Kinetics and mechanism of gold nanoparticle growth studied via optical extinction spectroscopy and computational modeling

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The successful design of nanoparticle synthesis protocols requires insight from mechanistic models, whose development relies on the availability of experimental data. For this purpose, optical extinction spectroscopy (OES) is rarely used in spite of being significantly less expensive and widely available when compared to frequently used synchrotron-based techniques. In this study, we developed protocols for the application of in situ OES to study the kinetics of gold nanoparticle (GNP) growth, serving as a model system. Spectra collected under six different experimental conditions were regressed using a physical model, built on extensive previous observations, calculating extinction by ensembles of GNPs. We considered the average size and shape of particles, and the possible electromagnetic interactions between them using a retarded effective medium theory. We identified the role of nucleation accompanying particle enlargement, the latter occurring via both molecular growth and aggregation. We further discovered instances of peptization consistent with previous experimental evidence.

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Since Faraday published his seminal work on the synthesis of colloidal gold nanoparticles (GNPs), there has been a tremendous effort to explore various nanoparticle synthesis routes in order to obtain better control over the properties of the final product.\textsuperscript{1,2} Every year numerous papers show up attempting to propose mechanisms for particular synthesis pathways. Most of these studies, however, miss the major point that it is extremely difficult, if possible at all, to interpret such a complicated process in terms of simplified models. This is true especially when dealing with a wide range of operating conditions. Here, mechanistic theoretical models, embracing various possibilities, come into the picture. By performing global uncertainty/sensitivity analysis one can map out various outcomes of the process vs. different possible combinations of the operating conditions.\textsuperscript{3}

The prerequisite to the foregoing powerful analysis is the development of a theoretical formalism with predictive capacity. For this purpose, extensive \textit{in situ} experimental data over a wide range of conditions has to be collected. In the case of nanoparticles, relatively expensive and laborious characterization techniques such as \textit{in situ} transmission electron microscopy (TEM),\textsuperscript{4,5} and synchrotron-based small- and wide-angle X-ray scattering (SAXS, WAXS) and X-ray absorption spectroscopy are typically employed.\textsuperscript{6-9} This is probably because of the simpler level of theory involved and/or the well-developed computational tools available for the analysis of the experimental data. Despite this popularity, both the electron beam and synchrotron light can drastically affect the system under investigation, e.g., accelerate the process of GNP formation and growth.\textsuperscript{4,5,9-12} For synchrotron-based methods, to circumvent this limitation one solution is the application of liquid jets so that a fresh sample is probed throughout the process.\textsuperscript{9,13,14} This method, however, adds to the complexity of the setup and does not allow for real-time measurements.\textsuperscript{14} On the other hand, optical extinction spectroscopy (OES) is rarely used to follow the formation of nanoparticles in spite of being noninvasive,\textsuperscript{10,12} significantly less expensive, and widely available. Indeed, to our knowledge very few articles have tried to quantitatively employ this characterization method and they are either dealing with relatively simple systems, where the particles behave as independent entities, or they simply neglect the interparticle interactions.\textsuperscript{15-17} For this reason, an immense need is felt to develop a general and easily adaptable theoretical framework in order to realize the practical application of \textit{in...}
situ OES in the study of nanomaterial formation. Thus, we developed such a protocol and applied that to study the kinetics and mechanism of gold nanoparticle growth. More specifically, citrate-mediated growth of colloidal gold served as a model system while the theoretical formalism can be applied to different scenarios such as other metallic and plasmonic nanoparticle systems.

**Results and discussions**

Several previous studies have addressed the mechanistic aspects during the (seeded) growth of GNPs using various characterization techniques such as atomic force microscopy (AFM),\textsuperscript{5,12,18} electrophoretic measurements,\textsuperscript{19,20} redox potential/pH measurements,\textsuperscript{18–20} dynamic light scattering (DLS),\textsuperscript{12,19,21} ex situ TEM,\textsuperscript{4,5,8,12,19–25} in situ TEM,\textsuperscript{4,5} and X-ray scattering.\textsuperscript{6,8,10,25,26} Many of these studies follow the process also using ex situ\textsuperscript{5,19–23} or in situ\textsuperscript{12,25,26} UV-vis spectroscopy but the information is treated merely qualitatively.

From the plethora of research, some of which was summarized above, we know that the processes of seeded growth is typically accompanied by nucleation of new particles.\textsuperscript{5,22,24,27} This could either be in a homogeneous fashion,\textsuperscript{22,27} or in the close vicinity of the already present seed surface\textsuperscript{5,24} (so called true catalytic secondary nucleation\textsuperscript{28} or, equivalently, near surface nucleation followed by particle mediated growth\textsuperscript{5}). Additional complication arises from the possibility of agglomeration/aggregation evoked in many studies to describe the transient enhanced extinction in the wavelength range 600-800 nm (namely, the temporary purple-greyish color of the suspension).\textsuperscript{18–20,22} Biggs et al.\textsuperscript{18} and Chow and Zukoski\textsuperscript{19} explained this in the light of the reduced colloidal stability in the presence of Au(III) in solution. Later, Rodriguez-Gonzalez and coworkers noticed that a homogeneous Au(III)→Au(I) reduction, followed by Au(I) diffusion toward the seed surface, and its subsequent disproportionation to Au(0) and Au(III) was more consistent with their experimental observations.\textsuperscript{20} Along the same lines, several workers have presented overwhelming evidence for the intermediacy of Au(I) in the reduction of Au(III) to metallic Au.\textsuperscript{5,21,29,30} Thus, it appears that Au(I) adsorption on the surface of GNPs tampers with their colloidal stability and as it is progressively reduced to Au(0), the surface is repopulated by the abundant citrate anions, and the colloidal stability recovers.\textsuperscript{19–21} Another notable
observation comes from recent experimental and theoretical findings by Cheng et al. who found that the local supersaturation in the region at the seed-solution interface exceeded that in the bulk of the reaction medium. Furthermore, as soon as secondary nuclei form in the vicinity of the seed surface, the gold ions tend to accumulate in the interparticle gap, replacing the citrate ions. This induces even further destabilization and brings the particles closer to each other, giving rise to large numbers of GNPs interacting inside mesoscale superclusters, several times large than the individual particles.

Beside the foregoing phenomena, a third and somewhat less addressed complexity concerns the electromagnetic interactions between the particles. As we discussed in the previous paragraph, enhanced particle number concentration and colloidal destabilization can bring particles closer to one another. This in turn provokes electromagnetic coupling between the neighboring particles. Plech et al., and also Förster et al. detected evidence for such “correlated assemblies” using SAXS, while Mikhlin et al. physically detected such liquid-like mesostructures using AFM, DLS, and TEM. In the literature, this effect has been frequently confused with agglomeration/aggregation wherein the particles are supposed to be in contact with each other (throughout this work we stick to the IUPAC definitions for agglomeration/coagulation and aggregation denoting the formation of physically and chemically bound multi-particle associates, respectively). In our theoretical framework, however, we explicitly distinguish between these effects in the sense that closely spaced particles are considered to be in electromagnetic interaction (and not agglomerated/aggregated) unless they touch each other (Supplementary Section 3).

With the introduction above in mind, it is clear that the optical extinction by colloidal metal nanoparticles may arise from two sources. The first is the extinction by well-separated nanoparticles whose interaction with the incoming light is practically independent from one another. On the other hand, the second contribution comes from nanoparticles lying close to each other (inside liquid-like superclusters, SCs), experiencing a superposition of the external field with the mean field produced by all the neighboring particles. Accounting for both possibilities in a suspension undergoing kinetic evolution requires the application of Gans formalism for the former and a
retarded effective medium theory (EMT)/Mie scattering framework\textsuperscript{37} for the latter (Methods and Supplementary Sections 2 and 3; hereafter, we simply refer to this combined Gans + EMT/Mie framework as the EMT model). Doing that, five physically well-defined parameters have to be estimated from regression to experimental spectra: $\bar{r}_{\text{GNP}}$ (average GNP radius), $\bar{\beta}$ (mean aspect ratio), $x_{\text{SC}}$ (number fraction of SCs out of all the scatterers, \textit{i.e.}, SCs + noninteracting GNPs), $f$ (filling factor, \textit{i.e.}, volume fraction of GNPs inside SCs), and $\bar{r}_{\text{SC}}$ (average radius of spherical SCs). In the rest of this paper, we will primarily focus on the results for the seeds synthesized with 15\% citric acid and grown at 70°C (experiment 15:85-70°C; Methods and Supplementary Section 1). Results for other experiments are either mechanistically similar or simpler and we have discussed them in Supplementary Sections 5-7.

Fig. 1 shows representative regressions for the experiment 15:85-70°C (see Supplementary Figs. 7-11 for all the temporal data). One can see that our theoretical framework provides excellent regressions to the experimental spectra throughout the kinetic process. Quantitatively, the range-normalized root mean square errors (NRMSE) are invariably less than 2\% for all the regressions while the deviations from experimental data at individual wavelengths and time points are never more than 5 \% of the extinction range (Supplementary Fig. 12). Additionally, the noninteracting GNP model (Gans formalism) is merely able to describe the early and the late spectra, when the interactions between the GNPs are vanishingly small. Contrarily, the EMT model closely fits the experimental spectra throughout the process (Supplementary Fig. 12 left). It is worth noting that previous attempts to theoretically describe the experimental spectra of DNA-linked GNP clusters, a system physically similar to our superclusters, yielded merely qualitative agreement as can be seen for example in Figure 5c of the article by Ross et al.\textsuperscript{38}

Fig. 2 presents the temporal evolution of the optimized model parameters (a-e) and the particle number concentration (f) for the experiment 15:85-70°C. In this figure, the red open circles represent the outputs of the EMT model regression whereas the black dots are those corresponding to the selected model along with their heuristically estimated\textsuperscript{39} 95\% confidence bounds (see Supplementary
Sections 3 and 9 for details). Besides, Fig. 3 provides some additional kinetic outputs obtained from regressing the experimental spectra (a-c), representative spectra (d), the evolution of peak width at half-maximum (PWHM) calculated from the experimental spectra according to Natan et al.\textsuperscript{40} (e), and the \textit{in situ} measured solution pH and reduction potential (Eh vs. Ag/AgCl/\textit{c}(KCl) = 3 mol/L; f). The grey-to-white shaded regions in Figs. 2 and 3 (denoted by Roman numerals in the first plots of each figure) characterize various mechanistic steps as discussed below.

