Supplementary Information

Fundamental Growth Principles of Colloidal Metal Nanoparticles

Jörg Polte*a

^a Humboldt-Universität zu Berlin, Department of Chemistry, Brook-Taylor-Strasse 2, 12489 Berlin, Germany

S1 Short Introduction to the concepts of colloidal stability

One of the most important aspects in colloid science is the mechanism of (metal) nanoparticle stabilization in the dispersing medium. In general, particles at the nanoscale are unstable and tend to agglomerate because at short interparticle distances they are attracted to each other by van der Waals, electrostatic or magnetic forces. Without any counteractive repulsive forces nanoparticles aggregate, agglomerate or undergo coalescent processes. In the theory of colloidal chemistry such repulsive forces can be achieved by electrostatic or steric stabilization.⁴⁷

Electrostatic stabilized nanoparticles possess at least one electrical double layer due to a surface charging. The resulting Coulomb repulsion forces between the particles decays exponentially with particle to particle distance. If the electrostatic repulsion is sufficiently high, it prevents the particles from any kind of coagulation. This is well known for the classical gold nanoparticle synthesis by reduction of tetrachloroauric acid with sodium citrate where the gold nanoparticles are surrounded by an electrical double layer formed by adsorbed citrate and chloride ions as well as the cations which are attracted to them.⁴

In the following section, important particle interactions are discussed briefly.

S1.1 Van der Waals Interaction - Nanoparticle Attraction Force

The common way to describe intermolecular forces is to use the so called Lennard-Jones potential which is an expression for the interaction energy of the pair potential W(r) of two molecules at a distance r:

$$W(D) = -\frac{C}{r^6} + \frac{B}{r^{12}}$$
(5)

with the constants C and B for the attractive Van der Waals and repulsive Born repulsion, respectively.^{48,49} At first, the second term (Born repulsion) will be neglected.

The Van der Waals interaction energy $W_a(D)$ between two particles with radius R_1 and R_2 can be theoretically obtained by adding all the intermolecular forces between all constituent molecules of the particles,

$$W_{a}(D) = \int_{V_{1}} dV_{1} \int_{V_{2}} \rho_{1} \rho_{2} \left(-\frac{C}{r^{6}} \right) dV_{2}$$
⁽⁶⁾

which finally yields for two spherical particles:

$$W_{a}(D) = -\frac{\pi^{2} \rho_{1} \rho_{2}}{6} C \left[\frac{2R_{1}R_{2}}{c^{2} - (R_{1} + R_{2})^{2}} + \frac{2R_{1}R_{2}}{c^{2} - (R_{1} - R_{2})^{2}} + ln \left(\frac{c^{2} - (R_{1} + R_{2})^{2}}{c^{2} - (R_{1} - R_{2})^{2}} \right) \right]$$
(7)

with the electron density ρ , the center to center distance between the two particles c and the distance between the two particle surfaces $D (D = c - (R_1 + R_2))$.

For two identical particles with $R = R_1 = R_2$ and $D \ll R$ (particles in close proximity) the equation reduces to approx.:

$$W_a(D) = -\frac{\pi^2 \rho_1 \rho_2 CR}{12D} = -\frac{AR}{12D}$$
(8)

with the Hamaker constant A.

The findings from Eq. (7) and (8) show that the surface interaction potential (thus the surface forces) decays less with respect to distance D than the interaction potential between two molecules (1/D compared to $1/r^6$) and that the potential is proportional to the particle size ($W_a(D) \sim R$).

S1.2 Electrostatic Interaction - Nanoparticle Repulsion Force

The attractive Van der Waals interactions discussed beforehand can promote reversible agglomeration or even irreversible aggregation of suspended particles. The preparation of stable nanoparticles demands forces opposing the Van der Waals attraction. This can be provided by the particle surface charge resulting in a repulsive interparticle forces.

In solution, solvated ions surround the particles and shield their surface charge. This can be described using the Stern-Gouy-Chapman theory in which the surface potential decreases within two layers known as the electric double layer (EDL) - a compact inner and a diffuse outer layer. The ions in the inner layer (Stern layer) are strongly bound and in the outer layer (diffuse layer) less firmly associated. Within the diffuse layer a boundary exists, known as the slipping plane, in which the particle acts as a single entity. The potential at this boundary is called the Zeta Potential (ζ potential). This is illustrated in Figure 2a together with the corresponding cross-section and the decrease of the electric potential.

