (*i.e.*, $N \geq 2$) the meaning of the term “just outside” becomes unclear since mirror charge formation distorts the shape of the barrier. Therefore, we define the work function W instead as the step in an *unperturbed* electric potential at the surface, *i.e.* without the mirror charge formation process. The value of W can thereby be obtained from measured or calculated E_{remove} by adding the Coulomb potential at the nanoparticle radius, see Fig. 2 and Eq. (2).

We make a case study of copper nanoparticles that are close to spherical in shape. An approximate jellium-model expression for the cost of electron removal, Eq. (3), is benchmarked against calculations using density functional theory (DFT) for nanoparticles with up to 16 atoms, and of various shapes and charge numbers. For nanoparticles of size $r_{NP} \geq 0.5$ nm or about 20 copper atoms, it is found that Eq. (3) gives an estimate of E_{remove} (and therefore also of the work function W) that lies within the natural scatter of ~ 1 eV due to deviations of these from spherical shape and the quantization of the motion of electrons. The work function W is reduced below W_{bulk} by an amount of δ which decreases with increasing size. This correction is not meaningful to make if δ is smaller than, say, 1/3 of the natural variation of W_{bulk} which depends on the metal crystallographic orientation planes of the surface. This variation is about 0.3 eV for copper [1]. If we therefore require $\delta < 0.1$ eV, and estimate δ from the jellium model, we find that the bulk work function is a sufficient approximation for radii $r_{NP} > 7$ nm.

In summary, we have three ranges regarding the work function

- $r_{NP} \geq 7$ nm, where $W \approx W_{bulk}$ within about 0.1 eV, and independent of both radius and charge number.
- $0.5 < r_{NP} < 7$ nm, where W is a function of radius but independent of charge number (in contrast to E_{remove} which depends on both the charge and radius), and Eq. (6) gives an approximation that lies within the unavoidable scatter (≈ 1 eV for the smallest sizes) due to deviations from spherical shape.
- $r_{NP} \leq 0.5$ nm, where the deviations from Eq. (6) are significant, up to 5 eV. In this size range the work function depends both on the radius and the charge number, and the most reliable values are probably the experimentally-based empirical expressions by Svanqvist and Hansen [18].

Let us now briefly discuss the implications of the results above for modelling nanoparticle charging in a plasma which is the subject of a separate study [7]. For large enough nanoparticle size, about $r_{NP} = 20$ nm, charging models from probe theory are sufficiently accurate for most purposes. In these the condition of zero net particle current (electrons and ions) from the plasma to the nanoparticle gives the floating potential ϕ_{NP} . Except at high pressure the ion current is given by orbital motion limited (OML) theory with the addition of collision-enhanced collection (CEC) of ions [7]. With decreasing size below 20 nm a sequence of complications set in. At about $r_{NP} \approx 10$ nm the number of electrons in a nanoparticle in a typical laboratory plasma is of the order of 10, and a statistical treatment with discrete charges of units e is needed. This complicates the models but is in principle straightforward to handle by replacing the electron and ion currents by probabilities, and following the charging process in time.

Below some critical radius $r_{NP.crit}$ electron field emission (EFE) become important for the charging. The reason is that, for a given value of ϕ_{NP} , the electric field at the surface of the nanoparticle is proportional to $1/r_{NP}$. A complication in assessing $r_{NP.crit}$ is that theoretical

calculations of EFE electron current I_{EFE} is increasingly uncertain below about $r_{NP} \approx 20$ nm. In a companion paper [7] however we show that, for a given ϕ_{NP} , the absolute value of $r_{NP.crit}$ is quite robust against these uncertainties. The physical reason for this robustness is an extremely steep variation in the EFE current with the electric field, *i.e.*, with the nanoparticle radius. It is also shown in [7] that the value of $r_{NP.crit}$ decreases slowly with increasing plasma density, is approximately proportional to T_e , and depends on the material of the nanoparticle. For a numerical example copper nanoparticles in a laboratory plasma with $n_e = 6 \times 10^{18} \text{ m}^{-3}$ and $T_e = 1$ eV have a critical radius $r_{NP.crit} \approx 1.4$ nm.

A case of particular interest regarding charging of clusters is below a radius of about 3 nm. Clusters at this size will generally not be doubly charged since the field emission rate for $N=2$ is much larger than the electron collection rate for $N=1$. For singly charged clusters however, the field emission current is zero for the simple reason that the electron in question cannot exert a force on itself. For these singly charged nanoparticles the decrease of W for radius below 1 nm probably has fundamental consequences for their charge. When $W \approx W_{bulk} \approx 4.6$ eV, as for larger nanoparticles, thermionic electron emission is safely negligible compared to other cluster-charging currents for typical plasma parameters. The lowering of the electron affinity shown in Fig. 3 (the $N=1$ curve) may enhance thermionic electron emission substantially. The result should be an appearance of a second critical radius, which depends on the temperature of the cluster, below which clusters are effectively neutralized by thermionic electron emission. Furthermore, in a plasma environment, neutralization by electron impact detachment, $NP^- + e \rightarrow NP + 2e$, also becomes a faster process with lower work function. Although electron impact detachment and secondary electron emission are not important processes in usual discharge plasmas they come into play in plasmas with a higher electron temperature, and can have a strong influence on dust charging both in fusion plasma devices [28] and in space plasmas [29].

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Appendix

Fig. 4. Visualization of the geometry optimized copper clusters with neutral charge.

Fig. 5. E_{remove} computed using two different DFT functionals for Cu clusters with 1 to 7 atoms. Circles represent the results of the M062X functional with the aug-cc-pVQZ basis set, and the crosses represent the results of the B3LYP functional with the 6-311G++(3df,3pd) basis set. Green, red and blue symbols correspond to charge number $N=0, 1$ and 2 respectively.

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