**Figure 1. Summary of spectral regressions.** Representative experimental UV-vis spectra (red curves composed of several open circles) and their corresponding theoretical fits (black lines) for the experiment 15:85-70°C.

Fig. 2a,b,f show that the EMT model approaches the Gans formalism when the interaction effects are negligible (that is, when \( \% \) GNP in SCs approaches zero; Figure 3b). We can see this self-consistent behavior more clearly in Supplementary Fig. 33 where the common parameters/outputs of the two models (\( \bar{r}_{\text{GNP}}, \bar{\rho}, \) GNP number concentration, and density) are plotted on the same axes. As expected, the discrepancy grows when the interaction effects become more prominent and it reaches a maximum around the same time the percentage of GNPs inside SCs is the highest. Having the self-consistency checked, we can scrutinize the temporal evolution during the seeded growth of GNPs by dividing the overall process time into five regions, as discussed below.
In region (I) (0-150 s), as soon as the concentrated Au(III) solution is injected into the seed suspension (Fig. 3d; the spectrum at 20 s) $\bar{\rho}_{GNP}$ drops from 7.4 to 6.1 nm (Figure 2a) while the number concentration of particles almost doubles (Figure 2f). This implies the occurrence of a nucleation event which quickly decelerates as a result of pH change (1.7 in the 20 mM Au(III) solution to 5.5 in the reaction medium at 70°C) converting the highly reactive [AuCl₄]⁻ species to its less reactive, hydrolyzed counterparts ([AuCl₄₋ₓ(OH)ₓ]⁻; x = 1-4). The sudden leap in PWHM and its subsequent stabilization correlates with this observation (Fig. 3e). Presumably, the new particles are generated by primary and secondary nucleation, as both mechanisms are possible under this operating condition. More specifically, the temperature, pH and number concentration of the seeds lie within a range where both nucleation types are viable (note that at the point of injection the high local supersaturation could induce an even faster nucleation). Alternatively, by lowering the temperature to 20°C (in a suspension prepared by only Na₃Cit) one can minimize primary nucleation (i.e., preserve the particle number concentration). In the latter case, all the injected Au(III) would be spent to enlarge the seeds through catalytic secondary nucleation and molecular growth (note that compared to primary nucleation, both processes have smaller free energy barriers). Indeed, Wuithschick et al. employed this notion to determine the reaction time at which primary nucleation stops during the method of Turkevich.

Another notable feature in region (I) is the formation of more anisotropic nanoparticles (increase in $\bar{\rho}$ from 1.25 to 1.5; Fig. 2b) which is also documented in TEM observations by many other workers. Such anisotropic secondary particles can arise due to either slow agglomeration/aggregation, or secondary nucleation. In this case, considering the short duration of region (I) and the near-bulk density of the population (Figure 3a), a secondary nucleation followed by integration to the seeds, via interparticle molecular growth, seems to be responsible for the anisotropy (see Supplementary Section 3 for the protocol to estimate density). A detailed discussion regarding the origins of anisotropy in secondary particles is presented in the classic paper by Enustun and Turkevich.
Figure 2. Kinetics of gold nanoparticle growth (experiment 15:85-70°C) from in situ UV-vis spectroscopy and model regression. a-e, Regressed physical parameters (and their corresponding 95% confidence bounds found by a heuristic search method\(^\text{39}\)) including mean particle radius (a), mean particle aspect ratio (b), number fraction of liquid-like superclusters (c), volume fraction of particles in superclusters (d), and mean supercluster radius (e). f, Temporal particle number concentration (along with 95% confidence bounds\(^\text{39}\)) obtained from scaling the calculated extinction cross sections with the experimental spectra. Legends are common in all the plots and the grey-to-white shaded regions characterize various mechanistic steps (denoted by Roman numerals in the first plot) as discussed in the main text.

After the nucleation event at the beginning of region (I), ensuing the reduced colloidal stability (due to Au(I) adsorption on the surface) and increased number concentration, there is a quiescent period during which particles start to gradually approach each other. This gives rise to electromagnetic interaction effects and the appearance of mesoscale liquid-like superclusters (Figure 2c-e and Figure 3b,c; Figure 3d,e enhanced extinction in the wavelength range 600-800 nm and peak broadening).\(^\text{12,18,19,31}\) Conferring the potential measurements (Figure 3f), we see that the pH continuously drops which is due to the injection of chloroauric acid solution and \([AuCl_4]^- \rightarrow Au(I)\) reduction by citrate.\(^\text{21,41}\) The latter, which dominates after the mixing period (probably less than a second), provides growth units/monomers for the densification of secondary particles (via molecular growth and neck formation\(^\text{5}\)) in addition to a subsequent nucleation event which happens in region (II) (see below). Looking at the Eh data (Figure 3f) in region (I), and knowing that Au(I)/Au(0) couple mainly determines the potential of the gold electrode,\(^\text{20,29}\) we understand that the quick initial drop in potential is related to the consumption of Au(I) by nucleation and molecular growth. Following this
shallow drop, Eh rises back up which indicates the buildup of Au(I) consistent with the pH behavior discussed earlier.

Figure 3. Complementary kinetic data (experiment 15:85-70°C) from in situ UV-vis spectroscopy and electrochemical potential measurements. a, Gold nanoparticle concentration (mM Au(0); obtained from extinction at 400 nm) and the estimated volumetric mass density of nanoparticles (with 95% confidence bounds found by a heuristic search method). b, Estimated percentage of electromagnetically interacting particles out of the overall population (i.e., interacting + noninteracting) along with the respective 95% confidence bounds. c, Mean center-to-center distance between electromagnetically interacting nanoparticles both normalized to the average particle radius and in absolute units (with 95% confidence bounds). d, Experimental extinction spectra at selected temporal points. e, Temporal evolution of peak width at half-maximum obtained from experimentally measured spectra. f, In situ measured solution pH and reduction potential (Eh vs. Ag/AgCl/κ(KCl) = 3 mol/L). The grey-to-white shaded regions (all the plots except for d) characterize various mechanistic steps (denoted by Roman numerals in the first plot) as discussed in the main text.

In region (II) (150-350 s) the formation of Au(0) accelerates (Figure 3a) due to a burst of new particles increasing the number concentration (Figure 2f) and lowering \( r_{\text{GNP}} \) (Figure 2a). This corresponds to a second nucleation event (both primary and secondary nucleation). One major difference compared to region (I) is the rapidly dropping density of GNPs (Figure 3a) which indicates that most of the Au(III) precursor is consumed in nucleation rather than molecular growth. This way, inside the resultant anisotropic secondary particles, mainly physical bonds hold primary particles together. We may identify these secondary particles as agglomerates but we should note that the mechanism behind their formation is true catalytic secondary nucleation and not agglomeration.

As we mentioned earlier, in region (I) the concentration of Au(I) builds up, which in turn provides a high supersaturation level that allows for significant primary nucleation alongside secondary
nucleation in region(II). Concurrent with the rapid increase in number concentration and in the presence of surface-adsorbed Au(I), colloidal stability decreases further and more GNP s approach each other to form liquid-like superclusters (Figure 2c-e and Figure 3b,c; Figure 3d enhanced extinction in 600-800 nm). Nanoparticles assemble into mesoscale structures ~ 350 nm in diameter (Figure 2e) with an average center-to-center distance ~ 15 nm (≈ 3 $\bar{r}_{\text{GNP}}$) between the GNP s (Figure 3c). The presence of both significant electromagnetic interactions and elongated nanoparticle agglomerates induces a two-fold rise in the experimentally measured PWHM (Figure 3e).

Consulting Figure 3f in region (II) the pH remains almost constant although the reduction of Au(III) by citrate releases protons.\(^{21,41}\) To explain this, we note that most of the highly reactive [AuCl\(_4\)]\(^-\) species has already converted either into Au(I) or [AuCl\(_4\)\(_x\)(OH)\(_x\)]\(^-\). For this reason, Au(III) speciation is shifted toward [AuCl\(_4\)]\(^-\) (Le Chatelier's principle), releasing OH\(^-\):\(^{1}\)

\[
[AuCl_4]^- + x OH^- \rightleftharpoons [AuCl_{4-x}(OH)_x]^+ + x Cl^-; x=1-4
\]  

This shift counterbalances the pH decreasing effect of Au(III) reduction and sustains until the end of the process, as witnessed by the continuous slow increase in pH. Finally, with Au(I)/Au(0) as the chief potential determining couple,\(^{20,29}\) the gradual decrease in Eh (Figure 3f) implies a continuous Au(I) $\rightarrow$ Au(0) reaction in region (II).

Region (III) (350-590 s) is accompanied by a precipitous drop in the number concentration of GNP s (Figure 2f) which come together and produce larger, secondary particles around 9 nm in radius (Figure 2a). These secondary particles have a quite spherical shape (Figure 2b) and are of lower density compared to bulk gold (Figure 3a). Therefore, they appear to be randomly packed fluffy agglomerates, whose morphology results from fast agglomeration under reduced colloidal stability.\(^{19,20,43}\) The high number concentration at the beginning of this period supports such fast coagulation process.\(^{8,18-20,43}\) Concurrently, growth continues to consume ionic Au as evidenced by the continuous increase in Au(0) concentration (Figure 3a).
Looking at the state of particle-particle interaction it continues to grow (Figure 3b) and reaches a maximum at the end of this period (more than 70% of GNP experiencing electromagnetic interactions with neighboring particles). This is consistent with the continued enhancement of extinction in the wavelength range 600-800 (Figure 3d). Consulting Figure 3e, initially PWHM does not significantly change but toward the end of this period, it rises toward a maximum of more than 300 nm (more than threefold the value in the seed spectrum). To explain this, we note that at the beginning the formation of more spherical agglomerates counteracts the peak broadening caused by enhanced electromagnetic interactions. Yet, eventually interaction effects dominate and broaden the localized surface plasmon resonance (LSPR) band (Figure 3e).

In region (III), the majority of Au(III) is in the hydrolyzed form (considering the pH level, Figure 3f) and they gradually reduce to Au(I), either directly or via [AuCl₄]⁻. Hence, unlike region (I) the level of supersaturation (Au(I) activity) is comparatively low. Consequently, contrary to the dense secondary particles in region (I), the agglomerates forming in region (III) do not have as extensive chemical bonds and they are less dense (Figure 3a). Towards the end of this region, Eh decreases quickly indicating the onset of another nucleation event, manifesting in region (IV) (Figure 3f).

