Theory of the Formation of Colloidal Crystals

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Latex polymer colloidal »crystals« were photographed microscopically by
N. Ise, H. Matsuoka, K. Ito, and H. Yoshida, *Faraday Discuss. Chem. Soc.*
90 (1990) 153, as apparent hexagonal lattices of one particle surrounded
symmetrically with six others. The apparent hexagonal lattice cannot exist
in reality, as supposed by the authors, because the vertical distance between
the planes is not defined. A cubic lattice is described in the present paper
which can explain the colloidal latex »crystals«. Experimentally, the »crys-
tals« were formed after elimination of electrolytes with ionexchangers. The
unavoidable quantity of the (1 − 1) electrolyte remaining after purification
is made responsible for the »inhomogeneity« of the system, *i.e.*, for the
separation of the system into the ordered, »crystal«, and the »disordered«
parts. The latex crystals are considered to be a realization of the model of
»quasi« crystals published by M. Mirnik, and K. Kvastek , A Lattice Model
for the Debye-Hückel Electrolytes, *Croat. Chem. Acta* **50** (1977) 321.

INTRODUCTION

Ordering phenomena of polymer latex particles in suspensions were described by
Ise *et al.*[1] The system is declared by the authors to be ionic and inhomogeneous. The
described colloidal phenomena represent, together with the Agl and latex coagulation
phenomena, important experimental observations which can serve for the deduction
and confirmation of the double layer theories. The double layer on colloidal particles
is always ionic: the inner layer consists of the ions adsorbed on ionic solids or in lat-
tices chemically bound ionogenic radicals. In the outer layer, the adjoining electrolyte
layer, there are statistically dispersed ions of opposite sign. Processes in such ionic sys-
tems can be well explained theoretically by the point charge double layer model. The
double layer is understood as the main factor causing either colloidal stability, coagula-
tion or electrokinetic phenomena.

Colloidal crystals are a new type of experiments, which can contribute towards a
better understanding of the double layer theories. The colloidal Agl type stability –

coagulation phenomena are theoretically explained by the author on the basis of the point charge double layer model in references 2 and 3. The experimental latex coagulation phenomena of formation of aggregates containing up to 12 primary particles[4] are theoretically explained in reference 5. A review of the author's work on double layers in electrokinetics is in preparation.[6]

The discussed latex system, containing monodisperse highly charged spherical particles, is defined by the following four parameters: (a) particle concentration, (b) electrolyte concentration, (c) particle diameter and (d) surface charge density. For theoretical analysis by the point charge double layer model they are transformed into: (a) particle number concentration, c_n, (b) ionic strength, I, (c) number of charges per particle, n_{cp} and (d) the distance between point charges on particle surface, i.e., the intercharge distance, l_{ic}.

The purpose of the present paper is to suggest a theoretical explanation of the colloidal crystals on the basis of the Debye-Hückel theory of ionic interactions as applied to the point charge double layer model. Also, an experiment is suggested to check the proposed theory.

THE CUBIC STRUCTURE OF COLLOIDAL CRYSTALS

Plates 1, 2 and Figures 1, 2 of reference 1 depict apparent hexagonal structures of one particle surrounded symmetrically by six other particles in a plane (from now on »apparent 1 + 6 particle lattice«!). The element of the apparent lattice is schematically drawn in Figure 1. In reality, the apparent hexagonal structure is impossible. It can be explained as a real cubic structure of 2 + 6 particles in the corners of a cube. Under the microscope, the vertical diagonals of the cubes are oriented parallel to the microscope observation axis (Figure 2) and they are perpendicular to the micrograph plane. The 1 + 6 depicted particles are projections of the real particles on the focus plane perpendicular to the microscope axis.

