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Particle size and sol stability in metal colloids*)

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With 4 figures

The calculation of *London-van der Waals* dispersion forces between metal surfaces leads to *Hamaker* constants of about $A = 5 \times 10^{-12}$ ergs. (1, 2). In model experiments (1, 2, 3) attractive forces of this order of magnitude have indeed been found. It is not clear how colloidal metals with such a large attraction between the particles can be stabilized by the repulsion of electrical double layers if the double layer potentials and the electrolyte concentrations are anywhere near the values which are pertinent for metal sols. Still, metal sols are the typical electrocratic colloids. For instance they beautifully obey the rule of *Schulze* and *Hardy*, which indicates that the stability and the coagulation of these sols are governed by the state of the electrical double layers.

Particle sizes of the order of 10^{-6} cm abound in metal sols. In non-metallic colloids the particles are typically larger by a factor of at least ten. So it occurred to us that the experimentally well known but theoretically not too well understood stability of colloidal metals might have to do with the smallness of the particles in metal sols. If this hypothesis proves correct coagulation concentrations in metal sols depend on the particle size in such a way that the highly disperse colloids are more stable than the coarser ones. This is a rather unorthodox position: it is traditional (4) to derive that coagulation concentrations are independent of particle size. From the analysis of coagulation kinetics on the basis of the slope of $\log W - \log c$ curves (5) it can even be inferred that in actual determinations of coagulation concentrations the coarser suspensions will seem more stable than those with small particles, and not the other way round.

Experimental

Series of monodisperse metal sols of increasing particle radius (50–1000 Å) were obtained. In these series coagulation concentrations were determined. It was found that in such a series of chemically identical monodisperse metal sols the coagulation concentration decreases when the particle size increases. In mixtures of two monodisperse colloids with small and large particles respectively it was observed that the larger particles coagulate at salt concentrations where the small particles remain as a stable sol.

a) Preparation of monodisperse metal sols

Monodisperse gold sols were obtained with the citrate method (6, 7), or with *Zsigmondys* method (8) where very small (nuclear) gold particles serve as a catalyst for the reduction of $HAuCl_4$ with hydroxylamine. Small particle silversols were obtained with *Carey Leas* method and purified by repeated coagulation with Na_3 citrate and $NaNO_3$ (9). Coarser silversols were prepared in a way analogous to the citrate method for gold sols: 2 ml 1% Na_3-citrate solution were added to 100 ml of a boiling solution of 10^{-3} M $AgNO_3$ and boiling was continued for 15 min. The large silver particles were centrifuged off, and the sediment was redispersed in water. After repeated centrifugation and redispersion in 50 ml water 1 ml 1% Na_3 citrate was added to the greenish brown silversol.

It was observed that monodisperse gold sols of different particle sizes are obtained by the citrate method when the citrate concentration during the preparation is varied, and the amount of gold to be reduced is kept constant. Details will be published separately. It seems that the available gold is distributed over more or fewer particles, the initial number of nuclear particles being determined by the citrate concentration.

b) The determination of coagulation concentrations

Colloids of different particle sizes were all brought to the same final concentrations (e.g. of gold and Na_3 citrate in sols prepared with the citrate method). In these sols coagulation concentrations were determined. It was used as a criterion for rapid coagulation that the color change which is typical for the coagulation of metal sols (10) was completed within a minute after the addition of inert electrolyte. Coagulating salts with monovalent, nonadsorbing ions (KNO_3, $NaNO_3$) were used. The lowest concentration at which rapid coagulation was observed will be called the coagulation concentration throughout this paper.

c) Fractionated coagulation

Mixtures were made of two chemically identical monodisperse metal (Au or Ag) sols of a rather different particle size (e.g. of sols with average radii of 75 Å and 800 Å respectively). These mixtures were left to equilibrate for a few days, but no changes were observed.

