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*Original Scientific Paper*

# Phase Transition in Monodisperse Gold Sol. Microscopic Observation of Gas, Liquid and Solid States

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A gold sol of narrow size distribution with particles 120 nm in average diameter undergoes phase transition from gaseous (dispersed) state to solid (crystalline) state *via* liquid state when the concentration of the counterions in the medium is increased. The phenomenon takes place in a very thin layer of the settled sol, as observed with a microscope at 2000× magnification. The transition from the gaseous to the liquid state occurs at the ion concentration of $\approx 0.02$ mol dm$^{-3}$ in a deposit of a number of small drops of a few micrometers in diameter. These »drops« start to crystallize at $\approx 0.03$ mol dm$^{-3}$. After ten hours, the sol is converted into a state in which the solid and its vapor (dispersed sol) coexist. The phenomenon is quite reversible. On dilution with water, the solid phase redisperses into the original gaseous state.

## INTRODUCTION

The possibility of phase transition in lyophobic colloids, as the effect of the secondary minimum in the interaction potential, has long been discussed[1,2] and sought.[3–6] Instead, reversible aggregations were observed in suspensions of very large particles. These phenomena were certainly an indication of the phase transition, but not of the thermodynamic phase transition. Particles in those suspensions were too large to participate in the lat-

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This article is dedicated to Professor Egon Matijević on the occasion of his 75th birthday.

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ter process. In contrast, with colloids of small particles the van der Waals force is weak and the potential minimum is too shallow to capture particles. This minimum can be made deeper by raising the electrolyte concentration of the medium; however, before the minimum becomes deep enough to capture the particles, the potential maximum, which is responsible for the stability of the system, disappears and the system coagulates irreversibly. This behavior, typical for the so called lyophobic colloids, originates from the small value of the Hamaker constant of particles. If this constant is very large, strong van der Waals force will produce a deep potential minimum at a moderate ion concentration where the dispersion stability is still maintained, and reversible aggregation can occur. The aggregates thus formed would be soft, allowing the particles to move around, corresponding to a liquid state. With the raise of the ion concentration, the potential minimum becomes deeper and the inter-particle distance shorter. As a consequence the particles in the aggregates are immobilized, causing a change from the »liquid« to the »solid« state. If the sol is monodisperse, the solid must have a crystalline structure. Thus, a lyophobic colloid of a large Hamaker constant, should appear in three states of matter, *i.e.*, gas, liquid, and solid. A gold sol of monodisperse large particles meets these conditions due to the exceedingly high Hamaker constant, which produces a strong van der Waals force.

This study describes such a sol and confirms the existence of the three states in it, which were observed clearly in a microscope, together with the dynamics of the phase transition phenomena.

## EXPERIMENTAL

### *Preparation of the Gold Sol*

The gold sol was prepared *in situ* by the reduction of a $NaAuCl_4$ solution with hydrazine, which is a common process,[7] by a modified procedure using seeds and a surfactant.

The amount of the sol was very small, since the preparation was carried out directly in a cell for microscopic observation. The latter was made from a glass tube 6 cm long and 18 mm in diameter, the bottom of which consisted of a cover slip cemented to one end of the tube with an epoxy resin. The surface of the bottom floor was cleaned with a 1% solution of a surfactant (sodium dodecyl benzene sulphonate), in order to avoid the gold particles from sticking to the glass and obscure the observation of the phenomena.

Reactant solutions were poured into the cell in the following order:

(1) 0.5 $cm^3$ of an 1% solution of the surfactant (sodium dodecyl benzene sulfonate).

(2) 4 $cm^3$ of a 0.002 mol $dm^{-3}$ $NaAuCl_4$ solution.

(3) 4 drops (1/20 $cm^3$) of a seed dispersion.*

(4) 2.4 $cm^3$ of 0.002 mol $dm^{-3}$ hydrazine sulfate solution.