The photographed apparent hexagonal structure of one particle surrounded by six others is in reality impossible because neither the hexagonal, nor any other symmetry is possible in the vertical planes. The photograph of such a hexagonal lattice would vary with the depth of focusing or with the direction of observation. It is impossible
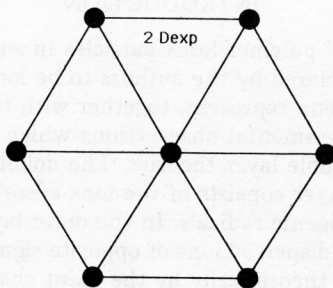

Figure 1. Schematic drawing of a hexagonal element on the micrograph of a latex crystal. Black points represent highly charged spheric particles. The apparent interparticle distance is $2\,D_{exp}$.
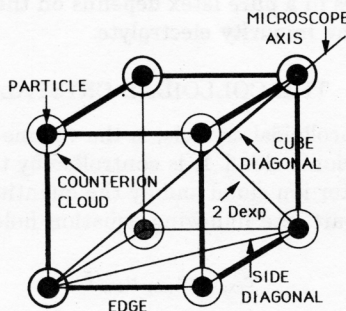
Figure 2. Schematic drawing of a cube element of the lattice. Black points represent spheric latex particles, circles the crossections of spheres of radius $= a / 2 + 1 / \kappa_p$. The microscope observation axis is parallel to the cube diagonal. The length of the cube edge is l_c. The projection of l_c is $2 D_{\exp}$. It equals the height of the triangle »cube diagonal — side diagonal — edge«.

to explain what would determine the real distance between the planes with the apparent 1 + 6 particle lattice. The »focus plane« of the microscope has necessarily a certain depth, d. The depicted apparent interparticle spacing is $2D_{\exp}$ and it is equal to the projection of the diagonal of the cube side plane or of the edge, l_c, on a plane perpendicular to the microscope axis. If d is bigger than the cube diagonal, l_d, then two or more particles in the vertical diagonals appear as single particles. The upper particles hide the lower ones. Only single particles are visible in the vertical diagonals if $d < l_d$. The possible real cubic arrangement of 2 + 6 particles, *i.e.*, the lattice of 8 particles in the corners of a cube, would be visible in all three directions of the diagonals as the constant hexagonal 1 + 6 particle arrangement. Also, irrespective of d, in any depth of the focus, the real cubic 2 + 6 particle lattice will appear as the apparent hexagonal 1 + 6 particle lattice. Experimental observations are in agreement with the described expectations.

INFLUENCE OF ELECTROLYTES

After purification with ion exchangers, some low concentration of an 1 – 1 electrolyte unavoidably remains in the latex. Any electrolyte present in a sufficiently small unavoidable impurity concentration or ionic strength, I, attracts a given quantity of water due to its dielectric properties. The electrolyte dissolved in water plus the latex particles dispersed in their quantity of water, *i.e.*, the »electrolyte + water volume« plus »particles + counterion cloud volume« constitute the disordered part of the system. The separation of the system into the part with the »colloidal crystal« and the part with the disordered particles is a consequence of the electrolyte which is expelled from the ordered part. The number concentration of the particles in the ordered region is bigger than that of the disordered region.

A pure latex crystal can be understood as an electrolyte »ion charges chemically bound on the surface of particles plus counterion cloud«. The charged particles with the counterion cloud show a tendency to repel each other as far as possible and, as a consequence, to occupy the available volume in dense packing. The distance between

the highly charged particles in a pure latex depends on the particle number concentration and the quantity of the impurity electrolyte.

THE COLLOIDAL CRYSTAL

The ordered part, the »colloidal crystal«, is the volume filled up solely with charged particles plus their counterionic cloud. It is controlled by the electrochemical potential of counterions in the counter ion cloud and by the quantity of the impurity electrolyte present. For the ordered part, the following equation holds:

$$c_{\exp} = c_{nexp}\, n_{ch}/L \tag{1}$$

Here $c_{\exp}$ is the counterion concentration and c_{nexp} the particle number concentration in the ordered part. The constant number of elementary charges per particle (= charge per particle number!) is n_{ch} and L is the Avogadro-Loschmidt constant.

The measurable apparent distance[1] between two neighbouring ordered particles on the micrograph is $2\,D_{\exp}$. It experimentally characterizes the cube as a lattice unit.

