Semnan University

Progress in Physics of Applied Materials

journal homepage: https://ppam.semnan.ac.ir/

Simulation of Nanoparticles Growth Synthesized from Laser Ablation in Liquid by Electrical Charging Mechanism with and without Inclusion of Ion Drift Motion

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ARTICLE INFO

Article history:
Received: 6 January 2022
Revised: 18 April 2022
Accepted: 1 June 2022

Keywords:
Electrical charging
Growth mechanism
Ion drift motion
Laser ablation in a liquid (LAL)
Orbital Motion Limited (OLM)

ABSTRACT

In this paper, investigation and simulation of nanoparticles grown by laser ablation in a liquid (LAL) are studied. Firstly, the probable growth mechanisms including "hydrodynamic condensation" and "electrical charging" are introduced. Then, using the Orbital Motion Limited (OML) theory, governing differential equations of growth by electrical charging mechanism (without surface evaporation) are obtained in the absence of plasma drift motion. By numerical solving of the equations in the hot and high-density plasmas (typical of laser ablation in liquids), the growth of nanoparticles is simulated and the upper limit of its size is obtained. The results show that the size of nanoparticles, by electrical charging mechanism, cannot be more than 10 nm. In the continuation, a drift motion is added to the plasma ions up to 8 km/s which is typical of an expanding plasma in liquid phase ablation. Simulation results show that such a drift motion will cause the nano-particles to miss their spherical shapes and get a pine-like shape. It is concluded that if the growth of nano-particles really obeys the electrical charging mechanism then the shape of the obtained nano-particles in the plasma phase of the LAL should not be spherical but must be pine-like and rather larger.

1. Introduction

There are various methods for the synthesis of nanoparticles, one of which is laser ablation technology [1]. In this method, a very short and strong laser pulse is incident on the target surface. This pulse causes local evaporation and produces nanoparticles of the target material (or its compounds) in the surrounding medium. Laser ablation can be accomplished in a vacuum or in gaseous media or even in a liquid (such as water) which is called Laser Ablation in Liquids (LAL) [2]. One of the characteristics of LAL compared to vacuum or gas ablation is that it produces finer and more uniform nanoparticles. Numerous new reports on the synthesis of nanomaterials (such as nickel nanoparticles, silicon, etc.) can be found with this method, which shows its importance [3,4]. The mechanism of LAL is such that when a strong laser pulse strikes the target, the process of local melting and evaporation occurs firstly. The material vapor, in interaction with the middle and end sections of the laser pulse, becomes a very hot and dense plasma (with a temperature of 4000-8000 K and a typical density of 10^{18} cm^{-3}). The heat transfer between the plasma and the surrounding fluid causes the contact layer to evaporate rapidly, forming an expanding cavitation bubble. As the plasma cools down, the bubble stops expanding and the pressure of the surrounding fluid causes it to collapse, and finally, the LAL process ends up in a fraction of a milli-second. Fig. 1 shows a schematic of the LAL process [5].

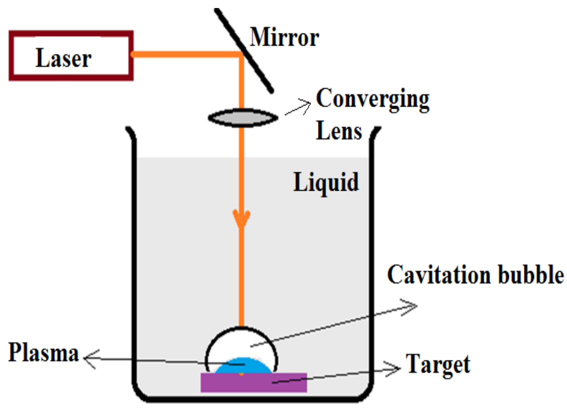

Fig. 1. Schematics of the laser ablation within a liquid.