The thickness of this double layer is called Debye length λ (κ^{-1}) and can be quantified using simple electrostatics. Obviously, the distribution of the electric surface potential $\psi(x)$ is required for the description of the double layer. The Poisson equation states:

$$\varepsilon \varepsilon_0 \frac{d^2 \psi(x)}{dx^2} = -\rho(x) \tag{9}$$

with x as the distance from the particle surface, the electrical potential $\psi(x)$, the permittivity of vacuum ε (8.854 e^{-12} $CJ^{-1}m^{-1}$), dielectric constant of the solution ε_0 and the charge density ρ . The physical meaning of the Poisson equation is that the total electric flux through a closed surface around the particle is proportional to the total electric surface charge (Gauss's flux theorem which is

one of the four Maxwell equations in classical electrodynamics). The ion distribution in the diffuse layer is determined by the balance between the electrostatic attractive force and the Brownian force of thermal diffusion described by Boltzmann:

$$n_i(x) = n_{i\infty} exp\left(-\frac{ez_i \Psi(x)}{k_B T}\right)$$
(10)

with the concentration of ion i n_i , $n_{i\infty}$ as the concentration of ion i at $x = \infty$, the valency of ion i Z_i , the Boltzmann constant k_B and the temparature T. The variation of the co-ion and counter-ion concentration can be described using the Boltzmann distribution and is displayed in Figure 2b. With $\rho(x) = \sum_{i} n_i(x) z_i e$ as the sum of all charges at distance x, Eq. (9) can be rewritten as:

$$\varepsilon \varepsilon_0 \frac{d^2 \psi(x)}{dx^2} = -\left(\sum_i z_i e n_{i\infty} exp\left(-\frac{e z_i \Psi(x)}{k_B T}\right)\right). \tag{11}$$

Due to the small potential the exponential functions can be linearized ($\exp(\pm x) = 1 \pm x + ...$) known as the Debye-Hückel linearization (DHL) yielding:

$$\varepsilon \varepsilon_0 \frac{d^2 \psi(x)}{dx^2} = -\left(\sum_i z_i e n_{i\infty} - \sum_i \frac{z_i^2 e^2 n_{i\infty}^2 \Psi(x)}{k_B T} \right)$$
(12)

and because of the charge neutrality, the first term is zero which finally gives:

$$\varepsilon \varepsilon_0 \frac{d^2 \psi(x)}{dx^2} = \sum_i \frac{z_i^2 e^2 n_{i\infty}^2 \Psi(x)}{k_B T} = \kappa^2 \Psi(x)$$
⁽¹³⁾

with the Debye constant κ

$$\kappa = \left[\sum_{i} \frac{z_i^2 e^2 n_{i\infty}^2}{k_B T}\right]^2.$$
(14)

The Debye screening length λ_D which measures the diffuse layer thickness is defined as $\lambda_D = \kappa^{-1}$. The simple solution for the differential equation (Eq. (9)) is:

$$\psi(x) = \psi_0(x) exp^{[m]}(-\kappa x) \tag{15}$$

with the surface potential ψ_0 at x = 0. This equation describes the decrease of the electric surface potential in the EDL, but actually the interaction between at least two EDLs are of interest to describe colloidal stability. The forces due to the EDL are caused by the overlap of the electric potential distribution and the overlap of the ion concentration (osmotic pressure). Finally, for the EDL interparticle force between two spherical particles with radius R and surface to surface distance Dusing the Derjaguin approximation the following expression is found to be a good approach (constant surface potential and particle radii much larger than the thickness of the EDL are assumed)⁴⁸:

$$F(D) = -2\pi\varepsilon\varepsilon_{0}\kappa R\psi_{\delta}^{2}exp^{[m]}(-\kappa D)$$

$$W_{R} = \int_{D}^{\infty} F(D)dD$$
with the interparticle energy
$$W_{R}(D) = 2\pi\varepsilon\varepsilon_{0}R\psi_{\delta}^{2}exp(-\kappa D)$$
(16)
(16)
(17)



Figure 2 (a) Formed electric double layer (EDL) around a nanoparticle due to the Gouy-Chapman model which consists of the inner Stern layer and the outer diffuse layer (b) corresponding decrease of the counter- and co-ion concentration with respect to the distance from the particle surface; (c) schematic of the EDL, Van der Waals and total interaction potential (TIP) of two nanoparticles; (d) and (e) influence of the ion concentration and the particle size on the TIP.