In region (IV) (590-750 s) the number concentration rises once again (Figure 2f) and \( r_{\text{GNP}} \) drops (Figure 2a). Meanwhile, \( \bar{\rho} \) rapidly increases due to the reappearance of anisotropic secondary particles. We can describe these observations by another nucleation event. Here, considering the relatively low supersaturation degrees (Figure 3f), the energetically more favorable secondary nucleation is probably more significant than primary nucleation. A second mechanism that can account for the increased number concentration is the (partial) peptization of the agglomerates formed in region (III). Chemical bond formation between primary particles inside these agglomerates gives rise to more dense secondary particles (Figure 3a). During this compaction, the loosely bound primary particles would have a chance to repeptize. This is assisted by the recovered colloidal stability due to the relatively low particle number concentration at the end of region (III) (Figure 2f) and the lower level of Au(I) (Figure 3f). Supplementary evidence for the regained colloidal stability comes from the rapidly disappearing interaction effects (Figure 2c,d and Figure 3b,c). As the interaction effects
vanish, PWHM decreases as well, with a deceleration towards the end of the period, the latter being due to the reappearance of anisotropic entities (Fig. 2b and Figure 3d).

In the last temporal region (750-1500 s), there is an abrupt drop in the number concentration (Figure 2f), and a fast rise in $\bar{r}_{\text{GNP}}$ (Figure 2a) and the average mass density (Figure 3a). Remarkably, Au(0) concentration does not perceptibly increase anymore (Figure 3a) implying an almost complete depletion of supersaturation. Eh being very close to its final equilibrium value further corroborates this hypothesis (Figure 3f). Hence, this period is dominated by an Ostwald ripening event (the amorphous nature of newly formed GNPs, as documented by Loh et al., can help the dissolution of small nanoparticles). Thus, larger particles grow at the expense of smaller particles and agglomerates coalesce to structures that are more dense (Figure 3a). In this period, coalescence along with intraparticle ripening render the particles more spherical. Finally, in the absence of electromagnetic interactions, the two optical theories (Gans + EMT/Mie and Gans) predict similar outputs (Supplementary Fig. 33).

Figure 4 schematically summarizes the mechanistic picture presented earlier, enumerating the most prominent events in each temporal region. Note that molecular growth, defined as particle enlargement by the addition of molecularly sized entities, can happen as long as the system is supersaturated. In region (V), this could be in the form of Ostwald/interparticle ripening. In Supplementary Section 8, we have presented further support for the proposed mechanism using principal component analysis.
**Figure 4. Proposed mechanism for the seeded growth of gold nanoparticles.** A Schematic representation portraying the sequence of processes encountered during the seeded growth of GNPs in the experiment 15:85-70°C. The degree of overlap between primary particles inside secondary particles correlates with the density of the latter (i.e., more overlap means a higher density). Seeds and final grown GNPs are shown as individual particles to denote coalescence into single entities. Molecular growth can happen throughout the process as represented by the continuous arrow at the bottom. To save space, the relative size of superclusters is not drawn to scale (they should be much larger than the individual secondary particles).

**Conclusions**

In summary, we developed a novel, comprehensive theoretical framework to extract kinetic and mechanistic information about the seeded growth of gold nanoparticles from time-resolved *in situ* optical extinction spectroscopy (OES). When compared to more sophisticated and expensive characterization techniques such as SAXS and *in situ* TEM, OES is appealing due to its availability, low cost, and relatively straightforward data collection procedure under various operating conditions. So far, the quantitative application of this technique was hampered by the complicated and undeveloped theory necessary to extract temporal kinetic information like particle size, shape, and concentration, as well as the state of particle-particle interaction (mesoscale aspects). In this article, we drew on the extensive previous research in the field and developed a physical model to describe the optical response of a growing gold sol. We demystified the complexity of the process, which may involve several temporally overlapping subprocesses, e.g. primary and secondary nucleation, molecular growth, agglomeration, and Ostwald ripening. We observed similar events for experiments performed under various conditions (e.g., different T and pH) and suggested a plausible mechanistic pathway to account for the various trends observed in the outputs of the spectral regression. In this respect, we identified the role of nucleation events accompanying the particle enlargement process.
Moreover, we showed that the particle enlargement might occur via a combination of molecular growth (in the form of Ostwald ripening, particularly close to the end of the process), secondary nucleation, and agglomeration. We further identified instances of peptization consistent with the previous experimental evidence reported by other workers.\textsuperscript{18-20} Besides, we addressed the longstanding question about the nature of moieties responsible for the purple-greyish color during the growth of gold nanoparticles. Concerning that, we distinguished the optical signature of electromagnetic interactions between the particles inside liquid-like superclusters, from that of relatively small fluffy agglomerates. Finally, we developed the theoretical formalism in a general form so that it can be transferred to other relevant systems such as various metal nanoparticles and quantum dots.

**Methods**

**Synthesis of GNPs and kinetic experiments.** Gold nanoparticle seeds were prepared by injecting 1 mL of a 50 mM H\textsubscript{Au}Cl\textsubscript{4} aqueous solution into 499 mL boiling solution of 2 mM citrate buffer. The buffer’s pH was tuned by adjusting the molar ratio citric acid/trisodium citrate (0%:100%, 15%:85%, and 25%:75%). We then used these particles in a seeded growth process, the kinetics of which was of interest. For this purpose, 0.75 mL 20 mM H\textsubscript{Au}Cl\textsubscript{4} solution was rapidly injected into 60 mL of a seed suspension at different temperatures (40, 60, 65, 70°C). The temporal evolution of the system was followed by UV-vis spectroscopy (one spectrum every 20 s for the experiments 25:75-40°C and 0:100-70°C, and every 10 s for the rest of the experiments), reduction potential (Eh) measurement, and pH measurement (Eh and pH data points collected every two seconds). Six sets of experimental data were collected under various conditions (T and pH) using different seed suspensions. This includes experiments at 60, 65, and 70°C using the 15%:85%-buffer seed, experiments at 70°C using 25%:75%- and 0%:100%-buffer seeds, and an experiment at 40°C using the 25%:75%-buffer seed suspension. Reference to each experiment denotes the buffer ratio followed by the experimental temperature, e.g., 15:85-70°C (experiment using 15%:85%-buffer seed at 70°C). See Supplementary Section 1 for further details on kinetic experiments.
**Optical extinction calculations.** Throughout our calculations, the bulk dielectric function of gold\textsuperscript{45} was modified to account for temperature and finite-size effects (Supplementary Section 2).\textsuperscript{33,36,46} The extinction of light by an ensemble of noninteracting GNPs was calculated using the quasi-static Gans formalism (GNP diameter $\lesssim 30$ nm) assuming prolate shaped particles with an average equivalent spherical radius $\bar{r}_{\text{GNP}}$, and a mean major-to-minor axis ratio $\bar{\beta}$.\textsuperscript{36} On the other hand, the optical response of ensembles composed of interacting GNPs was described using Maxwell-Garnett effective medium theory (EMT) with retarded polarization effects incorporated following Granqvist and Hunderi.\textsuperscript{47,48} Interacting GNPs are presumed to form spherical domains, denoted as liquid-like superclusters (SCs) wherein their local number concentration exceeds that of the bulk solution.\textsuperscript{11,12,26,31} The effective dielectric function estimated for a supercluster can then be inserted into the Mie scattering theory to calculate the corresponding extinction cross section.\textsuperscript{37} All the computational codes, both for the calculation of optical extinction and the regression of the experimental spectra, were developed in MATLAB R2017b. Mie scattering calculations were implemented using the MATLAB/Octave code written by Demers et al.\textsuperscript{49} A globalized bounded Nelder-Mead optimization scheme was employed for all the regressions.\textsuperscript{50} The 95% confidence intervals on various regression parameters and on different model outputs were obtained by a heuristic approach described by Schwaab et al.\textsuperscript{39} As a last note, throughout this work the theoretical framework that accounts for the extinction by both noninteracting and interacting GNPs is simply referred to as the EMT model (that is, EMT model $\equiv$ Gans theory for noninteracting GNPs + Retarded EMT/Mie for interacting GNPs). See Supplementary Sections 2 and 3 for further details on the theoretical framework and the regression protocol, respectively.

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Supplementary Information

Kinetics and mechanism of gold nanoparticle growth studied via optical extinction spectroscopy and computational modeling

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Supplementary Section 1. Additional experimental details

Materials. Metallic gold foil (99.99% pure) was purchased from Nuova Franco Suisse Italia. Hydrogen chloride (37 wt.% in H2O, 99.999% trace metals basis), nitric acid (70% HNO3, ≥99.999% trace metals basis), sodium citrate tribasic dihydrate (Na3Cit.2H2O, ACS reagent ≥99.0%), and citric acid (H3Cit, ACS reagent ≥99.5%) were purchased from Sigma Aldrich. Ultrapure water (18.2 MΩ cm, MilliQ) was used throughout the experiments. All the glassware and PTFE-coated magnetic stirring bars were cleaned with freshly prepared aqua regia and rinsed thoroughly with milliQ water before each experiment. A stock solution of HAuCl4 in water was prepared according to the procedure by Gross and used in all the syntheses.1 Fresh solutions of HAuCl4 and citrate buffer (with the desired concentrations) were prepared before each experiment and stored in tightly closed glass bottles.

Kinetic experiments. Among several seed synthesis protocols investigated, those synthesized in buffers with 15% citric acid provide a very good model system for kinetic studies because of the slow enough temporal evolution providing the chance to collect enough data with a reasonable time resolution of 10 seconds. On the other hand, the process is not excessively slowed down that the
particles interact for too long and aggregate (*i.e.*, form chemically cemented secondary particles) in an uncontrolled manner. This situation, which gives rise to large fractal-like structures, is thoroughly studied by Karg et al.\(^3\) The latter happens, for instance, for seeds synthesized using 100% Na\(_3\)Cit and grown at T < 60°C. Both the higher pH and the lower temperature in this sample hindered the reduction of Au(III), the presence of which favors attractive interactions between the particles.\(^4\)\(^5\) Throughout the main text, we have primarily focused on the results for seeds synthesized with 15% citric acid and grown at 70°C (named as 15:85-70°C). Results for the other experiments (including those for the same seeds grown at 60 and 65°C) are either mechanistically similar or simpler and we have discussed them in Supplementary Sections 5-7.