The turbidity appeared a few seconds after the injection of the solution No. 4, and the reaction ended in less than one minute, yielding a reddish brown suspension. SEM picture of particles are shown in Figure 1. The resulting particles were polydispersed with an average diameter of 120 nm, and their $\zeta$-potential was $-50 \pm 5$ mV.

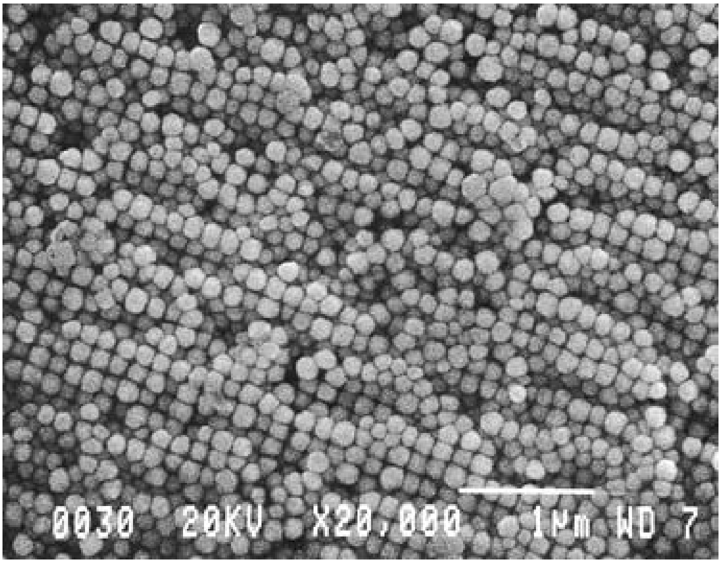

Figure 1. Scanning electron micrograph (SEM) of gold particles, having an average diameter of 120 nm. Despite their size distribution the particles tend to arrange themselves during the drying process of specimen preparation.

The sol so prepared was very stable and it was used in all experiments. The medium of the sol contained $Na^+$, $H^+$, $Cl^-$, $SO_4^{2-}$, and the surfactant ions. The total cation concentration in the medium is estimated to be $\approx 0.008$ mol $dm^{-3}$. In the study of the phase transition, KCl was used to vary the total ionic strength. Since the charge of the particles was negative, the cation concentration determined the dispersion behavior.

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* The seed sol was obtained by adding rapidly 4 $cm^3$ of a 0.02 mol $dm^{-3}$ sodium citrate solution into 10 $cm^3$ of a boiling solution of 0.001 mol $dm^{-3}$ $NaAuCl_4$. A few minutes after removing the solution from the heater, red color appeared. The sol was then diluted fiftyfold with water.

## RESULTS AND DISCUSSION

Gold particles settled completely in ≈ 20 hours, forming a thin layer at the bottom of the cell leaving a transparent supernatant solution above it. All phenomena took place in this thin layer, which were observed through the bottom floor with an inverted metallurgical microscope at 2000× magnification by using immersion. The addition of the KCl solution was carried out carefully not to disturb the sediment. To do so, the supernatant solution was removed with a pipet into a small beaker, to which KCl was added, and then the liquid was returned into the observation cell. The gold particles in the original sol were observed to move freely without aggregation, indicating the potential minimum to be very shallow at the ion concentration of 0.008 mol dm$^{-3}$.

On settling (after a sufficiently long time) the settled layer consisted of a dense population of particles, which were freely oscillating, corresponding to the state of a high density gas.