S1.3 DLVO Theory

More than 70 years ago, two Russian (Derjaguin and Landau) and two Dutch (Verwey and Overbeek) scientists developed a theory of colloidal stability which is still seen as one of the groundbreaking characterization models in the physics and chemistry of colloids - the DLVO theory.⁵⁰ The basic assumption is that the total force between colloidal particles is the addition of the Van der Waals (attractive) and the EDL (repulsive) forces. In the DLVO theory the effect of Van der Waals and double layer forces are combined, so that the potential interaction energy between two particles or two surfaces in a liquid is assumed to be the sum of the Van der Waals and EDL interaction energy:

$$W_{total}(D) = W_a(D) + W_r(D) \tag{18}$$

which can be rewritten with Eq. (8) and (17) for two identical particles with radius R in close proximity to:

$$W_{total}(D) = W_a(D) + W_r(D) = -\frac{AR}{12D} + 2\pi\varepsilon\varepsilon_0 R\psi_\delta^2 \exp(-\kappa D)$$
⁽¹⁹⁾

Note that in particular the second term changes with different assumptions (constant surface potential or surface charge, thin EDL compared to the particle size and vice versa etc.)

A representative resulting total interaction potential (TIP) is displayed in Figure 2c. The TIP demonstrates some fundamental features that become important in the explanation of particle growth processes. The shape of the curve is the consequence of the exponential and steep decay of the repulsive and attractive term, respectively. The resulting maximum of the curve represents the aggregation barrier and determines the colloidal stability. The barrier creates effectively an activation energy for aggregation that two particles have to overcome when they collide.

In this picture several factors affect the stability of the system (i.e. the barrier): (i) the ion type and concentration, (ii) the value of the surface potential and (iii) the particle size. Although, Eq. (16) is

limited to two identical particles, it describes the properties of the whole system quite well since the expressions for spherical particles with different sizes show similar dependencies with respect to size, surface charge, and ion concentration of the solution. The Van der Waals attraction is relatively independent of the ion concentration, but the repulsive term strongly depends on it since the counter-ions are the dominant ions in the Stern and diffuse layer. The ion concentration is directly proportional to κ and thus to the exponential decrease of the surface potential. This means that the higher the ion concentration (in particular the counter-ion concentration) the smaller is the EDL. In Figure 2d it is shown how the ion concentration in principle affects the TIP.

Moreover, Eq. (19) (i.e. with the assumption of a constant surface potential and a thin EDL), reveals that in close proximity the particle size is proportional to both the attractive and repulsive terms. Consequently, the TIP is directly proportional to the radius which means that with increasing size the shape of the curve and the position of the maximum remains whereas the aggregation barrier increases. As a more general rule, one can state that in almost all cases the aggregation barrier increases with increasing size and therefore also the colloidal stability. This is illustrated in Figure 2e.

S1.4 Steric Stabilization

Steric stabilization is a process in which colloidal particles are prevented from aggregating by adsorption of large molecules at the particle surface, such as polymers or surfactants, providing a protective layer. The prevention of coagulation of these large molecules can be explained via simple mechanisms. The density of the adsorbed molecules in the interparticle space would increase tremendously, if the interparticle distance would become smaller and smaller. This would cause a decrease in entropy, thus an increase of the free energy which is energetically less favorable. Due to the increased density, osmotic repulsive forces would also increase. Furthermore, a highly soluble molecule counteracts agglomeration.⁵¹

Hence, the interaction potential described in the DLVO theory has to be extended by a further term describing the repulsive forces due to the steric stabilization W_{steric} :

$$W_{total}(D) = W_a(D) + W_r(D) + W_{steric}$$
⁽²⁰⁾

The repulsive interaction potential W_{steric} is not a long range interaction and does not significantly depend on the particle size since the stability is mainly determined by parameters such as polymer concentration, temperature, average chain length and the solubility of the polymer.^{48,52}

S2 Experiment with subsequent addition

A simple experiment which illustrates the concentration influence on the growth, is the separation of the NaBH₄ synthesis in several growth steps. The experiment consist of three different mixing conditions of the precursor and reducing agent solution whereby all three final colloidal solutions have the same final concentrations.