The coagulation concentrations of the individual sols were determined (vide supra). It was found that highly disperse sols were more stable than coarse suspensions. The experiments with mixtures were under-

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taken to show that this was indeed an effect of particle size, and not of the chemistry or the concentration of the individual sols.

After the equilibration of the mixtures $NaNO_3$ was added to them in such amounts that the resulting salt concentration was near the coagulation concentration for the coarser particles, but well below the coagulation concentration which had been measured for the finer dispersion. The particle size distribution in the mixture before and at different times after the addition of salt was determined from electron micrographs.

d) Electron microscopy

Electron micrographs were made with a Philips EM 300 electron microscope, of sol droplets which were sprayed and dried on hydrophilic formvar. The particle size distributions of the mixed sols were obtained by counting at least hundred particles and assigning them on the basis of their markedly different size to one or the other of the original monodisperse sols. It was preferred to count all the particles that had been present in single droplets of the sol, so that the resulting distribution was independent of fractionation into groups of particles of different size which sometimes accompanied the drying up of a sol droplet.

Results

The coagulation concentration as a function of particle size in a typical series of chemically identical (citrate gold) monodisperse metal sols is given in fig. 1. Analogous results were obtained with other colloidal metals. It follows from our definition of a coagulation concentration that we determined concentrations of moderately rapid coagulation as coagulation concentrations. Under such circumstances there may still be a small maximum in the potential energy curve. As the potential energy of two particles is proportional with their radius a slight increase with the radius is expected of the determined coagulation concentrations. Instead we found a marked decrease of the coagulation concentration as the radius increases.

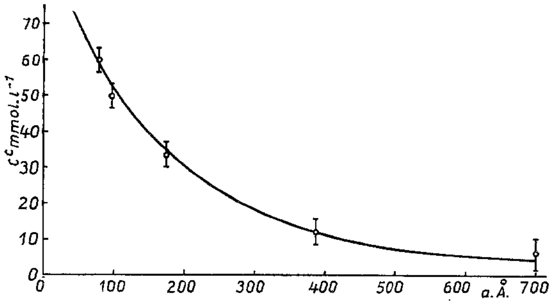
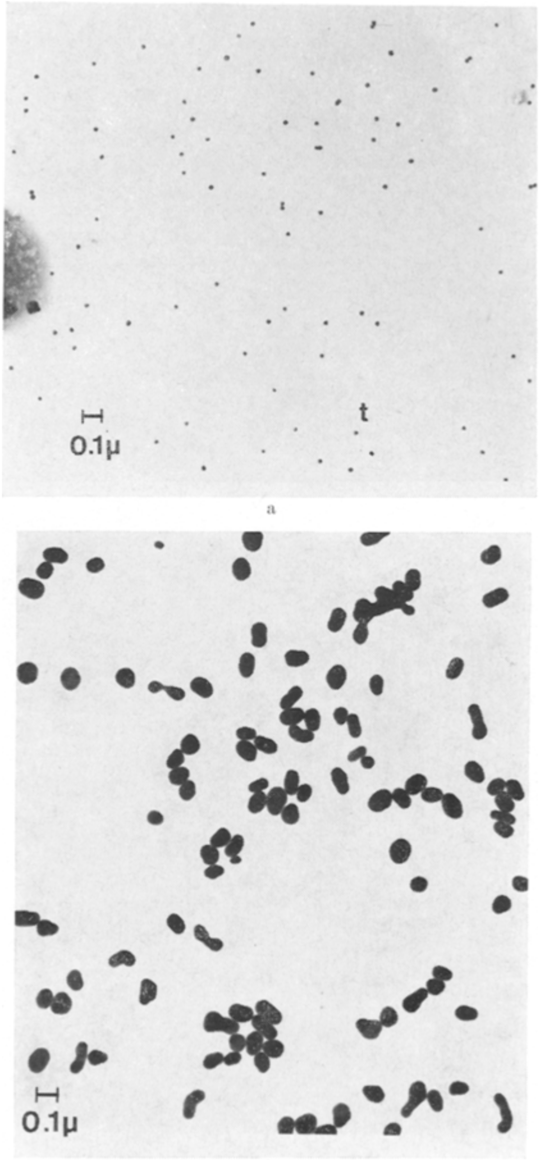