In the sufficiently high $(1-1)$ electrolyte concentration, which is equal to the ionic strength I, all particles are disordered (e.g., $I = 10^{-4}\mathrm{mol\ dm^{-3}}$, (see Reference 1, p. 158 – line 16) and the counted number of particles on a measured surface area, a, of a micrograph is n_O. The actual volume, $a\,d$, under the measured area, a, and thickness d, can be calculated by the equation

$$n_O = a\,d\,c_{nO} \text{ or } a\,d = n_O / c_{nO} \tag{2}$$

Since the particle number concentration, c_{nexp}, of the ordered part is higher than the average number concentration, c_{nO}, the number concentration of the disordered part, c_{ndis}, must be lower. In the presence of a sufficiently small concentration of electrolytes, instead of the average distribution, the system transforms into that of the ordered and disordered parts.

The interparticle spacings, $2\,D$, particle number concentrations, c_n, counted numbers of particles, n, on a given area of the micrograph, a, and volumes, v, of the system parts, change according to the following scheme:

$$\rightarrow \text{ ordered: } >2\,D_{\exp}, <c_{nexp}, <n_{\exp}, v_{\exp}$$
$$\uparrow$$
$$\text{Average: } 2D_O, c_{nO}, n_O, v_{sist}$$
$$\downarrow$$
$$\rightarrow \text{ disordered: } <2\,D_{dis}, >c_{ndis}, >n_{dis}, v_{dis}$$

In the ordered part, after purification and equilibration, the volume, v_{exp}, of the cube of edge, l_c can be calculated by:

$$v_{\exp} = l_c^3 = [D_{\exp}\,(3/2)^{1/2}]^3 \tag{3}$$

Here, $2\,D_{\exp}$ is the measurable apparent interparticle distance of the ordered part in the micrograph. It is equal in the real cube to the length of the projection of the edge, l_c, or of the side diagonal on a horizontal plane which is parallel to the cover

glass or perpendicular to the cube diagonal, l_d. It is equal to the height of the triangle »cube diagonal (l_d) – side diagonal – edge«.

In the colloidal »crystal«, each cube contains one particle in one corner. Consequently, the particle number concentration, c_{nexp}, is defined by:

$$c_{nexp} = 1/v_{exp} = [D_{exp} (3/2)^{1/2}]^{-3} \qquad (4)$$

Obviously, the depicted disordered particles are in reality in a given volume of thickness, d, and not just in a »focus plane« of zero thickness, as assumed in reference 1. The probability that the particles closer to the objective would hide particles that are further away is negligible if $d < l_d$.

In the presence of a small (trace) concentration of electrolyte, the counted number of particles is n_{dis} in the disordered part of the observed area, a. The particle number concentration, c_{ndis} can be estimated using the following equation:

$$c_{ndis} = n_{dis} / a \ d \qquad (5)$$

In support to this opinion, the following observation can be cited: in the presence of a sufficiently high electrolyte concentration (e.g., $I = 10^{-4}$ mol dm^{-3}, see reference 1, p. 158 – line 16), the ordered structure disappears completely and the disordered charged particles plus their conterions fill up, together with the added electrolyte, the total volume of the system, v_{syst}. The counted number of particles on a measured surface area a is n_O. The actual volume, $a \ d$, can be calculated by (2) and the total particle number concentration, c_{nO}, can be calculated from the mass concentration, particle size and density of the polymer.

During the ordering process, the number of particles in the system is necessarily always constant. Consequently, the following equation applies:

$$v_{syst} \, c_{nO} = v_{ord} \, c_{nexp} + v_{dis} \, c_{ndis} \qquad (6)$$

The volumes are of the system v_{syst}, of the ordered part v_{ord}, and of the disordered part, v_{dis}. Then, $v_{ord} + v_{dis} = v_{syst}$ holds. The relative volumes, of the ordered, $v_{rexp} = v_{exp} / v_{syst}$, and the disordered, $v_{rdis} = v_{dis} / v_{syst}$ parts, can be estimated in the following way:

$$v_{rexp} + v_{rdis} = 1 \ \text{or} \ v_{rdis} = 1 - v_{rexp} \qquad (7)$$
$$n_O / v_{rsyst} = n_{exp} / v_{rexp} + n_{dis} / v_{rdis}$$

or

$$c_{nO} = [n_{exp} / v_{rexp} + n_{dis} / (1 - v_{rexp})] \qquad (8.1)$$

It follows from the above equation:

$$v_{rexp} = (n_{exp} - n_{dis} + c_{nO}) / (2 \, c_{nO}) +$$
$$+ [(n_{exp} - n_{dis} + c_{nO})^2 / (4 \, c_{nO}^2) - n_{exp} / c_{nO}]^{1/2} \qquad (8)$$

THE DEBYE – HÜCKEL QUASI CRYSTAL LATTICE

The square root dependence of the Debye-Hückel radius on the ionic strength, I, can be calculated on the basis of a quasi crystal cubic lattice (see Figure 1^6!). It follows from the quasi crystal lattice that a great majority of ions of the Debye-Hückel electrolytes must be at small distances forming ion pairs and single ions must be in low concentrations at great distances.