In all synthetic procedures the reaction mixtures were continuously stirred with a teflon bar exactly fitting the reaction glass at 350 rpm. For each experiment a 3 mM NaBH₄ solution was freshly prepared by dissolving 113.5 mg of NaBH₄ in 1 l of MilliQ water.

In the standard synthesis Au NP's were synthesized by the fast 1:1 mixing of 5 ml of a 0.5 mM HAuCl₄ solution with 5 ml of a 3 mM NaBH₄ solution using Eppendorf pipettes. This synthesis results in Au NP's with a mean radius of 1.66 nm and a polydispersity of 10% that are stable for several minutes without the addition of any stabilizing agent.

In the second experiment the synthesis is separated in two steps. In the first step, 5 ml of Au-NP's with a radius of 1.66 nm were synthesized as described above. In a second step, 2.5 ml of a 3 mM NaBH₄ solution were added to the stirred AuNP solution followed by the rapid addition of 2.5 ml of a 0.5 mM HAuCl₄ solution using Eppendorf pipettes. The resulting NP's have a mean radius of 1.750 nm and a polydispersity of 10 %.

In the third experiment the addition of $HAuCl_4$ is separated in 30 steps. 5ml of Au-NP's with a radius of 1.66 nm were synthesized as described above. 2.5 ml of a 3 mM NaBH₄ solution were added to the stirred Au-NP's solution, followed by the addition of 2.5 ml of a 0.5 mM HAuCl₄ in 30 aliquots of 83 µl every 5-10 s using an Eppendorf pipette. The resulting NP's have a mean radius of 1.92 nm and a polydispersity of 10 %.



The scattering curves of the respective final NP's are displayed in Fig. 1.



The first experiment is the standard synthesis by mixing 1:1 the two reactants to obtain a 5ml colloidal solution with a final gold concentration of 0.25mmol (e.g. mixing with Eppendorf pipettes 0.5mmol HAuCl₄ with 3mmol NaBH4 solution in less than a second). The particles grow by coalescence to a size of ap-prox. 1.5 nm and are colloidal stable for minutes (e.g. within further 60min they grow to a size of approx. 1.8 nm). The addition of an appropriate stabilizing agents such as PVP prevents the further growth to 1.8nm. The second mixing comprises the separation of the synthesis in two steps. At first 2.5ml of a colloidal gold solution with the standard synthesis (with 1:1 mixing) is prepared and subsequently at first 1,25ml of 3mmol NaBH₄ and then 1,25ml of a 0.5mmol HAuCl₄ solution is added. For the third order, the 1,25ml HAuCl₄ solution is added to the 2.5ml colloidal gold solution (also prepared with the standard procedure) in 30 steps with additions of around 40µl every 5-10s (note that every growth step comprises around 3-4s). As expected the final particles of the first mixing condition (standard 1:1 mixing) have a mean radius of 1.44 nm at a polydispersity of 10%. For the second mixing condition at which HAuCl4 is reduced in the presence of existing particles (with 1.44nm) the final mean radius increased to 1.64 nm. The experiment revealed that around 50% of the added HAuCl₄ grow on existing particles and the remaining gold salt creates new particles. Therefore the final particle concentration in the second procedure equates to 75% of

the concentration in the first procedure. The growth mechanism of the second procedure can be deduced from known mechanistic knowledge of the standard synthesis. The existing particles with a size of around 1.5 nm are colloidal stable. The addition of $HAuCl_4$ (to the colloidal solution with sufficiently BH_4^- ions) will lead to an almost immediate reduction. The gold atoms can either grow on existing particles or form small metal clusters (dimers etc.) which are not colloidal stable. The probability for the growth on existing particles will be much lower than the formation of small clusters which is caused by the higher aggregation barrier but mainly due to the relatively low concentration of the existing particles. With the same argumentation the formed small molecular like metal clusters will further grow due to coalescence with themselves whereby the corresponding aggregation probability will decrease with increasing size caused by the increasing aggregation barrier and decreasing concentration. Consequently, less particles are created and more of the added gold salt grow onto existing particles. Thus, the final mean radius of the third procedure (i.e. 30 additions of around 40µI) is 1.75 nm and around 90% of the added gold salt grow onto the existing particles.