Fig. 1. Coagulation concentration C_c as a function of the particle radius a in a citrate sol

The observed decrease in the coagulation concentration in a series of individual sols could in principle still be related to the chemistry or the sol concentration of these colloids. This is not the case for experiments with mixed equilibrated sols.

The fractionation of a mixture according to particle size is illustrated by fig. 2. The small gold particles of fig. 2a and the larger ones of fig. 2b were mixed (fig. 2c). After the addition of enough $NaNO_3$ (e.g. 30 mmoll^{-1}) for the coagulation of the larger particles (cf. fig. 1) there remained a stable sol with the particle size distribution of fig. 2d.

The process of separation (fractionated coagulation) could be followed visually. The sol of small particles (2a) was a clear orange-



a

b

Fig. 2 (Legend vide p. 738)

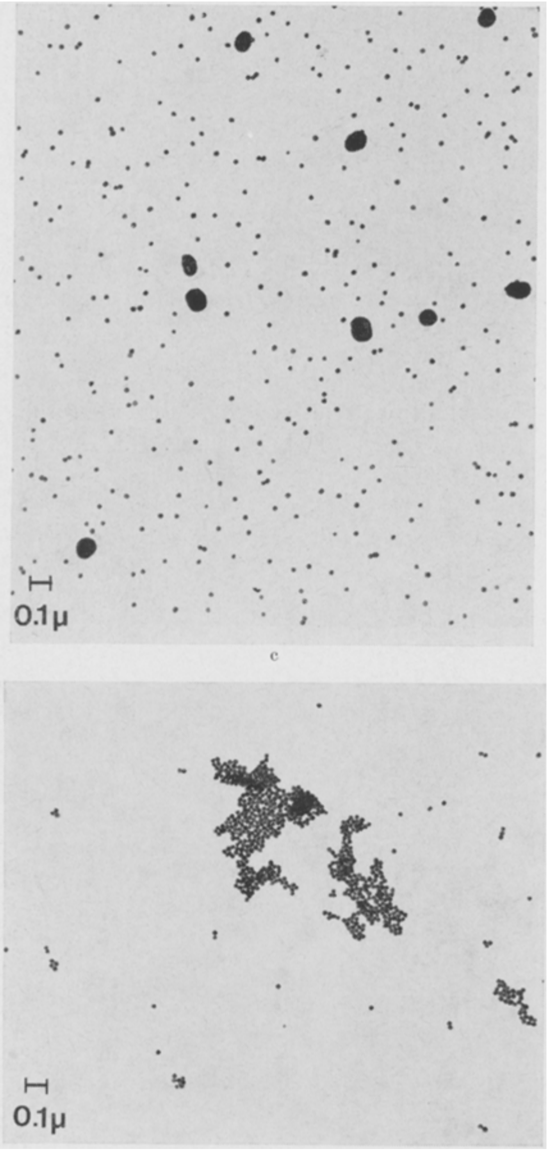


Fig. 2. Fractionated coagulation: 2a: the monodisperse sol of small particles; 2b: the monodisperse sol of large particles; 2c: mixture of the sols 2a and 2b; 2d: particles of the remaining sol after fractionation

red sol, but the sol of larger particles (2b) and by consequence also the mixture (2c) gave a strong *Tyndall* effect. When salt was added to the mixture a rapid decrease of the *Tyndall* effect could be observed. After an hour the *Tyndall* effect had disappeared completely. The sol, which had turned violet upon the addition of salt was clear red again, and a black sediment formed. The color of the supernatant red sol was the same as that of a sol with only the small particles and of the same or a slightly smaller concentration. This red color remained for hours, or even days, which indicates that the small particle colloid was completely stable at this concentration, and that no aggregates had formed in it (10).