The colloidal »crystals« are a physical realization of the quasi crystals. They strongly support the idea of imaginary quasi crystal lattices in electrolytes. They correspond to the lattice of Figure 1^6 in which the ion pairs were eliminated. Elimination of the ion pairs corresponds to the diffusion of the impurity electrolyte from the ordered into the disordered parts of the system.

The colloidal »crystal« lattice is characterized by cubes with particles in the corners. The counterion concentration, c, is by the power of 10 higher than the particle number concentration, n_{exp}, because the surface and charge density are extremely high, or, the number of charges per particle is extremely high ($= 1 - 6 \times 10^4$). The counterion cloud, are the counterions statistically distributed in the »crystal« volume. The average distance of the counterions from the particle charges corresponds to the Debye-Hückel distance, $1/\kappa_p$, which is defined by the well known equation:

$$1/\kappa_p = (1 / \kappa_p^\theta)I^{-1/2} \tag{9}$$

Here, κ_p and κ_p^θ are the reciprocal Debye-Hückel distance and its standard value at particles; the standard value is defined by $I = 1$ mol dm^{-3}.

The definition of κ_p^θ reads:

$$\kappa_p^\theta = (4 \pi L e_O^2 / \varepsilon k T)^{1/2} = 3,286 \ 10^{-8} \ (\text{dm/mol})^{1/2} \tag{10}$$

The remaining symbols have the conventional meaning. The definition of I for a binary electrolyte reads:

$$I = [(z_+ c z_-^2 + z_- c z_+^2)^{1/2} / (2 L) \tag{11}$$

Here: the particle number concentration $c = c_n$, the number of elementary charges per particle (= valency of the particle) $z_- = n_{ch}$, the counterion concentration $z_- c = c_n n_{ch} / L$, the counterion charge number $z_+ = 1$ and the term $z_- c z_+^2 = c_n n_{ch} / L$.

The same equation can be written for the purpose of the present latex electrolyte as:

$$I = (n_{ch}^2 c_n + n_{ch} c_n) / (2 L) \tag{12.1}$$

The characteristic of the present latices is their high charge per particle number ($\approx 2 - 6 \ 10^4$!) and, consequently, $n_{ch} >> c_n$. Then, $n_{ch}^2 c_n >> n_{ch} c_n$ and the same equation can be simplified to read:

$$I \cong n_{ch}^2 c_n / (2 L) \tag{12}$$

The counter ion cloud can be practically assumed to be a sphere of, with r variable, volume charge density. The maximal radial charge density forms a sphere of radius $r = a / 2 + 1 / \kappa_p$. Its center coincides with the center of the particle. The particle diameter is a.

Figure 2 describes schematically a cube of the same lattice. The black points represent the particles. The circles represent the crossections of the spheres of maximal radial charge density. The radius of the cloud circle equals the sum of the experimental particle radius plus $1/\kappa_p$. The order of magnitude is $10/\kappa_p < a/2 < 100 / \kappa_p$.

The average ion cloud potential exhibited by the counterion cloud upon the charges in the particle surface is determined by $1/\kappa_p$.

The conclusion can be made that a pure latex, like the present one, in the ordered part, with a big charge per particle number, $n_{ch} >> c_n$ and a low counterion concentration, c, forms the ordered cubic structure, the »colloidal crystal«.

THE DISORDERED REGION OF THE SYSTEM

Addition of a given quantity of ionexchangers to the latex for purification purposes, causes an equilibrium electrolyte impurity or trace concentration, I, to remain in the latex. The consequence is the observed separation of the system into the ordered and disordered regions. The final equilibrium is dynamical: some particles permanently diffuse from the ordered into the disordered parts and *vice versa*.