**Characterization.** The volume-averaged equivalent spherical radius for the seeds and grown GNP were found by TEM (JEOL-2010), measuring the semi-major and semi-minor axes of at least 100 particles using Fiji package and assuming prolate shaped particles (the axis perpendicular to the image is taken as a minor axis).\(^6\)\(^7\) *In situ* UV-vis spectra were collected using an Ocean Optics PEEK immersion probe with 1 cm optical path length (pure water was used as the reference). The probe was connected to a DT-mini-2-GS UV-Vis-NIR light source and a USB2000+XR1 spectrometer, both from Ocean Optics. Each spectrum was an average of four 2.5-second (5 s for the data in 0:100-70°C and 25:75-40°C experiments) acquisitions smoothed with a boxcar width two. Measurements of pH and Eh (vs. Ag/AgCl/c(KCl) = 3 mol/L) were done using a pH glass electrode (Unitrode Pt 1000) and a combined gold ring electrode, respectively, provided by Metrohm AG.

**Supplementary Section 2. Optical properties of gold nanoparticles and their ensembles**

The extinction of light by an ensemble of noninteracting GNPs is typically described using the Mie theory (in case of spherical particles) or the Gans formalism in the quasi-static regime (GNP diameter \(< \approx 30\) nm).\(^8\)\(^9\) However, more often than not, there are significant electromagnetic interactions between the particles.\(^10\)-\(^12\) Particularly in the case of metal nanoparticle synthesis (e.g., growth of GNPs), as we have elaborated on in Results and Discussion (main text), experimental evidence
support the presence of such interactions. In order to account for such interparticle interactions, there are two alternatives. One can take advantage of a plethora of numerical techniques employed to describe the optical extinction by (interacting) particle ensembles. This includes coupled dipole approximation, generalized Mie theory, and boundary element method to name a few. An alternative approach is the application of effective medium theories (EMTs). While the former alternative applies to any particle size and configuration, the latter is defined only in the quasi-static regime. Nevertheless, the numerical approaches are computationally prohibitive, particularly for ensembles with large numbers of particles. For this reason, having a large number of spectra collected during the growth process, and considering the small size of GNPs, in the current work we chose to employ an EMT formalism to account for the possible electromagnetic interactions between the particles.

**Dielectric function of gold and solvent (water).** The first step in developing an optical model for the extinction behavior of gold suspensions is the modification of bulk dielectric function so that temperature and finite size effects are properly taken into account. For the bulk data, we used the dielectric function of gold recently measured by Yakubovsky et al. on a 25 nm thick film (measured wavelength range 300-2000 nm). A smoothing spline was fitted to these data yielding the dielectric function of gold at room temperature every 1 nm (Supplementary Fig. 1). Intrinsic size effects for particles smaller than the mean free path of bulk gold were accounted for in the framework of the extended Drude model assuming size- and temperature-independent contribution from the interband transitions. Thus, the complex dielectric function of gold reads:

$$
\varepsilon(\omega, r, T) = \varepsilon_{IB}(\omega) + \left[1 - \frac{\omega_p(T)^2}{\omega(\omega + i\Gamma(r, T))}\right]
$$

(Supp. Eq. 1)

where $\varepsilon_{IB}$ represents the contribution of interband transitions by the bound electrons while the term in the square brackets comes from the free-electron contributions. In the latter, $\omega_p$ is the temperature-dependent bulk plasma frequency (rad/s), $\omega = \frac{2\pi c}{\lambda}$ is the vacuum angular frequency of the incident light (rad/s; $c$ and $\lambda$ are the speed of light and wavelength in vacuum, respectively), and $\Gamma$ is the
temperature \( (T) \)- and size (radius; \( r \)) - dependent damping frequency (rad/s) for the free electrons. The temperature dependence of \( \omega_p \) can be estimated considering the thermal expansion of gold, which in turn reduces the density of the conduction (free) electrons:

\[
\omega_p(T) = \frac{\omega_p(T_0)}{\sqrt{1 + \alpha_v(T - T_0)}}
\]  
(Supp. Eq. 2)

Here, \( T_0 = 298.15 \, K \) is a reference temperature (room temperature), \( \omega_p(T_0) = 1.37 \times 10^{16} \, rad/s \), and \( \alpha_v = 4.17 \times 10^{-5} \, K^{-1} \) is the volumetric thermal expansion coefficient of gold.\(^2^8\)

The damping of the free electrons arises from several processes including the interactions with phonons, electrons, lattice defects, grain boundaries, impurities, surface adsorbed species, and surfaces/interfaces themselves.\(^1^0,1^2,2^9,3^0\) The temperature dependences of the interactions with phonons (\( \Gamma_{e-ph} \)) and electrons (\( \Gamma_{e-e} \)) can be described as:\(^2^4,2^5,2^7\)

\[
\Gamma_{e-ph}(T) = \Gamma_{e-ph}(T_0) \times \left[ \frac{2}{5} + 4 \left( \frac{T}{\theta} \right)^5 \int_0^{\theta/T} \frac{z^4}{e^z - 1} dz \right]
\]  
(Supp. Eq. 3)

\[
\Gamma_{e-e}(\omega, T) = \frac{\pi^3 \Sigma \Delta}{12 \hbar E_F} \left[ (k_B T)^2 + \left( \frac{\hbar \omega}{2 \pi} \right)^2 \right]
\]  
(Supp. Eq. 4)

In these equations \( \Gamma_{e-ph}(T_0) = 7.09 \times 10^{13} \, rad/s \) (back calculated from \( \Gamma_{bulk}(T_0) = 1.2686 \times 10^{14} \, rad/s \)), \( \theta = 170 \, K \) is the Debye temperature of gold, \( \Sigma = 0.55 \) is the Fermi-surface average of scattering, \( \Delta = 0.77 \) is the fractional Umklapp scattering, \( E_F = 5.51 \, eV \) is the Fermi energy, \( \hbar \) is the reduced Planck constant, and \( k_B \) is the Boltzmann constant.\(^2^7\) In addition to these two damping mechanisms, the size-dependent damping due to interactions with surfaces/interfaces, grain boundaries, and defects (the free path effect,\(^1^0,1^2\) FPE) can be estimated using the following phenomenological approach:

\[
\Gamma_{FPE}(r) = A_{eff} \frac{V_f}{L_{eff}}
\]  
(Supp. Eq. 5)
where \( v_f = 1.4 \times 10^6 \text{ m/s} \) is the Fermi velocity of gold and \( L_{\text{eff}} = \frac{4 \times \text{volume}}{\text{surface area}} \left( \frac{4}{3} r \text{ for spheres} \right) \)
is the effective mean free path of electrons in nanoparticles with arbitrary shape.\(^{31}\) Further, \( A_{\text{eff}} \equiv \frac{4}{3} \eta \) with the factor \( \frac{4}{3} \) giving a typical proportionality constant 1 for surface-induced scattering in spherical nanoparticles (\( \eta \equiv 1 \)),\(^{10,12}\) and \( \eta \) accounts for the details of the scattering process and the additional contributions, e.g., by defects, adsorbed species, and grain boundaries.\(^{9,29,30,32}\) Having all the damping mechanisms in place one can calculate the overall damping frequency as

\[
\Gamma = \Gamma_{\text{e-ph}} + \Gamma_{\text{e-e}} + \Gamma_{\text{FPE}} \quad \text{(Supp. Eq. 6)}
\]

In practice, we can estimate \( \varepsilon_{IB} \) by subtracting the bulk Drude expression at room temperature \( (r \to \infty \Rightarrow \Gamma_{\text{FPE}} \to 0) \) from the experimental dielectric function:

\[
\varepsilon_{IB}(\omega) = \varepsilon_{\text{experimental}} - \left[ 1 - \frac{\omega_p(T_0)^2}{\omega(\omega + i\Gamma(\omega, r \to \infty, T_0))} \right] \quad \text{(Supp. Eq. 7)}
\]

Some workers have suggested that correcting only the imaginary part (of the dielectric function) for the intrinsic size effects provides superior fits to experimental data.\(^{8,26}\) However, our preliminary simulations proved the opposite in line with the works of Haiss et al.\(^{31}\) and Amendola and Meneghetti.\(^{9}\) For this reason throughout this work we will correct both the real and imaginary parts of \( \varepsilon \).

The dielectric function of water at different temperatures was calculated according to the correlation by Fernández-Prini and Dooley.\(^{34}\)
Supplementary Figure 1. Contributions of the interband transitions (bound electrons) and the free electrons to the real (left) and imaginary (right) parts of the gold’s bulk dielectric function taken from Yakubovsky et al.23

Calculation of extinction by gold nanoparticle ensembles. Extinction by ensembles of noninteracting GNPs was calculated using Gans formalism for prolate spheroids with an average equivalent spherical radius ($\bar{r}_{GNP}$) and a mean major-to-minor axis ratio ($\bar{\beta}$).9,12

In the literature, it is well documented that in the presence of Au(III), GNPs interact and tend to approach one another, possibly because of the reduced colloidal stability.4,5,13 The former affects the extinction behavior of the GNP ensemble due to electromagnetic coupling between the particles.3,5,11–14 This complication has so far hindered the application of OES to the kinetic studies on metallic nanoparticles. Here, the optical response of ensembles that have interacting GNPs is described using the Maxwell-Garnett effective medium theory with retarded polarization effects incorporated following Granqvist and Hunderi.20,21 For this purpose the interacting GNPs are presumed to form spherical domains wherein their local number concentration exceeds that of the bulk solution (Supplementary Fig. 2). The presence of such dense liquid-like superclusters (SCs) has been shown by a variety of characterization techniques (e.g., DLS, AFM, and in-situ TEM).13,14,35,36 Schatz and colleagues have used this picture to describe the extinction by arrays of plasmonic nanoparticles, i.e., DNA-linked GNP clusters with volume fractions 1-20%.16,22,37,38

Granqvist and Hunderi extended the Maxwell-Garnett EMT by introducing a phase factor in the Lorentz local-field equation.20,21 Doing that, they arrived at the following equation for the effective
dielectric function of an ensemble of nanoparticles embedded in a surrounding medium with dielectric permittivity $\varepsilon_m$:

$$
\tilde{\varepsilon} = \varepsilon_m \frac{1 + (1 - \frac{1}{3} e^{i\delta}) \sum_j f_j \alpha'_j}{1 - \frac{1}{3} e^{i\delta} \sum_j f_j \alpha'_j}
$$

(Supp. Eq. 8)

with

$$
\alpha'_j \equiv \frac{4\pi \alpha_j}{V_j} \equiv \frac{1}{3} \sum_{i=1}^{3} \frac{\varepsilon_j - \varepsilon_m}{\varepsilon_m + L_{ij}(\varepsilon_j - \varepsilon_m)}
$$