One of the open problems in LAL is about the growth mechanism of nanoparticles, which has not yet been answered clearly and convincingly. A number of researchers believe that the process of nucleation and growth of nanoparticles occur in the plasma phase of LAL due to the electrical charging process [6, 7]. Other researchers believe that these processes occur inside the

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DOI: 10.22075/ppam.2022.25821.1019

expanding vapor and bubble due to the hydrodynamic condensation caused by the supersaturated state of the material vapor, and that the growth phase continues even in the contraction phase of the bubble [8, 9]. It is clear from these discussions that the nucleation and growth of nanoparticles in the LAL method is a complex event that requires careful investigation. It seems that all the stages of LAL (i.e., plasma phase, expanding bubble, and bubble collapse) are, indeed, involved in the growth process each with its own mechanism. For this reason, different probable growth mechanisms in each of these stages must be carefully studied to completely determine the impact and contribution of each step.

Based on the studies conducted in the references, it can be said that the mechanisms of "electrical charging" and "hydrodynamic condensation" play the main role of the nucleation and growth of nanoparticles in LAL. References [6, 7] indicate that the electrical charging plays a major role, but articles [8, 9] claim that hydrodynamic condensation is the main factor in nucleation and growth. Overall, the electrical charging mechanism seems to be the dominant one in the plasma phase but the hydrodynamic condensation is mainly responsible in the vapor phase. Although it is true that the hydrodynamic condensation has more evidence, but the model proposed in the electrical charging mechanism is also logical and correct. In this method, electron and ion currents that enter the initial nanoparticle embryo from the surrounding plasma determine its growth. When this model is combined with other physical events such as nanoparticle surface evaporation as well as plasma lifetime, it can predict the growth of nanoparticles well. Of course, the validation of this theoretical model requires further study, which will be addressed in part in this article. In other words, it is clear from the above discussion that the mechanism of nanoparticle growth in LAL is still an unsolved problem that needs to be investigated more carefully.

In this paper, the mechanism of growth by electrical charging mechanism based on the theory of "Orbital Motion Limited " is studied. The effect of plasma drift motion (especially its positive ions) on the particle growth and its final shape is also simulated through the OML mechanism. The structure of the paper is as follows: the OML theory is explained first. Then the numerical results are mentioned and discussed. Conclusions are drawn at the last section.

2. Theory of Electrical Charging Mechanism The basic equations

In this section, the growth of nano-particles from laser ablation in liquids is theoretically considered based on the electrical charging mechanism. Two situations are studied: 1) the growth without drift motion of the plasma ions, and 2) growth with inclusion of ion drift motion.

2.1. No drift motion

The simplest model that can be considered for the growth of nanoparticles in plasma phase is the "Orbital Motion Limited" or OML theory. In a plasma that contains negative electrons and positive ions, electrons mobility is much greater than that of ions (because of their very smaller mass). This property causes an object that is placed inside the plasma (such as the initial nucleus of a nanoparticle) to get a negative charge over time. The negatively charged particle will, in turn, attract the positive ions which leads to its growth. The overall result is that an electron current and also an ion current enter the particle and its growth is continued. If the plasma conditions are stationary (i.e., independent of time), then the charge and potential of the particle will eventually reach a steady state and the electron and ion currents will equalize and neutralize each other. Such mechanism can be used to model the growth of nanoparticles in the plasma phase of the LAL method. It is assumed that an initial embryo of a nanoparticle which is going to grow, is present in the plasma. The nucleus is subjected to the electron and ion currents. The electron flux causes the particle charge to be negative and the ion flux causes it to grow. With this simple mechanism, the particle size gradually increases and growth occurs. Following the theory of OML, it can easily be proved that in a neutral plasma with equal electron and ion temperatures (and with first order ionization), the electron and ion currents entering the particle obey the following equations [6]:

$$I_e = -\pi r^2 en\sqrt{\frac{8kT}{\pi m_e}}e^{\frac{e\Phi}{kT}}$$

$$I_i = \pi r^2 en\sqrt{\frac{8kT}{\pi m_i}}\left(1-\frac{e\Phi}{kT}\right) \tag{1}$$