The best separation according to particle size – with the number of small particles in the mixture and the remaining stable supernatant sol practically the same and complete removal of the larger particles from the mixture – was obtained at electrolyte concentrations slightly below the coagulation concentration for the larger particles. At higher salt concentrations the aggregating large particles would carry small particles with them into the sediment even though the eventual supernatant was a stable sol of small particles.

Fig. 3 is direct experimental proof that the fractionation of mixed monodisperse metal sols is caused by the selective coagulation of the larger particles. It is a micrograph of a mixture of large and small (hydroxylamine) gold particles. Enough electrolyte was added to bring about the decrease of the *Tyndall* effect in the mixture which is the visual indication for fractionated coagulation. This time however the sol was sprayed onto the formvar for electron microscopic investigation shortly after the addition of salt and long before the aggregated particles had settled. In the electron microscope it was found that practically

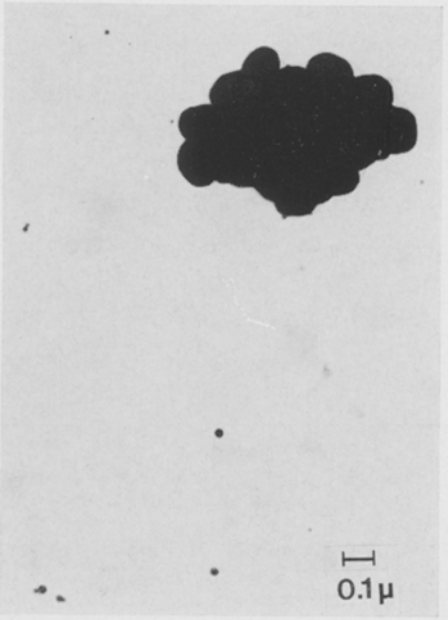


Fig. 3. An aggregate of large particles in a sol of stable small particles

all the large particles from the mixture had formed aggregates like the one in fig. 3, whereas the small particles were spread out on the formvar in the way which is usual for a stable sol. Inspection of the perimeter of the aggregates revealed that hardly any small particles take part in them even if the small particles outnumber the larger ones in the original mixture in a ratio of 10:1. In such preparations where coagulation was interrupted many aggregates like the one in fig. 3 were found and we have never observed that this type of aggregation was brought about in stable sols by the preparation techniques for electron microscopy. We believe therefore, that these aggregates are typical for the state of affairs in a mixture of monodisperse metal sols under the conditions of fractionated coagulation.

With mixtures of gold-(citrate or hydroxylamine) and of silver sols we obtained the same results. It seems therefore that the fractionated coagulation of metal sols is not dependent on the chemistry of the particular colloid, but that it is an effect common to metal sols, and perhaps other systems. The cause for fractionation appears not to lie in the polydispersity of the system as such, but in the lesser stability against electrolytes of the larger particles in a mixture.

Discussion and conclusions

Eq. [1] gives the non retarded *van der Waals* attraction between two spheres according to *Hamaker* (11):

$$V_A = -\frac{A}{6}\left[\frac{2}{S^2-4}+\frac{2}{S^2}+\ln\frac{S^2-4}{S^2}\right]. \qquad [1]$$

V_A is the potential energy of attraction; A is the *Hamaker* constant. $S = R/a = 2 + (H/a)$, with R the distance between the centers of two spheres of (equal) radius a, and H the shortest distance between the metal surfaces. For small values of H/a the approximate eq. [2] can be used.

$$V_A = -\frac{aA}{12H}. \qquad [2]$$

The eqs. [1] and [2] are represented in fig. 4. There is an important discrepancy between them for $0.1 < H/a$. For large H/a the exact formula [1] leads to a smaller attraction than [2].