(Supp. Eq. 9)

In these equations $f_j$ denotes the fractional filling factors (volume fractions) of various particle classes with $\sum_j f_j = f$, where $f$ is the total volume fraction of particles within the effective medium (individual superclusters). Additionally, $\alpha_j$ denotes the polarizability of particle $j$ with a volume ($V_j$),\textsuperscript{20,21} and $L_{ij}$ represents the triplet of depolarization factors along the different axes of the prolate spheroid $j$. Using the former quantities, for randomly oriented spheroids we can estimate the average volume-normalized polarizability ($\alpha'_j$).\textsuperscript{12,20,21} Moreover, $e^{i\delta}$ is a phase factor that accounts for the retarded nature of interaction with the depolarizing field and can be estimated knowing the mean center-to-center distance between the particles:

$$
\delta = \frac{2\pi\sqrt{\tilde{\varepsilon} d_{cc}}}{\lambda}
$$

(Supp. Eq. 10)

Assuming a uniform distribution of particles throughout the effective medium\textsuperscript{15,39} (Supplementary Fig. 2), the center-to-center distance between the particles can be estimated as:\textsuperscript{15,40}

$$
d_{cc} = 2\bar{r}_{GNP} \times \sqrt[3]{\frac{\pi}{\sqrt{18f}}}
$$

(Supp. Eq. 11)

In this equation the factor $\frac{\pi}{\sqrt{18}}$ is the close packing density of the equal spherical domains that belong to the individual GNPs (dotted black circles surrounding individual GNPs in Supplementary Fig. 2).
Considering the dependence of $\delta$ on $\bar{\epsilon}$, an iterative procedure is necessary to calculate the $\bar{\epsilon}$, starting with the non-retarded $\bar{\epsilon}$ as an initial guess.$^{20,21}$

A representative effective dielectric permittivity at 60°C for a supercluster of 10 nm GNPs in water with $f = 0.2$ is shown in Supplementary Fig. 3, calculated using both Maxwell-Garnet theory and its retarded extension by Granqvist and Hunderi.$^{20,21}$ Once we have the effective dielectric function of the spherical SCs, we can calculate the extinction cross section of noninteracting SCs using the Mie theory. Schatz et al. applied this method to calculate the extinction by DNA-linked nanoparticles and showed that the results match very well with those from the more rigorous coupled dipole approximation.$^{22,37}$

![Supplementary Figure 2](image.png)

**Supplementary Figure 2.** Schematic representation of an ensemble of electromagnetically interacting gold nanoparticles (yellow dots) composing a dense liquid-like supercluster (SC; large dashed circle in dark gray). Each black dotted circle around individual GNP's represents the portion of SC volume per particle.
Supplementary Figure 3. Maxwell-Garnett (MG) and retarded real (left) and imaginary (right) parts of the effective dielectric function of a GNP supercluster (water as the dispersing medium) with $r_{\text{GNP}} = 5\ \text{nm}$, 50% spherical-50% $\tilde{\rho} = 1.3$ particles, and $f = 0.2$ at 60°C.

Supplementary Section 3. Overall modeling workflow and regression to experimental spectra

We started the modeling procedure by converting the raw data, i.e., dark, reference, and temporal sample intensities, to extinction spectra. According to Parak et al. absorption by small noninteracting GNPs converges to zero at wavelength range 800-1200 nm.\textsuperscript{41} Therefore, the possibly drifted spectra of the seeds and grown particles were background corrected by shifting them to 0.01 and 0.03 absorption units at $\lambda = 800$ nm, respectively (these values are estimated from preliminary extinction calculations using the TEM characterized size and aspect ratio). The intermediate spectra were background-corrected using the shift factors estimated by linear interpolation between that of the seeds and the grown GNP. Several spectra collected on seeds before the injection of Au(III) solution were averaged to yield the seed data with improved signal to noise ratio. Background-corrected spectra were then fitted using smoothing splines with automatically selected smoothing parameters using the MATLAB’s curve fitting app and the data were saved with a 1 nm resolution.

We then started the regression procedure by calibrating the parameter $\eta$ using the mean volume-weighted particle radii of seeds and grown GNP estimated from TEM micrographs (Supplementary Section 4).\textsuperscript{9} The regression of these two experimental spectra was done by fixing the mean radii and globally fitting $\eta$ along with $\tilde{\beta}$ for both seeds and grown GNPs using the Gans formalism in the range
400-800 nm. The value of $\eta$ was constrained in the range [0.2,4]. The fitted $\eta$ values were used to derive a linear relation $\eta = \eta_0 + \eta_1 \bar{r}_{GNP}$ which was then used for all the intermediate spectra.

In the next step, we fitted all the intermediate spectra using the Gans theory with only two parameters ($\bar{r}_{GNP}$ and $\bar{\beta}$). The same was also done using the EMT model in which we considered possible contributions from both noninteracting GNPs as well as SCs composed of electromagnetically interacting particles (namely, EMT model $\equiv$ Gans theory for noninteracting GNPs + Retarded EMT/Mie for interacting GNPs). Assuming similar average size and aspect ratio for GNPs both inside and outside the SCs, we have five parameters to regress: $\bar{r}_{GNP}$, $\bar{\beta}$, $x_{SC}$ (the number fraction of SCs out of all the scatterers, i.e., SCs + noninteracting GNPs), $f$, and $\bar{r}_{SC}$ (the average radius of SCs). All the spectra were regressed searching over a wide space for $\bar{\beta}$ and the EMT parameters while constraining $\bar{r}_{GNP}$ to within 10% (50% for the second spectrum) of the previous optimized value (obtained from Gans theory for the first spectrum and EMT for the rest of the intermediate spectra):

$$\max(0.9\bar{r}_{GNP,j-1}, 2 \text{ nm}) \leq \bar{r}_{GNP} \leq \min(1.1\bar{r}_{GNP,j-1}, 15 \text{ nm})$$

$$1 \leq \bar{\beta} \leq 3$$

$$-8 \leq \log_{10}(x_{SC}) \leq 0$$

$$-3 \leq \log_{10}(f) \leq \log_{10}(0.4)$$

$$25 \leq \bar{r}_{SC} \leq 250 \text{ nm}$$

where $j$ represents the index of the current spectrum being fitted. There are three physical constraints to be considered when performing this regression:

$$N_{GNP/SC} = f \left( \frac{\bar{r}_{SC}}{\bar{r}_{GNP}} \right)^3 \geq 1000$$

$$\frac{f}{\frac{4}{3} \pi (\bar{r}_{GNP})^3} > (1 - x_{SC})C_t + x_{SC}C_t f \left( \frac{\bar{r}_{SC}}{\bar{r}_{GNP}} \right)^3$$

(Supp. Eq. 13)
with $N_{GNP/SC}$ denoting the average number of GNPs interacting inside each SC and $C_t$ being the total number concentration of the scatterers (noninteracting GNPs + SCs).

The first constraint (Supp. Eq. Supp. Eq. 13) specifies that there have to be at least 1000 particles for the interaction to be meaningful. This is a somewhat arbitrary lower bound considering the loosely defined stipulation of “large” number of particles ($N_{GNP/SC} \gg 1$) necessary for the mean-field averaging in the EMT derivation to be meaningful. This number was selected based on our preliminary regressions using a lower bound of two (the smallest physically meaningful value) which revealed that generally during the interaction period more than 1000 GNPs are involved inside SCs. Nevertheless, this would not introduce any problems because small $N_{GNP/SC}$ values happen in cases where the particle ensemble can adequately be described by a noninteracting Gans formalism. In these conditions, the size and aspect ratio fitted by an EMT model approaches that obtained by the Gans model.

The second constraint (Supp. Eq. 14), coming directly from our definition of superclusters as effective media for the interacting particles, requires that the local GNP number concentration inside an SC be higher than the bulk (i.e., averaged over all the suspension) concentration.

The third constraint (Supp. Eq. 15) finally states that the suspension volume cannot be filled with GNPs and SCs beyond the close sphere packing density. This constraint is rarely violated during an optimization problem, as it requires an extremely high concentration of scatterers.

Being only dependent on the optimization variables, Supp. Eq. 13 can be introduced as a nonlinear constraint in the optimization scheme. Instead, the other two constraints have the parameter $C_t$, which is calculated by scaling the computed extinction cross section with the experimental spectrum in the vicinity of the surface-plasmon resonance band ($\lambda_{spr} \pm 1 \text{ nm}$). Therefore, to exert the constraints in Supp. Eqs. 14 and 15, the objective function is written so that it returns infinity (“Inf”) in case either of them is violated.
Having the constraints in place, a globalized bounded Nelder-Mead optimization\(^{44}\) run from 20 randomly generated start points (complying with the first constraint), was used to find the set of model parameters that fit the intermediate spectra optimally. Since the search space for the parameters \(x_{SC}\) and \(f\) span several orders of magnitude, the random sample was generated on their \(\log_{10}\) transformation. Moreover, in order to bring all the variables in the order of unity and make the optimization more robust the \(\log_{10}\)-transformation of the three EMT parameters \((x_{SC}, f, \text{ and } \bar{r}_{SC})\) were optimized and all the parameters (including the GNP parameters, \(\bar{r}_{GNP}\) and \(\bar{\beta}\)) were centered and scale in the range \([-1,1]\).\(^{45}\) The objective function \((fval \equiv \chi^2 = \sum_i (A_{\text{experimental}} - A_{\text{calculated}})^2)\) was also scaled to be in the order of unity close to the optimal point. Throughout the optimization, we saved the function evaluations whose \(fval\) were within the 95% confidence bounds of the optimized point. This information was then used in order to estimate the corresponding confidence regions on the optimized parameters as well as the other ancillary model outputs (e.g., \(N_{\text{GNP}/SC}\)). Details of this heuristic approach to the construction of 95% confidence bounds are presented in the work of Schwaab et al.\(^{46}\)

When all the spectra are fitted using both the noninteracting GNP model as well as the EMT model, the former is selected as the superior one whenever the following condition holds:

\[
\frac{|\bar{r}_{GNP,EMT} - \bar{r}_{GNP,Gans}|}{\bar{r}_{GNP,EMT}} \leq 0.01
\]

(Supp. Eq. 18)

\[
\frac{|\bar{\beta}_{EMT} - \bar{\beta}_{Gans}|}{\bar{\beta}_{EMT}} \leq 0.01
\]

This condition coincides with % GNP in SCs (obtained from the EMT regressions) approaching zero. This practically corresponds to a situation where there is no tangible electromagnetic interactions between the particles. For periods during which relatively weak interaction effects are present, typically at the beginning and close to the end of the seeded growth process, regressions are repeated over a narrower search space that is compatible with the intermediate data points (that is, when the interaction effects are typically stronger). This is done either by setting a more stringent bound (e.g.,
setting $lb_{\log_{10}(f)} = 0.1$ or by constraining the parameter(s) to a neighborhood of the previous optimal output (e.g., $\max(0.8 \times \bar{r}_{SC,j-1}, 25 \text{ nm}) \leq \bar{r}_{SC} \leq \min(1.2 \times \bar{r}_{SC,j-1}, 250 \text{ nm})$). This new regression is retained as long as it does not deteriorate the quality of the fit substantially. This would help to obtain more reliable estimates for various parameters, especially the EMT variables.

