Nucleation of plasmonic resonance nanoparticles

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We predict the electromagnetic field driven nucleation of nanoparticles that provide plasmonic oscillations in resonance with the field frequency. The oscillations assume a phase that maximizes the particle polarization and energy gain due to nucleation. We derive closed-form expressions for the corresponding nucleation barrier and particle shape vs field frequency and strength, metal plasma frequency, conductivity, and the host dielectric permittivity. We show that the plasmonic polarization allows for nucleation of particles that would not be stable in zero field.

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I. INTRODUCTION

Accelerated nucleation in response to laser or dc electric fields has been observed in a number of systems.[1–4] The phenomenon is typically attributed to the lowering of the nucleation barrier by the field-induced polarization of the new phase particle. Similar observations have been reported for nanoparticles of various shapes.[5–8] Existing theoretical models[4,9–11] consider an essentially static field. However, for ac fields, especially near plasmonic resonances, frequency-dependent effects can strongly modify the nucleus polarization and exponentially change the nucleation rate.

This paper introduces the concept of plasmonic mediated nucleation. The underlying idea is that the nucleated particle provides a narrow resonance and phase of plasmonic oscillations that maximize its polarizability in the external electromagnetic field; that makes such particles energetically more favorable and lowers their nucleation barriers. As a result, an ac field will favor the nucleation of a particular geometry, such that the plasmonic frequency of the particle is in resonance with the field frequency. Furthermore, we will show that the plasmonic related energy gain can be significant enough to change the phase equilibrium, thereby triggering nucleation of particles that would not form in zero field.

II. ELECTRIC-FIELD EFFECT IN CLASSICAL NUCLEATION THEORY

Our consideration is based on the classical nucleation theory (CNT)[11–13] where the system free energy is approximated by the sum of the bulk and surface contributions of the new phase particle. Adding an electric-field-dependent term, F_E, the free energy takes the form

$$F = F_E + \mu V + \sigma A. \tag{1}$$

Here, μ is the difference in chemical potential (per volume) due to nucleation, and σ is the surface tension, V and A are the particle volume and area, respectively. The case of $\mu < 0$ corresponds to a metastable system in which nucleation is naturally expected without external field; $\mu > 0$ describes the case where metal particles are energetically unfavorable in zero field, yet, as shown below, they can appear in a sufficient electromagnetic field.

For a static field,[4,9–11] F_E represents the polarization energy gain similar to that of an induced dipole $\mathbf{p} = \alpha\mathbf{E}$ in an electric field $\mathbf{E}$. Given a particle of polarizability α in a dielectric material with permittivity ϵ, the polarization induced gain in a static field is represented as[11]

$$F_E = -\epsilon\alpha E^2. \tag{2}$$

Although not immediately obvious, the factor ϵ makes Eq. (2) different from the energy of a dipole in an external field. It reflects the contributions from all charges in the system, including those responsible for the field; this factor has been confirmed by several authors.[9–11]

To introduce useful notations, we briefly review the case of a spherical metallic nucleus of radius R in a static field where $\alpha = R^3$, $V = 4\pi R^3/3$, $A = 4\pi R^2$. Assuming $\mu < 0$, the nucleation barrier W and radius R are determined by the maximum of the energy in Eq. (1),

$$W = W_0(1+\xi/2)^{-2} \quad \text{when} \quad R = R_0(1+\xi/2)^{-1}. \tag{3}$$

The corresponding zero-field CNT quantities and the dimensionless field strength parameter ξ are

$$W_0 = \frac{16\pi}{3}\frac{\sigma^3}{\mu^2}, \quad R_0 = \frac{2\sigma}{|\mu|}, \quad \xi = \frac{\epsilon E^2 R_0^3}{W_0}. \tag{4}$$

Their ballpark values are $W_0 \sim 1$ eV, $R_0 \sim 1$ nm, and $\xi \ll 1$ for a moderate field of $E = 30$ kV/cm.

Since we are considering electromagnetic fields of frequency $\omega \gg \omega_{at}$, where $\omega_{at} \sim 10^{13}$ s^{-1} is the characteristic frequency of atomic vibrations, the induced polarization will be predominantly of electronic origin. The corresponding part of the electronic energy, proportional to $-\mathbf{p}\cdot\mathbf{E}$, will oscillate in time with frequency ω. According to the standard procedure of adiabatic (Born-Oppenheimer) approximation, its time average can be treated as a contribution to the potential energy of the atomic subsystem. Using the known recipe for time averages,[14] the latter contribution to the free energy of an atomic subsystem can be presented in the form

$$F_E = -\epsilon\frac{E}{2}\mathrm{Re}(\alpha), \tag{5}$$

where E is now understood as the field amplitude and $\mathrm{Re}(\alpha)$ represents the real part of the polarizability.