where m_e and m_i are the mass of electrons and ions, k is the Boltzmann constant, e is the magnitude of the electron charge, r is the particle radius, and Φ is its electrical potential, n and T are, the density and temperature of the plasma respectively. Assuming the particle is spherical, its electric potential can be obtained by the following equation [6]:

$$\Phi = \frac{Q}{4\pi\varepsilon_0 r} \tag{2}$$

Q in the above equation is the total charge (due to electrons and ions) which is being accumulated on the growing nanoparticle. Eq. (2) is of good accuracy when the particle size is much smaller than the Debye length [6]. Using the above equations, the equation governing the temporal evolution of the particle radius can be obtained. The temporal derivative of the particle charge is indeed the net current:

$$I_e + I_i = \frac{dQ}{dt} = 4\pi\varepsilon_0\left(\Phi\frac{dr}{dt} + r\frac{d\Phi}{dt}\right) \tag{3}$$

If the mass density of the target material is ρ and its molar mass is M, then the atomic radius will be as follows:

$$a = \left(\frac{3}{4\pi}\frac{M}{N_A\rho}\right)^{1/3} \tag{4}$$

Where N_A is the Avogadro number. Since the addition of each ion to the particle causes it to grow, then the rate of increase of the particle radius will read:

$$r^2 \frac{dr}{dt} = \frac{I_e a^3}{3e} \tag{5}$$

Equations (3) and (5) are, in fact, a set of first-order differential equations. By solving them, the radius of the particle (i.e., r) and its potential (i.e., Φ) can be obtained. Of course, this requires that the plasma temperature and density (i.e., n and T) to be known. In typical LAL experiments performed with nanosecond laser pulses, the plasma lifetime is about a few hundreds of nanoseconds. Assuming exponential damping, plasma density can be considered as [6]:

$$n = n_0 e^{-\frac{t}{\tau}} \tag{6}$$

where n_0 is the initial plasma density and τ is the plasma lifetime. With a good approximation, the plasma can be modeled to be isothermal with temperature $T = T_0$. Now, it is possible to study the growth of nanoparticles by solving coupled equations (3) and (5).

It should be noted that other factors that can affect the particle size (such as surface evaporation) are not included in the above model. The reason is that the main purpose of the present study is to find the highest growth rate (free from any growth-limiting factors) in order to find the maximum radius of the nanoparticles which is achievable by electrical charging mechanism.

2.2. With drift motion

In the previous section, the effect of drift motion of the expanding plasma was not considered in the formulation. It is known that, the expanding plasma during the initial stage of the ablation can have high supersonic speeds up to 24 km/s [2]. In this section, a simple model for inclusion of drift motion in the growth mechanism is developed.

The currents in Eq. (1) are correct only when the nanoparticle is moveless and the surrounding plasma has also no motion except for thermal internal motions. In other words, in Eq. (1) the environment has no velocity and a thermal equilibrium is present. To account for the drift motion of the plasma around the particle, the Maxwell velocity distribution in the presence of a uniform motion along the positive z-direction is considered:

$$p(\vec{v}) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{\frac{-mv_x^2}{2kT}} e^{\frac{-mv_y^2}{2kT}} e^{\frac{-m(v_z-v_0)^2}{2kT}} \tag{7}$$

Where v_0 is the drift velocity along the z-axis. Using the above distribution and averaging over the velocity, the differential ion current entering the nanoparticle from the differential solid angle of $d\Omega = Sin\theta d\theta d\varphi$ is obtained as follows:

$$dI_i = (2r^2)\, en \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{\frac{-m{v_0}^2}{2kT}} \left[\int_0^\infty \left(1 - \frac{2e\Phi(r)}{mv^2}\right) v^3 e^{\frac{-m(v^2-2vv_0\,Cos\,\theta)}{2\pi}} dv\right] Sin\,\theta\, d\theta d\varphi \tag{8}$$

With this anisotropic ion current, a model for particle growth and its final shape can be proposed. The simplest model that can be assumed is the linear growth rate which is dependent on the local polar angle. Such a model is seen in figure 2:

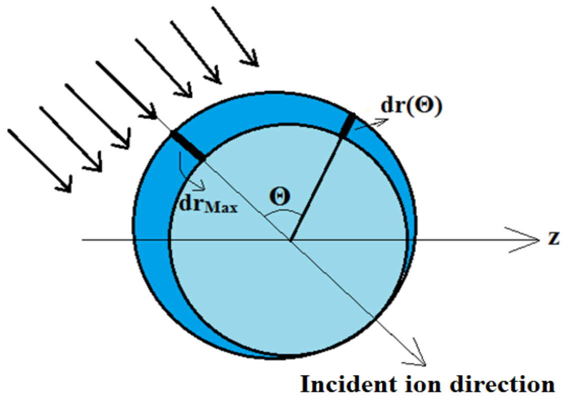

Fig. 2. Nanoparticle growth with linear dependence on local polar angle.

According to this model, during the incidence of ions from a spatial angle, the highest growth will be in front of the particle and the lowest growth (i.e., zero) will be in the opposite side. Assuming a linear dependence, increase of the radius in different parts of the particle can be modeled as follows:

$$dr(\Theta) = dr_{Max}\left(\frac{\pi - \Theta}{\pi}\right) \tag{9}$$

Where Θ means the angle between the direction of the differential ion current and the observation point as is seen in Fig. 2. Other terms in Eq. (9) are as follows:

$$dr_{Max} = \frac{dV}{2\pi r^2} \tag{10}$$

$$dV = \frac{dI_i dt}{e}\left(\frac{4}{3}\pi a^3\right) \tag{11}$$

where dV is the volume element. The electrical potential of the growing nanoparticle is again assumed to be found form Eq. (2) but with an averaged value of the nanoparticle radius (i.e., $\langle r \rangle$) in place of 'r':

$$\Phi = \frac{Q}{4\pi\varepsilon_0 \langle r \rangle} \tag{12}$$

With the above equations and solving them for the entire spatial angle and during the plasma lifetime, the growth of the nanoparticle and its shape evolution can be studied. Unfortunately, the solving procedure cannot be done analytically and one must recourse to numerical calculation. After discretizing the time and spatial angle, the following algorithm is applied to find the numerical solution: For each time step, the differential ion current is first obtained from Eq. (8). Then, the contribution of the dI_i to the radius growth of the nanoparticle is calculated from Eq. (9). At the end of the time step, the total ion and the electron charge deposited on the particle are calculated and the potential of the particle is updated through Eq.

(12). The process is repeated for all time steps to simulate particle growth dynamically and to find its final size and shape. In the following section, the simulation results are present for 'without' and 'with' drift motion.

3.Results and discussion

3.1. No drift motion

Numerical solutions of Eqs. (3) and (5) are used to simulate the growth of nanoparticles. To do this, a Mathematica code written by the authors is used. A nickel target with a mass density of 9.8 cm^{-3} is considered with the initial plasma density of $n_0=10^{18}$ cm^{-3} and a constant (i.e., isothermal) temperature of $T_0=6000$ *K*. The radius of the primary embryo is assumed to be r_0 = 0.8 *nm* with initial charge of $Q_0=0$ *C* and the plasma duration is considered to be $\tau=100$ *ns* [6]. Fig. 3 shows the temporal evolution of the nanoparticle radius as well as its electric charge. It is clear from Fig. 3-*a* that the particle radius starts increasing and finally reaches a saturation at about 3 *nm*, and then its growth stops. The electric charge of the nanoparticles (Fig. 3-*b*) decreases from 0 and eventually becomes saturated. If other embryos with different initial radii were used in the simulation, almost the same final saturated values would be obtained [6]. Calculations show that the model presented in Eqs. (1) to (5) has very little sensitivity to plasma temperature but is strongly dependent on plasma density. If the plasma density is twice that of used, then the nanoparticle radius will increase to 5 *nm*.