The kinetics of coagulation are governed by the sum of V_A and the repulsion energy V_R. This sum has a maximum at about $\varkappa H = 1$, when the particles are approximately one *Debye* length apart. In our experiments coagulation concentrations were at *Debye* lengths of 20 Å or thereabout. With the small particles (100 Å) of metal sols this makes $H/a > 0.1$ when the potential energy of interaction is at its maximum. In the coarser non-metallic systems eq. [2] can fruitfully be applied for coagulation problems but this is not so for the small particles which are described in this paper. At the maximum of the interaction of the small particles V_A is given by the exact eq. [1].

The repulsion energy V_R has been calculated numerically (12, 13). It remains proportional with a down to $\varkappa H = 1$, $H/a = 0.2$ and beyond. V_R at $\varkappa H = 1$ can be represented by a straight line in fig. 4, just like $-V_A$ at $H = 1/\varkappa$ according to eq. [2] since both are at a constant interparticle distance and proportional with a. These lines for V_R and $-V_A$ are parallel. As long as $V_R > V_A$ there is a positive potential energy at $\varkappa H = 1$, near the maximum. If however the line for V_R at $\varkappa H = 1$ is below that for eq. [2] it must intersect the exact curve of eq. [1] for V_A at $H = 1/\varkappa$. In that case the potential energy at $\varkappa H = 1$

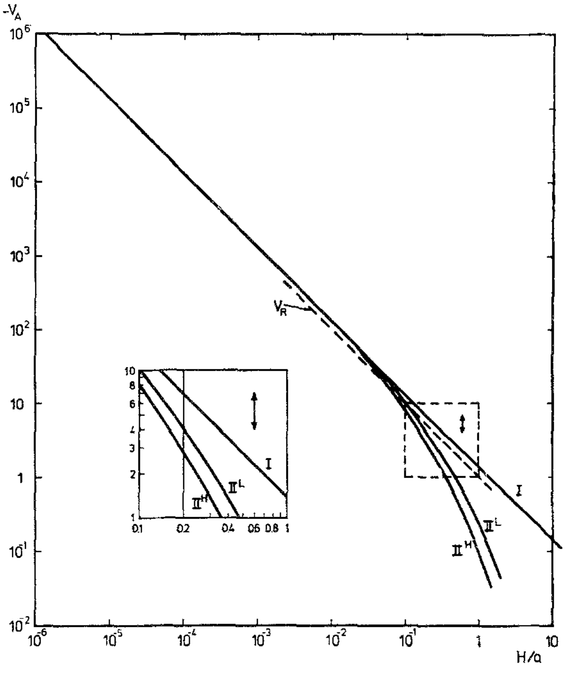


Fig. 4. Interaction energies as a function of H/a. Curve I: eq. [2]; curve $\mathrm{II^H}$: eq. [1]; curve $\mathrm{II^L}$: $-V_A$ for metals according to ref. (15)

becomes negative with large particles and positive for small particle radii. Coarse sols are unstable under these circumstances, whereas highly disperse colloids on the other side of the intersection can remain stable if $V_R + V_A$ at the maximum is large relative to kT.

The arrows in fig. 4 are a measure for the effect of particle smallness on colloid stability. With $1/\varkappa = 20$ Å, $\varkappa H = 1$ and $A = 5 \times 10^{-12}$ erg they represent $20\,kT$, but with $A = 5 \times 10^{-13}$ their length is only $2\,kT$ and the effects of smallness on stability are negligible. This is only a crude example, but it illustrates that *Hamaker* constants can in principle be obtained from experiments on the kinetics of fractionated coagulation.

The effects of particle smallness on colloid stability explain why there is such a discrepancy between the calculated *Hamaker* constants and those obtained from coagulation experiments on metal sols when the smallness of the particles was left out of consideration (e.g. by the use of eq. [2]). It remains to be seen how this observation affects the data on coarser but crystalline materials with sharp edges on the particles.