III. QUALITATIVE ANALYSIS

Prior to the rigorous derivation, we show next that all the major results of this work can be obtained qualitatively [Eqs. (6)–(9)]. We start with noting the high polarizability,

$$\alpha \sim (H/R)^2 V \gg V, \tag{6}$$

of needle-shaped particles, e.g., a prolate spheroid or a cylinder of height $2H$ and radius $R \ll H$ aligned to the field (Fig. 1). Indeed, the field-induced charges, $\pm q$, induced at the opposite poles are estimated from the balance of forces, $q^2/H^2 = qE$, which gives the dipole moment $p \sim Hq \sim EH^3 \sim V(H/R)^2 E \equiv \alpha E$.

The plasmonic resonance in a needle-shaped metal particle can be qualitatively explained by considering small parallel displacements $x \ll H$ of the free electrons along the cylinder axis. This will result in small charges $q \sim \pm\pi R^2 x N e$ on the two poles of the cylinder where N and e are the electron concentration and charge, respectively. The corresponding forces $-qe/H^2$ on individual electrons can be interpreted as the restoring forces $-m\omega^2 x$, which yields the resonant frequency

$$\omega_r \sim \omega_p (R/H) \ll \omega_p, \tag{7}$$

where m is the electron mass and we have used the standard definition of the plasma frequency, $\omega_p = \sqrt{4\pi N e^2/m}$. The plasmonic frequency ω_r has been experimentally observed in light scattering.[15]

When ω_r is in resonance with ω, the plasmonic oscillation energy is accumulated in the particle to the extent allowed by its quality factor (Q factor) $Q \sim \omega\tau \gg 1$ with τ being the electron relaxation time. Because that energy is proportional to the square of the internal electric field, one can say that the latter increases the polarizability effectively by the Q factor.

Combining the latter with Eqs. (6) and (7) gives the resonant ($\omega \approx \omega_r$) polarizability,

$$\alpha_r \sim V(\omega_p/\omega)^2 \omega\tau \gg V. \tag{8}$$

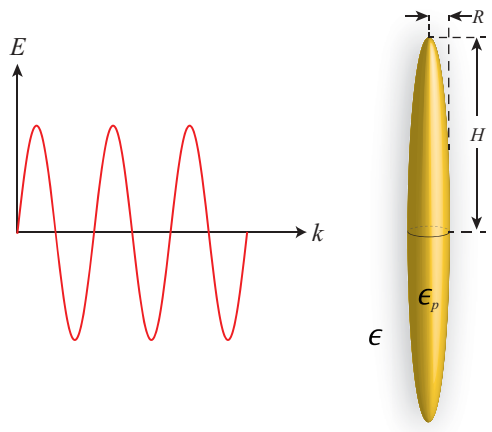

FIG. 1. (Color online) Illustration of a plasmonic resonance nanoparticle. A metallic prolate spheroid of semimajor axis H (aligned with the electric field E) and semiminor axis R is formed with its aspect ratio tuned to the frequency ω of the ac field such that $H/R \approx \omega_p/\omega$, where ω_p is the plasma frequency. ϵ and ϵ_p are the permittivity of the dielectric medium and particle, respectively.

This gigantic increase in polarizability takes us to the major prediction of this work: an ac field of frequency ω can drive the nucleation of needle-shaped particles with resonant aspect ratio $H/R \sim \omega_p/\omega \gg 1$.

We note that the first amplification factor $(\omega_p/\omega)^2 \sim (H/R)^2 \gg 1$ reflects the needle-shaped geometry of the particle and remains as such in a static field,[4] while the Q factor enhancement $\omega\tau \gg 1$ is specific to ac fields. Taking into account the amplification ratio in Eq. (8), an approximate result for the ac resonant nucleation barrier can be guessed from the known static result,[4] or even from Eq. (3), with $\xi \to (\omega_p/\omega)^2(\omega\tau)\xi \gg 1$, which yields

$$W \sim \left(\omega/\omega_p^3\tau^2\right)\left(W_0/E^2R_0^3\right)^2 W_0. \tag{9}$$