When the ion concentration was raised stepweise to 0.02 mol dm$^{-3}$, the sol became unstable showing vigorous density fluctuation and in a few tens of seconds separated into two phases depositing a number of small round

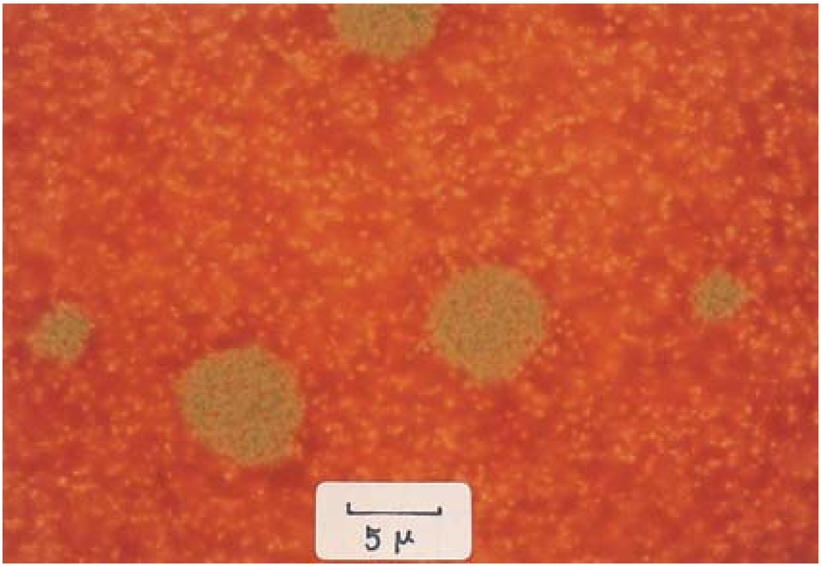

Figure 2. The state of phase separation in the dense sediment of sol particles at the 1–1 ion concentration or 0.02 mol dm$^{-3}$. Yellow round regions are drops of liquid state sol, which undergo Brownian motion, forming larger drops by coalescence of the small ones.

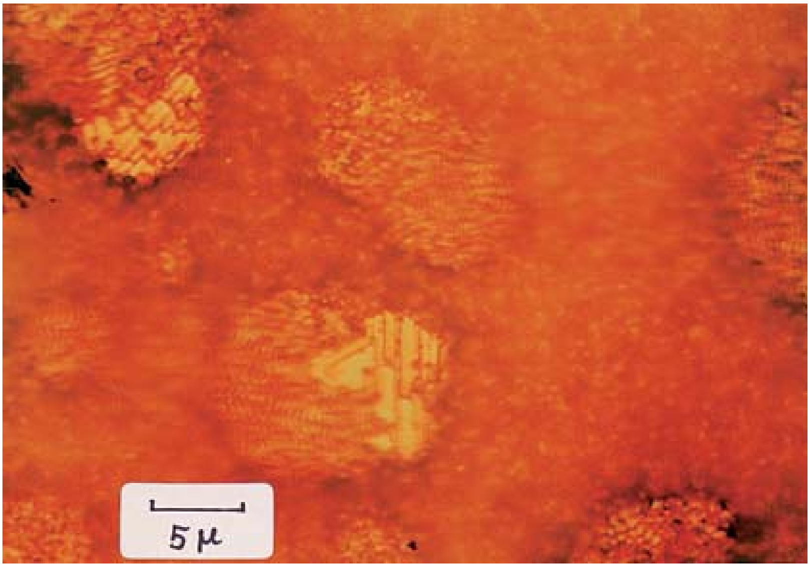

Figure 3. The start of the crystallization of gold sediment at an ion concentration of 0.03 mol $dm^{-3}$. The bright yellow regions are the crystalline phase in the progress of growing. Although three phases are seen, they do not represent the state of triple point in equilibrium.