The $1 - 1$ electrolyte is present in a trace concentration, $c = I$, and it is dissolved in a given quantity of water. The volume of the electrolyte plus water, v_{el}, plus the volume of ordered particles, v_{exp}, is larger than the volume of the sole ordered particles, *i.e.*, $v_{dis} = v_{exp} + v_{el} > v_{exp}$. The electrolyte counterions (plus coions) diffuse into the disordered parts till their electrochemical potential becomes equal to their electrochemical potential in the ordered part. Due to the tendency of counterions to diffuse to lower counterion concentrations (lower electrochemical potentials!), the impurity electrolyte diffuses of the ordered region and concentrates in the disordered region. As a consequence, in a part of the system, in v_{dis}, the cubic structure is destroyed.

A POSSIBLE EXPERIMENTAL VERIFICATION
OF THE ORDERING THEORY

The proposed theory could be verified by the following experiment. Several systems should be prepared by increasing sufficiently small additions (*e.g.* multiples of $\cong$ 10^{-6} mol dm^{-3}) of an $(1 - 1)$ electrolyte. They would cause a gradual increase of the counted n_{diss} and calculated v_{rdis} or a decrease of the ordered region, v_{rexp}. That minimal concentration of the electrolyte should be estimated which eliminates the ordered part, *i.e.*, which causes its volume to become zero. This would be the minimal concentration in which no $1 + 6$ ordered hexagonal structure could be observed. In this way, also, the concentration of the electrolyte impurity that remained after purification could be estimated. The minimum value of I of the $1 - 1$ electrolyte which transforms the ordered into the disordered region is equal to the constant I of the disordered region.

LIST OF SYMBOLS

a	particle diameter
a_m	area in the micrograph used for counting particles
c, c_l	concentration of (counter) ions, latex concentration by mass
$c_{ndis}, c_{nexp}, c_{nO}$	disordered particle number concentration, ordered, average
d	thickness of the microscope focus layer
L	Avogadro – Loschmidt constant
D_{dis}, D_{exp}, D_O	half of the disordered interparticle distance, ordered, average
e_O	elementary charge
l_{ic}, l_c, l_d	distance between charges on the particle surface, length of the cube edge, of its diagonal
I	ionic strength
k	Boltzmann constant
n_{ch}	number of elementary charges per particle
n_{dis}, n_{exp}, n_O	counted number of particles of the disordered, ordered, average parts
$v_{dis}, v_{exp}, v_{el}, v_{syst}$	volume, of the disordered, ordered parts, of the electrolyte, of the system
v_{rexp}, v_{rdis}	relative volume of the ordered, disordered, parts
z, z_+, z_-	charge number (valency), of cations, anions
ε	permittivity of the solution
$\kappa_p, \kappa_p^{\theta}$	variable reciprocal Debye-Hückel distance at particles, standard defined by the well known definition of the reciprocal DHT radius if $I = 1$ mol dm^{-3}

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SAŽETAK

Teorija tvorbe koloidnih kristala

M. Mirnik

N. Ise, H. Matsuoka, K. Ito i H. Yoshida (*Faraday Discuss. Chem. Soc.* **90** (1990) 153) objavili su mikroskopske snimke prividne simetrične heksagonske rešetke u kojima je jedna čestica okružena sa šest drugih polimernih čestica lateksa. Dokazuje se da je prividna heksagonska rešetka u stvarnosti nemoguća. Opisana je teseralna rešetka kojom se može protumačiti snimljena prividna heksagonska rešetka, tzv. »koloidnog kristala«. Ti »kristali« nastaju nakon eliminacije elektrolitnih nečistoća ionskim izmjenjivačima. Stvaranje nesređenog dijela sustava, uz sređeni tj. uz kristalni dio, protumačeno je prisutnošću ostatka elektrolita neuklonjivog ionskim izmjenjivačima. Za definiranje eksperimentalnih sustava nužni su parametri: koncentracija čestica, tj. broj čestica u jedinici volumena, površina i oblik čestica, broj elementarnih naboja na svakoj čestici i koncentracija elektrolita. Teorije, koje ne uključuju sva ta četiri parametra potrebna za definiranje ekperimentalnih sistema u koloidnoj su kemiji neupotrebljive.