The complementary scenario would describe the resonance nucleation of a cavity in a metal host.[16]

IV. FORMAL CONSIDERATION

Our rigorous analysis begins with the polarizability of a spheroid:[17]

$$\alpha = \frac{V}{4\pi}\frac{\epsilon_p - \epsilon}{\epsilon + n(\epsilon_p - \epsilon)}. \tag{10}$$

Here, ϵ_p is the dielectric permittivity of a metal particle and ϵ is that of the medium, n is the depolarizing factor of a strongly anisotropic prolate spheroid,

$$n \approx (R/H)^2[\ln(2H/R) - 1] \equiv (R/H)^2\Lambda \ll 1. \tag{11}$$

Also, we use the dielectric permittivity of a metal,

$$\epsilon_p = 1 - \frac{\omega_p^2}{\omega^2} + i\frac{\omega_p^2}{\omega^3\tau}. \tag{12}$$

ϵ is assumed to be a real number, and $\tau^{-1} \ll \omega \ll \omega_p$.

Using Eqs. (10)–(12) with Eq. (5) yields

$$\mathrm{Re}(\alpha) = \frac{V}{4\pi}\frac{(n - n_\omega) + bn}{(n - n_\omega)^2 + bn^2}, \tag{13}$$

where $b = 1/(\omega\tau)^2$, and

$$n_\omega = \frac{\epsilon\omega^2}{\omega_p^2 + (\epsilon - 1)\omega^2} \approx \frac{\epsilon\omega^2}{\omega_p^2} \ll 1. \tag{14}$$

The polarizability $\mathrm{Re}(\alpha)$ has a sharp minimum when

$$n \approx n_\omega - \sqrt{b}n_\omega, \tag{15}$$

which reflects the presence of the plasmonic resonance. Since $n \sim (R/H)^2$ from Eq. (11), the expression for n_ω is fully consistent with the qualitative result in Eq. (7). The relationship between nanoparticle aspect ratio and the field frequency is illustrated in Fig. 2.

Given the sharpness of the resonance, all other n-dependent quantities, in particular the prolate spheroid volume and area,

$$V = 4\pi H^3 n/3\Lambda, \quad A = \pi^2 H^2\sqrt{n/\Lambda}. \tag{16}$$

can be evaluated at $n = n_\omega$. That yields

$$[\mathrm{Re}(\alpha)]_{\min} \approx -H^3/6\Lambda\sqrt{b}, \tag{17}$$

consistent with our earlier estimate in Eq. (8).

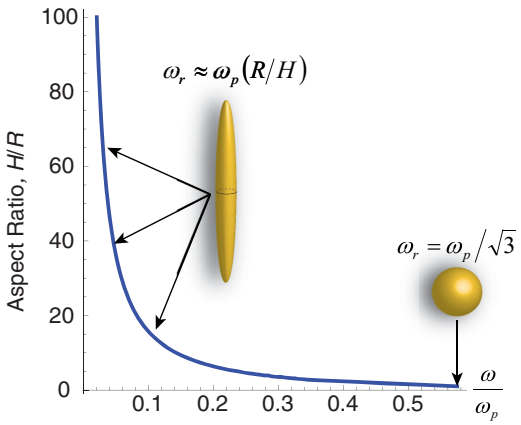

FIG. 2. (Color online) Aspect ratio of the metallic nucleus as a function of frequency. The resonance frequency for a sphere is $\omega_r = \omega_p/\sqrt{3}$, while for a prolate spheroid the resonance frequency depends on the aspect ratio, as shown.

Normalizing the free energy in Eq. (1) with respect to the classical barrier, it takes the form

$$\frac{F}{W_0} = \frac{H^3}{R_0^3}\left(\frac{\omega}{\omega_p}\right)^2 \frac{2\epsilon}{\Lambda}\left[-\frac{E^2\epsilon R_0^3}{24W_0}\left(\frac{\omega_p}{\omega}\right)^2(\omega\tau) \pm 1\right] + \frac{3\pi}{4}\sqrt{\frac{\epsilon}{\Lambda}}\frac{\omega}{\omega_p}\frac{H^2}{R_0^2}. \quad (18)$$

Here $\pm$ corresponds to the cases when the original phase is metastable $(-)$ and stable $(+)$, in the latter case, nucleation impossible is in zero field. The effect of the resonance on the free energy is illustrated in Fig. 3.