Our observation that the separation of large and small particles by fractionated coagulation is most effective at salt concentrations which are just enough to coagulate the larger particles is now readily explained. At the coagulation concentration the maximum in $V_R + V_A$, which is approximately proportional with the particle radius vanishes. When this happens for the larger particles there is still a positive maximum in the interaction of small particles since their attraction is qualitatively smaller – as if they had smaller *Hamaker* constants but obeyed eq. [2]. And although this maximum is rather small due to the small particle radii, it is still the highest when the salt concentrations are low. The smallest concentration which can be used to coagulate the larger particles is therefore the best for fractionated coagulation.

Since metal suspensions owe their stability at least partly to the smallness of the particles it should be all but impossible to repeptize coagulated metal sols. In a floc H/a is small, even for small a. To bring about repeptization it is not enough to make $V_R > -V_A$ at $\varkappa H = 1$ – which is facilitated by the smallness of the particles. It is necessary for the repeptization of a floc that $V_R > -V_A$ at the distance of closest approach, i.e. for small H/a (14). With $A = 5 \times 10^{-12}$ erg and reasonable double layer potentials this seems hardly possible. That the repeptization of metal sols is indeed very difficult is still another indication that our working hypothesis is valid: metal sols rely for their stability on the smallness of their particles.

Summary

It is shown experimentally that the stability of metal sols depends on particle size. Sols with small particles are more stable against electrolyte coagulation than coarser suspensions. It is possible to separate metal particles of different radii by fractionated coagulation. Results are explained from the diminished *van der Waals* attraction between small particles. Consequences for the repeptization of metal sols and for the measurement of *Hamaker* constants are discussed. It is concluded that the smallness of the particles is a decisive factor for the stability of metal colloids.

Zusammenfassung

Es wird gezeigt, daß die Stabilität von Metallkolloiden von der Teilchengröße abhängig ist. Systeme aus kleinen Teilchen sind bei Elektrolytkoagulation wesentlich stabiler als Systeme mit größeren Teilchen. Durch fraktionierte Flockung werden Kolloidteilchen dem Teilchenradius nach getrennt. Die Erklärung dieser Ergebnisse folgt aus der verringerten *van der Waals*schen Anziehung zwischen kleinen Teilchen. Konsequenzen für die Repeptisierung von Metallkolloiden und für die Bestimmung der *Hamaker*schen Konstante werden diskutiert. Die Stabilität der Metallkolloide wird von der Teilchengröße weitgehend beeinflußt.

Acknowledgement

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References

1) *Krupp, H.*, Adv. Coll. Int. Sc. **1**, 111 (1967).
2) *Deryagin, B. V., V. M. Muller*, and *Ya. T. Rabinovich*, Koll. Zh. **31**, 304 (1969).
3) *Rouweler, G. C. J.*, Chem. Phys. Lett. **8**, 275 (1971).
4) *Ottewill, R. H.* and *J. N. Shaw*, Disc. Far. Soc. **42**, 154 (1966).
5) *Reerink, H.* and *J. Th. G. Overbeek*, Disc. Far. Soc. **18**, 74 (1954).
6) *Turkevich, J., J. Hillier*, and *P. C. Stevenson*, Disc. Far. Soc. **11**, 55 (1951).
7) *Frens, G.*, to be published.
8) *Zsigmondy-Thiessen*, Das kolloide Gold, pg. 48, 64 (Leipzig 1925).
9) *Frens, G.*, Kolloid-Z. u. Z. Polymere **233**, 922 (1969).
10) *Holliday, A. K.*, Trans. Far. Soc. **43**, 661 (1947).
11) *Hamaker, H. C.*, Physica **4**, 1058 (1937).
12) *Hoskin, N. E.* and *S. Levine*, Phil. Trans. Roy. Soc. **A 248**, 433 (1956).
13) *McCartney, L. N.* and *S. Levine*, J. Coll. Int. Sc. **30**, 345 (1969).
14) *Frens, G.*, J. Coll. Int. Sc., in press.
15) *Langbein, D.*, J. Phys. Chem. Solids **32**, 1657 (1971).