One of the ancillary outputs of the current theoretical framework is the volumetric mass density of nanoparticles. Estimating the concentration of GNP s (in mM Au(0)) from the linear correlation with absorbance at $\lambda = 400 \text{ nm} \ (\text{Abs}_{400})$, one can calculate the density of nanoparticles by comparing the previous value with that computed using the bulk gold density (19.3 g.cm$^{-3}$), the regressed $\bar{r}_{GNP}$, and the number concentration. Practically, the seeds and the grown particles have an apparent mass density similar to the bulk value (bear in mind a $\sim 5\%$ uncertainty in the concentration from $\text{Abs}_{400}$, as well as possible uncertainties in the sizes and concentrations of the initial and final GNP s).

As discussed in the main text, in our theoretical framework we explicitly distinguish between agglomeration/aggregation and electromagnetic interactions between the particles. To this end, closely spaced particles are considered to be in electromagnetic interaction (and not agglomerated/aggregated) unless they touch each other. This is straightforwardly implemented by setting an upper bound of 0.4 for the filling factor, which is equivalent to a center-to-center distance of $\sim 2.5\bar{r}_{GNP}$ (the minimum filling factor at which particles may be touching each other corresponds to random loose packing of spheres which has a filling factor of 0.55$^{48}$).

**Supplementary Section 4. TEM images and particle size distributions**

In this section, we have summarized the number-based particles size distributions (PSD) and the representative TEM micrographs for different seed and grown GNP suspensions. For each PSD the normal distribution with the same mean and standard deviation is plotted as well. Note, however, that the mean volume-weighted particle radii are used throughout the spectroscopic analyses as the extinction signal is weighted by particle volumes.$^9$
Supplementary Figure 4. Particle size distributions (left panel) for the seeds and grown GNPs prepared with a 15%-85% citric acid/trisodium citrate buffer along with their representative TEM images (right panel).
Supplementary Figure 5. Particle size distributions (top panel) for the seeds and grown GNPs prepared with a 25%:75% citric acid/trisodium citrate buffer along with their representative TEM images (bottom panel).

Supplementary Figure 6. Particle size distributions (top panel) for the seeds and grown GNPs prepared with 100% trisodium citrate along with their representative TEM images (bottom panel).
Supplementary Section 5. Regression plots and fit qualities

Supplementary Figure 7. Experimental spectra (red curves) and their corresponding theoretical fits (black lines) for the 15:85-70°C experiment (t = 0-320 s).

Supplementary Figure 8. Experimental spectra (red curves) and their corresponding theoretical fits (black lines) for the 15:85-70°C experiment (t = 330-640 s).
Supplementary Figure 9. Experimental spectra (red curves) and their corresponding theoretical fits (black lines) for the 15:85-70°C experiment (t = 650-960 s).

Supplementary Figure 10. Experimental spectra (red curves) and their corresponding theoretical fits (black lines) for the 15:85-70°C experiment (t = 970-1280 s).
Supplementary Figure 11. Experimental spectra (red curves) and their corresponding theoretical fits (black lines) for the 15:85-70°C experiment (t = 1290-1450 s).

Supplementary Figure 12. Range-normalized root mean square error (NRMSE; a) and range-normalized errors for individual wavelengths and temporal points (b) for the fits on spectra in the 15:85-70°C experiment.
Supplementary Figure 13. Representative experimental UV-vis spectra (red curves composed of several open circles) and their corresponding theoretical fits (black lines) for the 15:85-65°C experiment.

Supplementary Figure 14. Range-normalized root mean square error (NRMSE; a) and range-normalized errors for individual wavelengths and temporal points (b) for the fits on spectra in the 15:85-65°C experiment.
Supplementary Figure 15. Representative experimental UV-vis spectra (red curves composed of several open circles) and their corresponding theoretical fits (black lines) for the 15:85-60°C experiment.

Supplementary Figure 16. Range-normalized root mean square error (NRMSE; a) and range-normalized errors for individual wavelengths and temporal points (b) for the fits on spectra in the 15:85-60°C experiment.
Supplementary Figure 17. Representative experimental UV-vis spectra (red curves composed of several open circles) and their corresponding theoretical fits (black lines) for the 25:75-70°C experiment.

Supplementary Figure 18. Range-normalized root mean square error (NRMSE; a) and range-normalized errors for individual wavelengths and temporal points (b) for the fits on spectra in the 25:75-70°C experiment.
Supplementary Figure 19. Representative experimental UV-vis spectra (red curves composed of several open circles) and their corresponding theoretical fits (black lines) for the 25:75-40°C experiment.

Supplementary Figure 20. Range-normalized root mean square error (NRMSE; a) and range-normalized errors for individual wavelengths and temporal points (b) for the fits on spectra in the 25:75-40°C experiment.
Supplementary Figure 21. Representative experimental UV-vis spectra (red curves composed of several open circles) and their corresponding theoretical fits (black lines) for the 0:100-70°C experiment.

Supplementary Figure 22. Range-normalized root mean square error (NRMSE; a) and range-normalized errors for individual wavelengths and temporal points (b) for the fits on spectra in the 0:100-70°C experiment.
Supplementary Section 6. Regression outputs for experiments other than 15:85-70°C

In this section, we have presented the regression results for all the datasets not discussed in the main text. The major experimental conditions varied from one set to another is the pH of the seed suspension, tuned by the citric acid/trisodium citrate ratio, and the temperature at which the growth process happened. Both lower pH and higher temperature favor a more facile reduction of Au(III) to Au(I) which in turn accelerates the whole process. In all the experiments performed with buffer (that is, all the experiments but 0:100-70°C) the overall mechanism of the seeded growth process is very similar to that of the experiment 15:85-70°C discussed in the main text. The essential difference from one experiment to another is the time scale corresponding to each mechanistic region (Supplementary Figs. 23-30). On the other hand, in the experiment conducted with 100% trisodium citrate (Na₃Cit) the mechanism appears to be slightly different (Supplementary Figs. 31 and 32). In this experiment, the electromagnetic interaction effects are generally much weaker than the rest of the experiments (Supplementary Fig. 32b). The significantly smaller enhancement of the extinction in the range 600-800 nm (Supplementary Fig. 32d), as well as the invariably lower PWHM values (almost half the values in other experiments, close to the maximum; Supplementary Figure 32e) support this hypothesis.

For the experiment 0:100-70°C, the overall seeded growth process can be divided into four mechanistic regions (grey-to-white shaded regions in Supplementary Figures 31 and 32 denoted by Roman numerals). As soon as the Au(III) solution is injected into the seed suspension, a rapid jump happens in Eh (Supplementary Fig. 32f) denoting the formation of Au(I) which couples with Au(0) to control the potential.⁴⁹,⁵⁰ Following that, there is an immediate drop in Eh indicating the conversion of Au(I) to Au(0). This provides the necessary monomers for a nucleation event, both primary and secondary, at the beginning of region (I) (0-600 s). The sudden drop in the average GNP radius and
the leap in number concentration notify such an event. At the same time, similar to the experiment
15:85-70°C, true catalytic secondary nucleation gives rise to relatively anisotropic scatterers
(Supplementary Fig. 31b). In the presence of Au(I) and enhanced number concentration,45,50 the
colloidal destabilization of nanoparticles bring them closer to each other inducing electromagnetic
interaction effects (Supplementary Fig. 31c-e; Supplementary Figure 32b,c; Supplementary Fig. 32d,e
enhanced extinction in the wavelength range 600-800 nm and peak broadening). Here, a notable
difference is that the average GNP density starts to drop below the bulk value early on
(Supplementary Fig. 32a). Furthermore, the molar concentration of Au(0) exhibits no quiescent period
in its temporal evolution. This means that in region (I) a continuous but slow primary nucleation
competes with secondary nucleation and molecular growth. As a result, the number concentration
keeps increasing slowly while the former competition preserves a more or less constant particle size
(Supplementary Fig. 31a,f). In the meantime, secondary nucleation keeps increasing the mean aspect
ratio of the GNP scatterers (Supplementary Fig. 31b). From what we described here, region (I) in this
experiment resembles a combination of regions (I) and (II) of the typical mechanism presented in the
main text.

In region (II) (600-1500 s), following a deceleration in nucleation, colloidal destabilization induces an
agglomeration event. Consequently, the mean particle size increases while the GNP number
concentration goes down. Slow but continuous provision of Au(I) (Supplementary Fig. 32a,f) allows
for the densification of these agglomerates into aggregates (Supplementary Fig. 32a). Here, the
agglomeration being slower than in the typical mechanism, the rate of decrease in $\bar{\beta}$ is smaller. Close
to the end of this region, simultaneous with a quick drop in Eh (Supplementary Fig. 32f), the decrease
of $\bar{\beta}$ accelerates. The could be due to an accelerated coalescence of the agglomerates into
more compact morphologies.51

In region (III) (1500-1800 s), the previous aggregation process decelerates (Supplementary
Fig. 31a,f) while slow molecular growth continues to consume ionic gold (Supplementary Fig. 32a).
By the end of this region, the suspension is practically depleted from ionic Au (Supplementary Fig. 32a).

Finally, with no more ionic gold available in region (IV) (1800-3000 s) Ostwald ripening/interparticle ripening induces further enlargement in the average size and reduction in the average aspect ratio (Supplementary Fig. 31a,b,f and Supplementary Figure 32f).\textsuperscript{36,51,52} During this period, as the electromagnetic interaction effects disappear, the two optical theories (the EMT model and Gans) approach to similar outputs (Supplementary Fig. 38).