It follows from Eq. (18) that the plasmonic resonance can significantly accelerate nucleation in metastable systems. For the case of stable systems, the field can induce nucleation when

$$E > E_\omega \equiv E_c\sqrt{\frac{\omega}{\omega_p^2\tau}}, \quad E_c \equiv 2\sqrt{\frac{6W_0}{\epsilon R_0^3}}. \quad (19)$$

Below we concentrate on the case of field dominated nucleation, satisfying the condition of Eq. (19) and neglecting the second term in the square brackets of Eq. (18). In minimizing F with respect to H we keep

$$\Lambda \approx \ln(2\omega_p/\sqrt{\epsilon}\omega) - 1 \quad (20)$$

constant. The resulting nucleus semimajor axis and nucleation barrier are, respectively,

$$H = \frac{\pi}{4}\sqrt{\frac{\Lambda}{\epsilon}}\left(\frac{E_c}{E}\right)^2\frac{1}{\omega_p\tau}R_0, \quad (21)$$

$$W = \frac{\pi^3}{64}\sqrt{\frac{\Lambda}{\epsilon}}\frac{\omega}{\omega_p^3\tau^2}\left(\frac{E_c}{E}\right)^4 W_0. \quad (22)$$

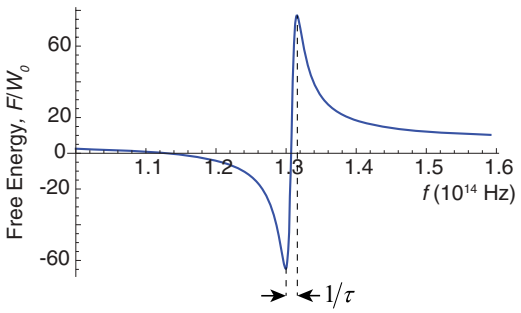

FIG. 3. (Color online) Normalized free energy of a prolate spheroidal metallic particle vs field frequency $f = \omega/2\pi$, with $E = 3 \times 10^5$ V/cm. The sharp resonance of width $1/\tau$ determines the aspect ratio $H/R \approx \omega_p/\omega \approx 10$. Parameters values are typical for nucleation in solids: $R_0 = 1$ nm and $W_0 = 1$ eV, with $\omega_p = 10^{16}$ rad/s, $\tau = 10^{-13}$ s, and $\epsilon = 1$.

V. PLASMONIC MEDIATED NUCLEATION IN THE PROXIMITY OF A PHASE TRANSITION

Our theory applies most easily to a system close to some bulk phase transition at temperature T_c, so that $\mu = \mu_0(1 - T/T_c)$. Correspondingly, the classical nucleation radius and barrier become

$$R_0 = R_{00}(1 - T/T_c)^{-1}, \quad W_0 = W_{00}(1 - T/T_c)^{-2}, \quad (23)$$

and $E_c = E_{c0}(1 - T/T_c)^{1/2}$, where R_{00}, W_{00}, and E_{c0} are obtained from their definitions in Eqs. (4) and (19) with $\mu = \mu_0$. This allows macroscopically large R_0, consistent with CNT; also, it corresponds to lower E_c, making the plasmonic nucleation easier to observe.

Using the above scaling, the results for particle nucleation length and barrier turn out to be temperature independent: they retain their form of Eqs. (21) and (22) with the trivial substitutions,

$$R_0 \to R_{00}, \quad W_0 \to W_{00}, \quad E_c \to E_{c0}.$$

This is in striking difference with CNT, which predicts a diverging nucleation radius R_0 and barrier W_0 towards the phase-transition temperature in Eq. (23). Note that the conclusion of temperature-independent nucleation radius and barrier remains valid for the case of static field induced nucleation as well.[18]

A practical significance of the latter observation is that it justifies the lack of attention (by CNT and related theories) to the role of the latent heat absorbed or liberated in the course of nucleation event. Simply stated, the finding of temperature-independent nucleation barrier means that cooling or heating due to the latent heat will not affect the nucleation rate.