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Discussion

J. Lyklema (Wageningen, Holland):

Können Sie noch ein wenig eingehender den physikalischen Unterschied zwischen Metallen und Nichtmetallen behandeln?

Wenn man zeigen kann, daß die Effekte, worüber Sie soeben berichtet haben, wirklich auf Metalle beschränkt bleiben, muß man für stabile Sole von Nichtmetallen mit sehr kleinen Teilchen (z. B. Mikroemulsionen) andere Ursachen finden.

G. Frens (Eindhoven, Holland):

In der Theorie sind die Effekte der Geometrie (H/a) natürlich nicht auf Metallteilchen beschränkt. Im Vergleich mit der Energie der Wärmebewegung sind die geometrischen Effekte aber nur groß bei Systemen mit starker Attraktion, wie bei den Metallen. Bei diesen Kolloiden erwartet man dann auch fraktionierte Koagulation. Bei sehr kleinen Teilchen mit kleinen *Hamaker*-Konstanten sind die Dispersionskräfte überhaupt sehr klein.

Ihre Frage nach dem physikalischen Unterschied zwischen Metallen und Nichtmetallen hat aber weitere Aspekte: Ganz unabhängig von der Teilchengröße wäre diskutabel, inwiefern die *Hamaker*sche Anschauungsweise in kondensierten Medien überhaupt zutrifft. Für Metalle gelten Formeln, wie z. B. die von *Langbein*, schon besser. Auch in diesen alternativen Darstellungen der Theorie von Dispersionskräften bleiben die geometrischen H/a-Effekte bestehen, wie das auch in Abb. 4 gezeigt wurde.

Dann ist vom Standpunkt der Festkörperphysik aus die Kleinheit selbst der kolloiden Metallteilchen interessant. Der Unterschied zwischen Nichtmetallen und Metallen liegt in den frei beweglichen Leitungselektronen. Das „freie" Elektronengas in einem Metall wird charakterisiert durch Kenngrößen sowie die freie Weglänge der Elektronen, welche die atomaren Dimensionen weit übersteigen. In kolloiden Metallteilchen ist dieses Elektronengas in kleinen Kügelchen – der Größenordnung der freien Weglänge eines Elektrons – ganz eng eingeschlossen, und dies kann die Eigenschaften und damit den Anteil des Elektronenplasmas an den Dispersionskräften beeinflussen. Bei quantitativer Deutung der experimentellen Ergebnisse aus Abb. 1 fanden wir, daß die Attraktionskonstante, die doch eine Materialkonstante ist, um einen Faktor 2 kleiner ist bei kleinen Teilchen als bei großen. Wir sollen diese „preliminary remark" natürlich noch gründlicher überprüfen. Es sieht aber so aus, daß es in der „Welt der vernachlässigten Dimensionen" auch geänderte Materialeigenschaften gibt.

I. Varuch (Basel, Schweiz):

Was passiert, wenn man zur Flockung andere Flockungsmittel benutzt als die verwendeten Elektrolyte? Könnte man es anhand von Ihren Vorstellungen vorhersagen?

G. Frens (Eindhoven, Holland):

Bei der Flockung mit Polymeren, wie sie z. B. von *Fleer* und *Lyklema* beschrieben wurde, kann man gegen die viel größeren Energien bei der Adsorption von Polymersegmenten an der Teilchenoberfläche und bei der gegenseitigen Abstoßung von Polymerketten die *van der Waals*schen Attraktionskräfte vernachlässigen. Daher bleiben unsere Betrachtungen für Flockung dieser Art ohne Konsequenzen.