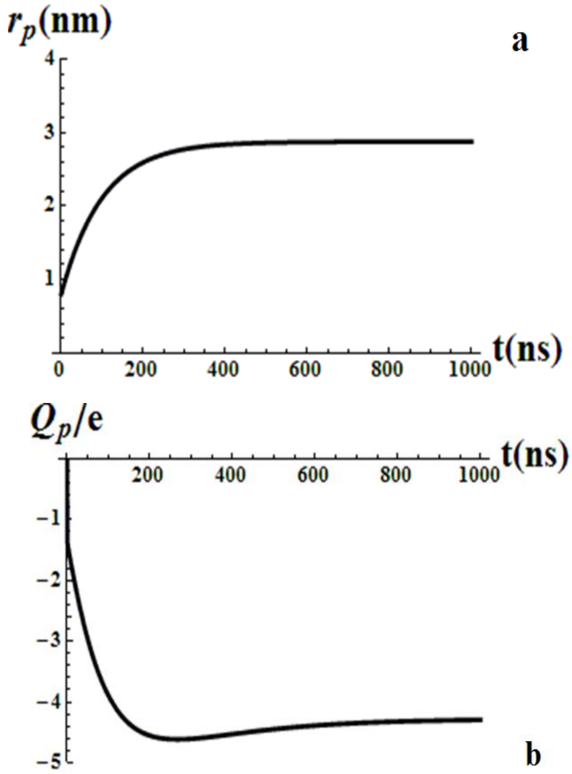

Fig. 3. a) temporal evolution of the nanoparticle radius r_p; b) temporal evolution of its electric charge Q_p.

As mentioned above, this model does not include evaporation and other probable factors that prevent the particle from growing. In other words, the size obtained for the nanoparticle by this assumption is, in fact, the maximum size that can be expected from the model of electric charging for LAL method. The above discussion shows that with the mechanism of electrical charging, the nanoparticle diameter cannot be larger than 10 *nm* in LAL plasma stage, and if the limiting factors such as evaporation is included, the particle diameter must be even smaller. Experimental reports in the literature on the synthesis of nickel nanoparticles by LAL, observed such small nanoparticles which can be regarded as a reason for the accuracy and ability of the electrical charging mechanism [3]. However, other experimental researches can be found in the references that report larger nanoparticles. Perhaps, a reason for this can be the continuation of the growth process in the bubble phase and its collapse. However, it should be noted that the maximum growth that a nanoparticle can get in the plasma-stage of LAL is less than 10 *nm*, and no further growth is possible in this phase.

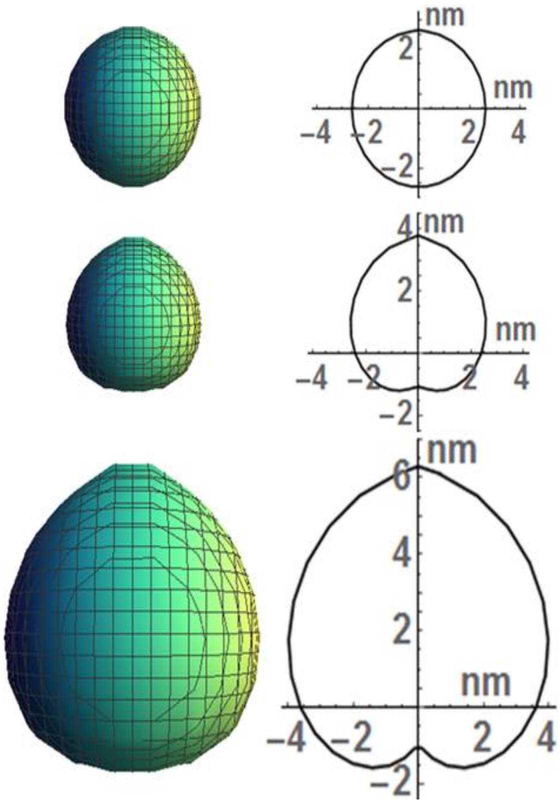

Fig. 4. Effect of drift velocity on the final shape and size of the nanoparticles. The top is for 0 speed, the middle is for 4000 m/s, and the bottom is for 8000 m/s.