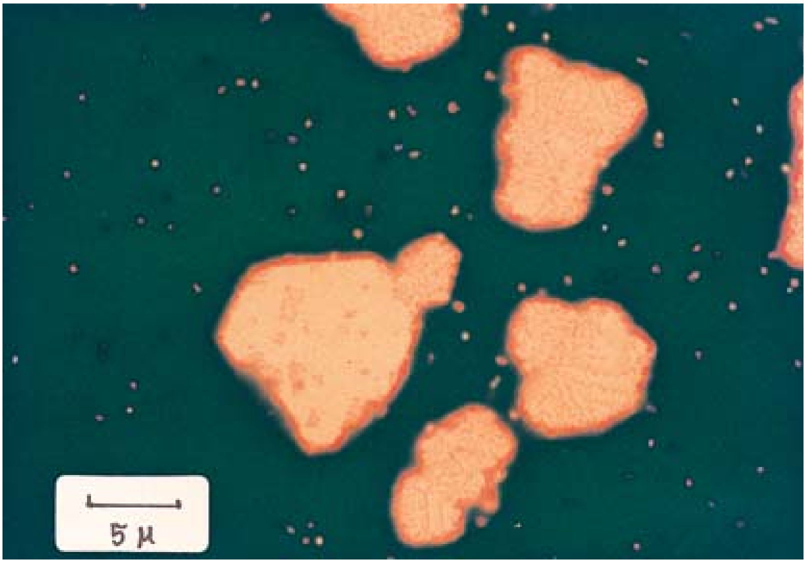

Figure 4. The state of the sol 24 hours after the onset of crystallization. All droplets are recognized to be in the crystalline state, although the picture is out of focus. It is significant that the vapor (dispersed) phase is very thin.

domains, a few micrometers in diameter, as shown in Figure 2. These domains were yellow and contained a high density of particles, which were moving sluggishly. The round shape of the domains must have been the effect of the surface tension, and the new phase was without doubt in the liquid state. These domains, now to be called liquid drops, were the subject of the Brownian movement, which on contact coalesced into larger drops. The figure shows the condition several minutes after the phase separation.

At the ion concentration of 0.03 mol $dm^{-3}$, the second new phase appeared in every drop, which was bright yellow and grew fast into geometrical shapes, triangular or trapezoidal, as shown in Figure 3. This second new phase was a crystalline solid, which finally occupied the entire area of each drop in contact with its »vapor« (the dispersed sol), as shown in Figure 4. Although the picture is out of focus, the geometrical shape of the solid phase is evident. Blurred periphery is due to the motion of particles at the »solid-vapor« boundary. The low density of the vapor phase indicates that the minimum in the DLVO-potential is now very deep.

The described phenomena were perfectly reversible; on dilution with water, the solid phase re-dispersed into the liquid phase.

## CONCLUSIONS

Gold particles having average diameter of 120 nm, undergo phase transition from a gas to a solid *via* liquid state, caused by an increase in the ion concentration of the medium, which is a form of reversible aggregation in a lyophobic sol. The analogy between molecular and colloid system is now established.

In spite of the clear evidence of the phase transition, any quantitative information about the depth of the secondary minimum was not obtained in the present study. To do so a comparison of particle density between two phases at equilibrium, vapor and solid, or vapor and liquid, is needed. The former case seems to be promising, if larger sol particles were used.

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## SAŽETAK

### Fazni prijelaz u monodisperznom solu zlata. Mikroskopska promatranja plinovitog, tekućeg i čvrstog stanja

*Sei Hachisu*

Sol zlata s česticama uske raspodjele, promjera 120 nm, podložan je faznoj promjeni. Povećanje koncentracije protuiona uzrokuje prijelaz plinovitog (dispergiranog) stanja u čvrsto (kristalno) stanje. Ta se pojava zbiva u vrlo tankom sloju istaloženog sola što je zapaženo pomoću mikroskopa s povećanjem od 2000 ×. Pri koncentraciji iona od oko 0,02 mol dm$^{-3}$ zbiva se prijelaz iz plinovitog u tekuće stanje s brojnim malenim kapljicama. Te »kapljice« počinju kristalizirati kod koncentracije iona od oko 0,03 mol dm$^{-3}$. Nakon deset sati sol prelazi u stanje u kojem koegzistiraju čvrsto i plinovito stanje (dispergiran sol). Ta je pojava reverzibilna. Čvrsta faza prelazi u prvotno plinsko stanje razrjeđivanjem pomoću vode.