As one can see from the discussion above, the overall mechanism during the experiment 0:100-70°C is very similar to the general picture explained in the main text. In this respect, the decelerated rate of Au(I) production, due to the higher pH levels, renders the process more gradual and continuous compare to the experiment 15:85-70°C. Slower Au(I) formation also reduces the electromagnetic interaction effects which consequently introduces much less deviation from the predictions of the Gans theory (compare Supplementary Figure 38 with Supplementary Figure 33-37). Additional support for the proposed mechanism is presented in Supplementary Section 8 (using principal component analysis).
Supplementary Figure 23. Kinetics of gold nanoparticle growth (15:85-65°C experiment) from in situ UV-vis spectroscopy and model regression. a-e, Regressed physical parameters (and their corresponding 95% confidence bounds found by a heuristic search method\textsuperscript{46}) including mean particle radius (a), mean particle aspect ratio (b), number fraction of liquid-like superclusters (c), volume fraction of particles in superclusters (d), and mean supercluster radius (e). f, Temporal particle number concentration (along with the respective 95% confidence bounds\textsuperscript{46}) obtained from scaling the calculated extinction cross sections with the experimental spectra. Legends are common in all the plots and the grey-to-white shaded regions denote various mechanistic steps (denoted by Roman numerals in the first plot).
Supplementary Figure 24. Complementary kinetic data (15:85-65°C experiment) from *in situ* UV-vis spectroscopy and electrochemical potential measurements. a, Gold nanoparticle concentration (as mM Au(0); obtained from extinction at 400 nm²) and the estimated volumetric mass density of nanoparticles (with 95% confidence bounds found by a heuristic search method⁴⁶). b, Estimated percentage of electromagnetically interacting particles out of the overall population (i.e., interacting + noninteracting) along with the respective 95% confidence bounds.⁴⁶ c, Mean center-to-center distance between electromagnetically interacting nanoparticles both normalized to the average particle radius and in absolute units (with 95% confidence bounds⁴⁶). d, Experimental extinction spectra at selected temporal points. e, Temporal evolution of peak width at half-maximum obtained from experimentally measured spectra.⁶ f, *In situ* measured solution pH and reduction potential (Eh) (vs. Ag/AgCl/c(KCl) = 3 mol/L). The grey-to-white shaded regions (all the plots except for (d)) denote various mechanistic steps (denoted by Roman numerals in the first plot).
Supplementary Figure 25. Kinetics of gold nanoparticle growth (15:85-60°C experiment) from in situ UV-vis spectroscopy and model regression. a-e, Regressed physical parameters (and their corresponding 95% confidence bounds found by a heuristic search method) including mean particle radius (a), mean particle aspect ratio (b), number fraction of liquid-like superclusters (c), volume fraction of particles in superclusters (d), and mean supercluster radius (e). f, Temporal particle number concentration (along with the respective 95% confidence bounds) obtained from scaling the calculated extinction cross sections with the experimental spectra. Legends are common in all the plots and the grey-to-white shaded regions denote various mechanistic steps (denoted by Roman numerals in the first plot).
Supplementary Figure 26. Complementary kinetic data (15:85-60°C experiment) from in situ UV-vis spectroscopy and electrochemical potential measurements. a, Gold nanoparticle concentration (as mM Au(0); obtained from extinction at 400 nm) and the estimated volumetric mass density of nanoparticles (with 95% confidence bounds found by a heuristic search method). b, Estimated percentage of electromagnetically interacting particles out of the overall population (i.e., interacting + noninteracting) along with the respective 95% confidence bounds. c, Mean center-to-center distance between electromagnetically interacting nanoparticles both normalized to the average particle radius and in absolute units (with 95% confidence bounds). d, Experimental extinction spectra at selected temporal points. e, Temporal evolution of peak width at half-maximum obtained from experimentally measured spectra. f, In situ measured solution pH and reduction potential (Eh) (vs. Ag/AgCl/c(KCl) = 3 mol/L). The grey-to-white shaded regions (all the plots except for (d)) denote various mechanistic steps (denoted by Roman numerals in the first plot).
Supplementary Figure 27. Kinetics of gold nanoparticle growth (25:75-70°C experiment) from in situ UV-vis spectroscopy and model regression. a-e, Regressed physical parameters (and their corresponding 95% confidence bounds found by a heuristic search method\textsuperscript{46}) including mean particle radius (a), mean particle aspect ratio (b), number fraction of liquid-like superclusters (c), volume fraction of particles in superclusters (d), and mean supercluster radius (e). f, Temporal particle number concentration (along with the respective 95% confidence bounds\textsuperscript{46}) obtained from scaling the calculated extinction cross sections with the experimental spectra. Legends are common in all the plots and the grey-to-white shaded regions denote various mechanistic steps (denoted by Roman numerals in the first plot).
Supplementary Figure 28. Complementary kinetic data (25:75-70°C experiment) from in situ UV-vis spectroscopy and electrochemical potential measurements. a, Gold nanoparticle concentration (as mM Au(0); obtained from extinction at 400 nm) and the estimated volumetric mass density of nanoparticles (with 95% confidence bounds found by a heuristic search method). b, Estimated percentage of electromagnetically interacting particles out of the overall population (i.e., interacting + noninteracting) along with the respective 95% confidence bounds. c, Mean center-to-center distance between electromagnetically interacting nanoparticles both normalized to the average particle radius and in absolute units (with 95% confidence bounds). d, Experimental extinction spectra at selected temporal points. e, Temporal evolution of peak width at half-maximum obtained from experimentally measured spectra. f, In situ measured solution pH and reduction potential (Eh) (vs. Ag/AgCl/c(KCl) = 3 mol/L). The grey-to-white shaded regions (all the plots except for (d)) denote various mechanistic steps (denoted by Roman numerals in the first plot).
Supplementary Figure 29. Kinetics of gold nanoparticle growth (25:75-40°C experiment) from in situ UV-vis spectroscopy and model regression. a–c, Regressed physical parameters (and their corresponding 95% confidence bounds found by a heuristic search method) including mean particle radius (a), mean particle aspect ratio (b), number fraction of liquid-like superclusters (c), volume fraction of particles in superclusters (d), and mean supercluster radius (e). f, Temporal particle number concentration (along with the respective 95% confidence bounds) obtained from scaling the calculated extinction cross sections with the experimental spectra. Legends are common in all the plots and the grey-to-white shaded regions denote various mechanistic steps (denoted by Roman numerals in the first plot).
Supplementary Figure 30. Complementary kinetic data (25:75-40°C experiment) from in situ UV-vis spectroscopy and electrochemical potential measurements. a, Gold nanoparticle concentration (as mM Au(0); obtained from extinction at 400 nm) and the estimated volumetric mass density of nanoparticles (with 95% confidence bounds found by a heuristic search method). b, Estimated percentage of electromagnetically interacting particles out of the overall population (i.e., interacting + noninteracting) along with the respective 95% confidence bounds. c, Mean center-to-center distance between electromagnetically interacting nanoparticles both normalized to the average particle radius and in absolute units (with 95% confidence bounds). d, Experimental extinction spectra at selected temporal points. e, Temporal evolution of peak width at half-maximum obtained from experimentally measured spectra. f, In situ measured solution pH and reduction potential (Eh) (vs. Ag/AgCl/c(KCl) = 3 mol/L). The grey-to-white shaded regions (all the plots except for (d)) denote various mechanistic steps (denoted by Roman numerals in the first plot).
Supplementary Figure 31. Kinetics of gold nanoparticle growth (0:100-70°C experiment) from *in situ* UV-vis spectroscopy and model regression. a–e, Regressed physical parameters (and their corresponding 95% confidence bounds found by a heuristic search method46) including mean particle radius (a), mean particle aspect ratio (b), number fraction of liquid-like superclusters (c), volume fraction of particles in superclusters (d), and mean supercluster radius (e). f, Temporal particle number concentration (along with the respective 95% confidence bounds46) obtained from scaling the calculated extinction cross sections with the experimental spectra. Legends are common in all the plots and the grey-to-white shaded regions denote various mechanistic steps (denoted by Roman numerals in the first plot).
Supplementary Figure 32. Complementary kinetic data (0:100-70°C experiment) from in situ UV-vis spectroscopy and electrochemical potential measurements. a, Gold nanoparticle concentration (as mM Au(0); obtained from extinction at 400 nm") and the estimated volumetric mass density of nanoparticles (with 95% confidence bounds found by a heuristic search method\(^{46}\)). b, Estimated percentage of electromagnetically interacting particles out of the overall population (i.e., interacting + noninteracting) along with the respective 95% confidence bounds.\(^{46}\) c, Mean center-to-center distance between electromagnetically interacting nanoparticles both normalized to the average particle radius and in absolute units (with 95% confidence bounds\(^{46}\)). d, Experimental extinction spectra at selected temporal points. e, Temporal evolution of peak width at half-maximum obtained from experimentally measured spectra.\(^{6}\) f, In situ measured solution pH and reduction potential (Eh) (vs. Ag/AgCl/c(KCl) = 3 mol/L). The grey-to-white shaded regions (all the plots except for (d)) denote various mechanistic steps (denoted by Roman numerals in the first plot).
Supplementary Section 7. Temporal regression results common to both EMT and noninteracting (Gans) models

Supplementary Figure 33. Temporal evolution of optimal model outputs common between the Gans and the EMT formalisms (15:85–70°C experiment). a, Mean particle radius. b, Mean particle aspect ratio. c, Particle number concentration. d, Estimated particle density. 95% confidence bounds were found by a heuristic search method\textsuperscript{46} and the legends are common in all the plots. The grey-to-white shaded regions denote various mechanistic steps (denoted by Roman numerals in the first plot).
Supplementary Figure 34 Temporal evolution of optimal model outputs common between the Gans and the EMT formalisms (15:85-65°C experiment). a, Mean particle radius. b, Mean particle aspect ratio. c, Particle number concentration. d, Estimated particle density. 95% confidence bounds were found by a heuristic search method and the legends are common in all the plots. The grey-to-white shaded regions denote various mechanistic steps (denoted by Roman numerals in the first plot).
Supplementary Figure 35 Temporal evolution of optimal model outputs common between the Gans and the EMT formalisms (15:85-60°C experiment). a, Mean particle radius. b, Mean particle aspect ratio. c, Particle number concentration. d, Estimated particle density. 95% confidence bounds were found by a heuristic search method\(^{46}\) and the legends are common in all the plots. The grey-to-white shaded regions denote various mechanistic steps (denoted by Roman numerals in the first plot).
Supplementary Figure 36. Temporal evolution of optimal model outputs common between the Gans and the EMT formalisms (25-75-70°C experiment). a, Mean particle radius. b, Mean particle aspect ratio. c, Particle number concentration. d, Estimated particle density. 95% confidence bounds were found by a heuristic search method and the legends are common in all the plots. The grey-to-white shaded regions denote various mechanistic steps (denoted by Roman numerals in the first plot).
Supplementary Figure 37. Temporal evolution of optimal model outputs common between the Gans and the EMT formalisms (25-75°C experiment). a, Mean particle radius. b, Mean particle aspect ratio. c, Particle number concentration. d, Estimated particle density. 95% confidence bounds were found by a heuristic search method and the legends are common in all the plots. The grey-to-white shaded regions denote various mechanistic steps (denoted by Roman numerals in the first plot).
Supplementary Figure 38. Temporal evolution of optimal model outputs common between the Gans and the EMT formalisms (0:100-70°C experiment). a, Mean particle radius. b, Mean particle aspect ratio. c, Particle number concentration. d, Estimated particle density. 95% confidence bounds were found by a heuristic search method and the legends are common in all the plots. The grey-to-white shaded regions denote various mechanistic steps (denoted by Roman numerals in the first plot).