3.2. With drift motion

The Mathematica code is generalized to simulate the nanoparticle growth in the presence of plasma drift motion. Again, the nickel target with the foregoing characteristics is considered. The final three-dimensional shape of the grown nanoparticle and a cross-sectional view of it for drift velocities of 0, 4000, 8000 m/s is shown in figure 4. It is clear from the figure that the plasma drift velocity has a considerable effect especially on the final shape and size of the nanoparticles. The final shape, as is seen, is pine-like. At higher velocities, the overall size of the nanoparticles is also larger. On the other hand, as reported in the references, the expansion velocity of the plasma in the LAL method can be as has high as 5000-24000 m/s [2]. Such a rapid expansion can bring about a large drift motion within the plasma. This means that the inclusion of drift motion in the plasma phase is necessary for correct calculation of final size and shape of the nanoparticles.

Dependence of the nanoparticle size on the drift velocity is also shown in figure 5. According to this plot, the nanoparticle size grows more with increasing the drift velocity (except for low velocities in which it has a descending behavior).

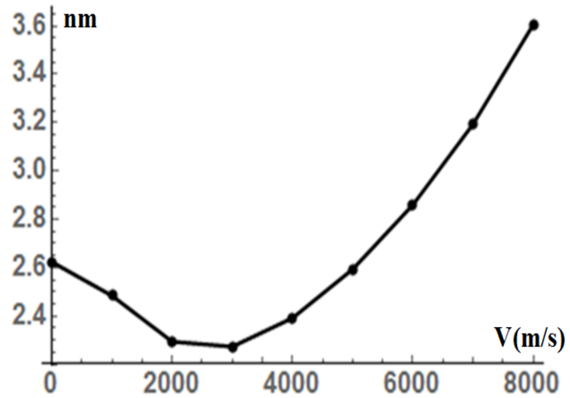

Fig. 5. Final size of the nanoparticles as a function of the plasma drift velocity.

The above simulation shows that the effect of ultrasonic velocity of the plasma-phase expansion is to convert the spherical shape of the nanoparticle into a pine-fruit-like shape. Of course, the prediction is only for the plasma-phase stage of the LAL. In other words, if one wants to confirm the obtained results, he needs to get nano-particles grown only in this phase. Unfortunately, there is no experimental reports in the literature regarding the growth dynamics only in the plasma-phase regime and the obtained nanoparticles have experienced possible growth mechanisms in plasma phase as well as bubble formation and its collapse phases.

4. Conclusions

In the first section of the paper, the growth process of nanoparticles in liquid-phase laser ablation (or LAL) was simulated by the mechanism of electrical charging without considering growth limiters (such as evaporation). It turned out that for a typical plasma generated in LAL, the final size of the nanoparticles would be smaller than 10 nanometers. Taking into account effects such as thermal emission and field emission of the electrons as well as surface evaporation of nanoparticles would lead to even smaller sizes. Of course, inclusion of such effects was not considered in this article. The important conclusion to be drawn is that if the growth process of nanoparticles in the LAL method is limited to the plasma phase only, then their size should not exceed 10 *nm*. It should be noted that, if other growth phases such as cavitation bubble and its collapse were taken into account, then even bigger nanoparticles would be obtained.

In the second section of the paper, the effect of plasma expansion velocity on the final shape and size of the nanoparticle in LAL obeying electrical charging mechanism was studied. It turned out that if this OML is correct, the final shape of the nanoparticles should be larger in pine-like shapes. Unfortunately, there is no experimental reports in the literature regarding the nanoparticle's growth dynamics only in the plasma phase and the reported nanoparticle growth mechanisms are for the overall duration of the LAL including all phases, i.e., plasma, cavitation bubble and collapse. The prediction of the paper is that if the OML theory is true then due to the fast drift motion of the expanding plasma, the nanoparticles must have pine-like shapes, otherwise, the electrical charging mechanism falls into somewhat doubt.

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