VI. NUMERICAL ESTIMATES

Numerically, there is a broad window wherein the plasmonic resonance nucleation takes place. Indeed, the Q factor in Eq. (19) can be represented[19] as $\omega_p\tau = 160/(\sqrt{Na_B^3}\rho) \sim 10^3$, where a_B is the Bohr radius, $1/\sqrt{Na_B^3}$ is in the range 5–10, and the resistivity ρ (in units of $\mu\Omega$ cm) is smaller than unity. Also, it is reasonable to assume $\omega \lesssim 0.1\omega_p$. To estimate E_c in Eq. (19), consider $R_0 \sim 3$ nm and $W_0 \sim 2$ eV typical of, e.g., conductive (crystalline) nuclei in the prototype phase change material $Ge_2Sb_2Te_5$ (see Refs. 4 and 20, and references therein) and other metal nuclei.[11,21] For the case of $Ge_2Sb_2Te_5$), we use $\varepsilon = 16$, which yields $E_c = 4 \times 10^6$ V/cm. The other multipliers in Eq. (19) make E_ω much lower, say $E_\omega \sim 30$ kV/cm,

corresponding to laser power density $P \sim 10$ W/μm^2, an order of magnitude below that used with DVD burners. Assuming much lower dielectric permittivity $\varepsilon \sim 3$–5 for nucleation in a liquid or a glass will increase the latter P by a factor of $16/\varepsilon$ still keeping it rather low.

The above estimate of Q factor and P may become less optimistic if τ is reduced by surface scattering when the particle dimension is small.[22] In addition, quantum effects arise in the range of very small particle sizes ($\lesssim$1 nm) broadening and suppressing plasmonic resonances.[23] We note, however, that our considered mechanism falls beyond the quantum range since the resonance of importance is in the long axis direction corresponding to $H \gtrsim 10$ nm (see the caption to Fig. 3).

VII. DISCUSSION AND CONCLUSIONS

We now briefly discuss possible implications of our theory. A system near phase transition under a moderate intensity laser beam would be most suitable for experimental verification. The predicted high aspect ratio particles are optically accessible and can be identified via the unique features of prolate spheroids in light scattering and absorption.[15,22] Another unique feature is that the laser beams that create the nanoparticles can simultaneously play the role of optical tweezers. That can be exploited to observe and control the positions of nucleated metal particles that would be unstable in zero field.

A comment is in order regarding possible melting of a metal embryo created in the course of plasmonic mediated nucleation. The above consideration did not specify the state of a newly created nucleus except its metal-like conductivity. Therefore all the above predictions remain valid for the case when the power density is high enough to melt the metal particle. Furthermore, the analysis in Sec. V shows that the melting phase transition will not have any effect on plasmonic dominated nucleation barrier.

Another comment concerns the postnucleation stages of plasmonic triggered transformations. Assuming a continuing laser beam, the needle-shaped nuclei predicted by the above consideration will further evolve in parameter space along the trajectories maintaining their minimum energies and corresponding aspect ratio $R/H \sim \sqrt{\varepsilon}\omega/\omega_p \ll 1$. As a result, particles observed upon laser beam removal can be considerably larger than predicted by Eq. (21) yet exhibiting the characteristic needle-shaped geometry. Note that often used beams of diameters 10–100 μm $\gg H$ can generate multiple nucleation events per spot.

There have been several observations that are possibly consistent with the above-predicted mechanism; a few of note include the formation of metallic nanorods under laser beams, which did not nucleate in zero field,[5] many orders of magnitude acceleration of metal nanoparticle formation under laser irradiation,[6] laser induced nucleation of silver nanoparticles in glasses,[7] and a versatile, comprehensive study of laser induced nanowire nucleation.[8] In all those cases, different mechanisms may have been responsible for the observations (except, perhaps, for the case[5] that specifically identifies the frequency-dependent effect and the possible role of plasmonic excitations). Further experimental verification is required to attribute the observations to the phenomenon predicted here. Verifiable features include frequency-dependent nanoparticle nucleation and shape, rates exponentially accelerated with laser power with Arrhenius temperature dependence.

Given the abundant current literature on the topic, we can safely omit the discussion of important practical applications of nanoparticle plasmonic resonances. However, we emphasize that because of its resonant nature, the mechanism introduced in this work can be useful in controlling nanoparticle sizes, shapes, and distributions.

As a particular example of practical effects we note the possibility of phase change memory via electric-field-induced nucleation of metal particles in dielectric hosts. It was previously analyzed in the static approximation.[24] The above consideration shows that the corresponding barrier is lower than estimated in Ref. 24 by the factor $\sim 1/Q \ll 1$, which makes the nucleation rate exponentially higher.

In conclusion, we have predicted a phenomenon of plasmonic driven nucleation of metallic nanoparticles. There are many important practical implications. More work is called upon to describe the growth stage of such resonant particles and relate them to the observations.

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