Supplementary Section 8. Principal component analysis on temporal spectra

Principal component analysis (PCA) is a useful and accessible tool to identify the major contributors to an overall signal. For an evolving colloidal suspension, the optical response can be decomposed into linearly uncorrelated variables, called principal components (PCs), giving coefficients (or loadings) with their corresponding temporal scores. In simple words, each coefficient represents the spectral signature of a PC while the score correlates with the weight (significance) of that PC at a specific time. PCA has a limitation in the sense that each spectrum is assumed to be a linear combination of several pure spectra. A tacit assumption in the previous statement is the constancy of
the pure spectra (over time), which does not hold for a growing colloidal metal suspension. Therefore, PCA would detect artificial compounds, the linear combinations of which give the temporal spectra. Nevertheless, it is not possible to assign the coefficients to particular species.\textsuperscript{53,54} In spite of these limitations, PCA allows for estimating the number of contributing phenomena and provides approximate optical signatures for each of them.

With the introduction above in mind, PCA over a spectral range 400-800 nm on the data from the experiment 15:85-70°C implies that there are three main contributors (Supplementary Fig. 39; the fourth PC is practically capturing noise as implied by its noisy coefficient and low score throughout the process; the data are centered before PCA). Note that there is no contribution from the dissolved ionic gold species nor from the organic compounds in the selected spectral range. Therefore, only three PCs, all originating from the colloidal nanoparticles, capture > 99.8% of the temporal variation in the spectra with individual contributions 75.9, 22.8, 1.3% for PCs 1 to 3, respectively.

Taking a closer look at the coefficient plot reveals that the first PC (Supplementary Fig. 39a; red dots) is mainly related to individual GNPs with their localized surface plasmon resonance (LSPR) band around 520 nm. The corresponding score plot (Supplementary Fig. 39b) indicates a monotonic evolution toward the final GNPs that are larger.

The second PC (Supplementary Fig. 39a; gray dots) exhibits an inverse behavior close to the LSPR band (LSPR damping) while it correlates with the enhanced extinction in the range 600-800 nm. The corresponding score grows to a maximum and drops subsequently (Supplementary Fig. 39b). Thus, this PC majorly represents the electromagnetic interactions between the particles that appear early on, grow as the particles approach each other, and fade out as they peptize back to noninteracting scatterers. Mikhlin et al. identified very similar temporal evolution during the one-pot synthesis of GNPs, where large (100-500 nm) 3D networks of GNPs suspended in aqueous droplets appeared early on and disintegrated as the process proceeded to the end.\textsuperscript{13,14,35} As discussed in the main text, the electromagnetic interactions arise from colloidal destabilization caused by the replacement of citrate ions by Au(I) moieties on the surface of GNPs which brings the particles closer to each other. This
has been confirmed by previous AFM, DLS, electrophoretic, SAXS, and UV-vis spectroscopic measurements. In addition, very recent in situ TEM studies on a seeded growth process discovered the possibility of new GNP nucleation in the close vicinity of the already present particles and correlated this observation with similar optical behavior (Fig. 1 Ref. 51). This can inherently bring about an electromagnetic interaction between the particles.

Finally, the third PC (Supplementary Fig. 39a; purple dots) demonstrates a similar coefficient behavior as PC2 but with a narrower peak around 580 nm and a sharper contrast between this peak and the LSPR-damping band. The contrast signifies the distinction between longitudinal and transversal extinction cross sections in prolate-shaped particles. Therefore, this PC can mainly be ascribed to the particle shape evolution that dampens the LSPR band and enhances the extinction in the red region. Looking at Supplementary Figure 39b, the temporal variation in the corresponding score plot correlates quite closely with the evolution observed in $\tilde{\beta}$ (Fig. 2b in the main text).

As we discussed in Supplementary Section 6, all the datasets exhibit very similar mechanistic behavior (with different time scales). PCA plots reflect this similarity as well (Supplementary Figs. 39-43). The most important difference is in the experiment 0:100-70°C, where the electromagnetic interaction effects are far less significant compared to the rest of the experiments. Quantitatively, PC1 to PC3 account for 94.9, 5, and 0.1% of the variance, respectively. Therefore, the contribution of electromagnetic interactions is around 4.5 times less than that in the experiment 15:85-70°C. The corresponding PCA plots also validate this statement. In this respect, conferring Supplementary Fig. 44b we see that the score corresponding to PC2 is considerably smaller than in the other datasets (Supplementary Figs. 39-43b).

As noted earlier, the collective nonlinear combination of the three effects identified by PCA (i.e., the average size of individual GNPs, their aspect ratio, and the electromagnetic interactions between them) dictates the temporal optical behavior of the particle ensemble. This nonlinear (and correlated) dependence does not allow for a one-to-one quantitative correlation between the PCs and the physical characteristics. That is why we tackled the problem directly adopting the nonlinear regression of a
physicochemical model to the experimental data. Nevertheless, as we discussed above PCA does provide qualitative insight about the physics of the problem and provides support for the proposed theoretical framework.

Supplementary Figure 39. Principal component analysis on temporal UV-vis spectra (15:85-70°C experiment). a, PCA coefficients. b, PCA scores. Legends are common in both plots.

Supplementary Figure 40. Principal component analysis on temporal UV-vis spectra (15:85-65°C experiment). a, PCA coefficients. b, PCA scores. Legends are common in both plots.
Supplementary Figure 41. Principal component analysis on temporal UV-vis spectra (15:85-60°C experiment). a, PCA coefficients. b, PCA scores. Legends are common in both plots.

Supplementary Figure 42. Principal component analysis on temporal UV-vis spectra (25:75-70°C experiment). a, PCA coefficients. b, PCA scores. Legends are common in both plots.

Supplementary Figure 43. Principal component analysis on temporal UV-vis spectra (25:75-40°C experiment). a, PCA coefficients. b, PCA scores. Legends are common in both plots.
Supplementary Figure 44. Principal component analysis on temporal UV-vis spectra (0:100-70°C experiment). a, PCA coefficients. b, PCA scores. Legends are common in both plots.

Supplementary Section 9. Representative confidence regions at the onset of interaction effects

In this section, we have presented representative 95% confidence (likelihood) regions estimated for individual model parameters obtained from regression with the EMT model. The confidence regions are estimated using the approach presented by Schwaab et al. This heuristic method of constructing the confidence bounds provides an invaluable and easy-to-use visual tool to assess the behavior of the model at hand. Below, we have provided such plots for the experiment 15:85-70°C at several time points during the seeded growth process. Initially, in the absence of electromagnetic interaction between the particles, only parameters common with the Gans theory ($\bar{r}_{\text{GNP}}, \bar{\beta}$, and GNP concentration) are well constrained (Supplementary Figs. 45 and 46). For these parameters, $f_{\text{val}} \equiv 100 \times \chi^2 = 100 \times \sum_i (A_{\text{experimental}} - A_{\text{calculated}})^2$ assumes a parabolic shape near the minimum (Supplementary Fig. 45a,b,f and 46a,b,f). On the contrary, $x_{\text{SC}}, f$, and $\bar{r}_{\text{SC}}$ adopt very broad confidence regions, which implies model insensitiveness with respect to these parameters (Supplementary Figs. 45c,d,e and 46c,d,e). As the interaction effects emerge, parabolic basins of attraction develop for the EMT parameters as well (Supplementary Figs. 47-52). Particularly at the onset of interaction, there might be several basins of attraction and/or oddly shaped likelihood regions (Supplementary Figs. 48-51). This is a common observation in nonlinear regression problems and
similar examples are provided by Schwaab and coworkers.\textsuperscript{46,55} On the other hand, when the interaction effects are strong enough, the likelihood regions become narrow and close to parabolic for all the parameters (Supplementary Fig. 52).

**Supplementary Figure 45.** 95\% confidence regions (for individual model parameters) as estimated by the heuristic method of Schwaab et al.\textsuperscript{46} (15.85-70\degree C experiment; t = 20 s).
Supplementary Figure 46. 95% confidence regions (for individual model parameters) as estimated by the heuristic method of Schwaab et al. (15:85-70°C experiment; t = 60 s).

Supplementary Figure 47. 95% confidence regions (for individual model parameters) as estimated by the heuristic method of Schwaab et al. (15:85-70°C experiment; t = 110 s).
Supplementary Figure 48. 95% confidence regions (for individual model parameters) as estimated by the heuristic method of Schwaab et al. (15:85-70°C experiment; t = 120 s).

Supplementary Figure 49. 95% confidence regions (for individual model parameters) as estimated by the heuristic method of Schwaab et al. (15:85-70°C experiment; t = 130 s).
Supplementary Figure 50. 95% confidence regions (for individual model parameters) as estimated by the heuristic method of Schwaab et al.46 (15:85-70°C experiment; t = 140 s).

Supplementary Figure 51. 95% confidence regions (for individual model parameters) as estimated by the heuristic method of Schwaab et al.46 (15:85-70°C experiment; t = 150 s).
**Supplementary Figure 52.** 95% confidence regions (for individual model parameters) as estimated by the heuristic method of Schwaab et al.\textsuperscript{46} (15:85-70°C experiment; t = 350 s).

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