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CONCERNING THE APPEARANCE OF THE STRING OF PEARL CHAIN FORMATION OF EMULSION PARTICLES UNDER THE EFFECT OF AN ALTERNATING FIELD.

by Ernst Muth

In the course of experiments concerning the creaming of milk, especially concerning the aggregation of fat droplets to greater complexes, measurements were undertaken of charge and double layer potentials of the droplets. With regard to the complicated composition of milk relative to the degree of dispersal of its individual constituents[1] - in addition to the fat we find in milk various albumens in more or less highly dispersed distribution and in ion- and molecular distribution, milk sugars and salts - only the direct, microscopic measurement of the cataphoretic velocity of particles could provide somewhat exact values. Coincidentally with these measurements the secondary potential of a small Ruhmdorff inductor was once attached to the electrodes, to learn of the effect of an alternating field on the particles. The effect was completely unexpected. The globules of the size order 0.5μ to 5μ, distributed in the diluted milk at intervals of about 5μ, which in part rose quietly (fall in the microscopic picture) - the observations were made with a horizontal microscope - in part were in lively Brown movement, at the moment of connection with the alternating potential formed string of pearl chain-like formations, such as Thomson[2] observed in the, by steam, saturated air of an iron light arc under the influence of a magnet; and R. Whytland and Speakman[3] found with the oxide vapors of Zn, Mg, Al, Cd, Sb. After a few seconds almost all particles were in the order of a string of pearls. In addition to this movement a one-sided cataphoretic movement was observed, such as H. R. Kruyt[4] found under similar circumstances in his experiments with vanadinpentoxide under the effect of an alternating field. He traces these anomalies, which occur mostly during the first seconds after activation of the inductors, to suspected isolation errors in the current

conduction and the still not stationary work of the just activated inductor. - If the current was broken, the formed chains disintegrated again, and after some time the original picture prior to alternating potential connection, was reconstructed.

This effect shall be described in more detail. In order to observe the arrangement of the particles in chains in more detail, it was necessary to connect lower alternating potentials and to avoid the above mentioned disturbances as much as possible. Both conditions were met when high frequency alternating potentials were used in the investigations. A cathode tube served as alternating current producer in the generator connection. The tube was chosen so that the vibrations began already at less than 100 volt anode potential, and alternating potentials of less than 25 volt could be taken at the ends of the self induction spool in the anode circle of the tube. By changing the size of the self induction (exchangable spools) and the capacity of the anode circle, frequencies of $2 \cdot 10^4 - 2 \cdot 10^6$ Hertz could be obtained. Glass capillaries of various inner width, diameter 0.1 mm to 0.25 mm, served as observation chambers. The electrodes were copper wire of 0.05 mm to 0.1 mm thickness, led into the capillaries from both sides. The capillaries filled with the emulsion, were closed with paraffin at both ends and glued to an object bearer with paraffin. The use of capillaries as chambers in these experiments could be undertaken without hesitation. Tests with the simple chamber as described by O Blueh[5], gave the same effect of chain formation. Even without a chamber, by bringing the emulsion between two stanniol strips as electrodes, fastened to an object bearer without using a cover glass, the chain formation resulted. This last test already eliminates the possibility to trace the observed effect to an electro-osmosis of the fluid in the alternating field. In order to avoid as much as possible observation errors, occurring at the disturbing fluid currents alongside the capillary walls on the basis of electroosmosis, only particles at greater

distances from the walls were observed - Using the capillary as the chamber with measurements on microscopic particles has an advantage over other chambers, in that the electrode distance can be chosen large and may be varied. - AS mentioned at the beginning, the observations were made with a horizontal microscope in order to avoid the collection and adhesion of the above mentioned particles -. We used milk, washed out cream emulged in water, butter-fat-water, and petroleum-water-emulsions.

Under great magnification (1545 times) the mechanics of the string of pearl chain formation of the particles could be followed in great detail. At the second of connection of the alternating potential the particles begin to arrange themselves and the chain formation starts. In a 20 times diluted milk solution one can observe after a fraction of a second, chains of 5 - 10 - 15 single members. The axis of the chains lie in the direction of the field. New members are constantly added to the ends of the chains. One can clearly see, how individual globules in the vicinity of the chain ends, suddenly are caught in the effective sphere of the end members and from a distance of 4 μ - 6 μ - 8 μ are pulled to the chain ends. (Thedistances were calculated on hand of a gauged ocular-micrometer; 1 scale part = 1 μ). However, particles at a distance from the chain ends, opposite the course of the chain, no matter how close, are not attracted. Unless they are small and pulled to another small one which adheres to a larger one (Fig. 1).

It is also worth mentioning, that the particles are not drawn to the free chain ends in the direction vertical to the chain formation, but mostly only in pointed angles to the chain axis.

After a few seconds, almost all globules have arranged themselves in chains, and gradually these too hang themselves to each other (Fig. 2).

Again one clearly see, how two chains lie closely alongside each other

without showing a tendency to attract one another (Fig. 2a).

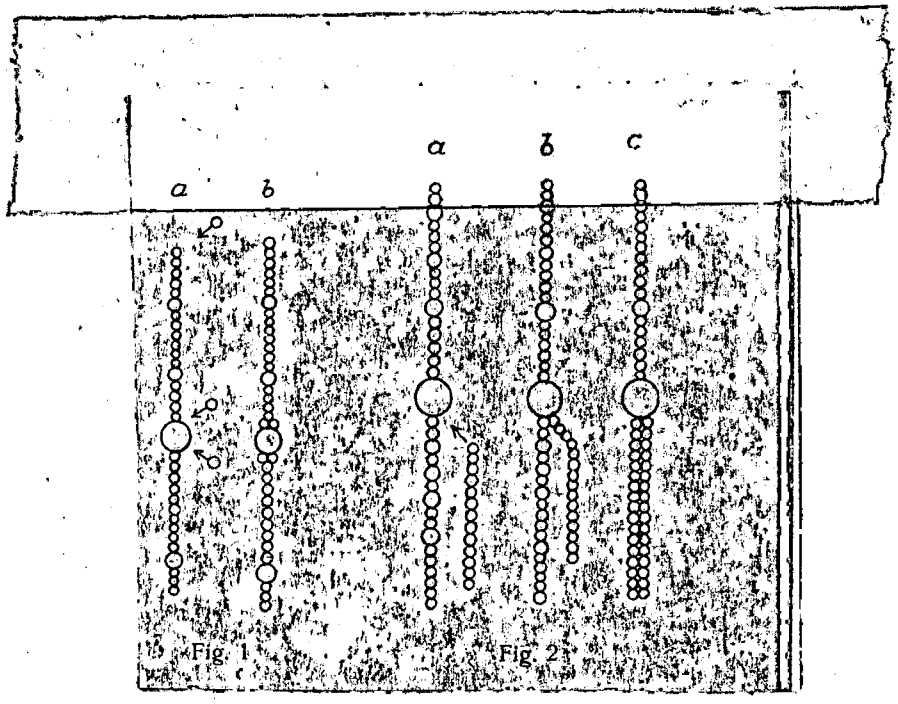

Fig. 1 Fig. 2

However, when the free end of a chain comes to the vicinity of a greater part of a second, to which only a relatively small one adheres, the free end member positions itself, drawing its chain, alongside (Fig. 2b). The attracted, at its end bent chain places itself into the field direction and then places itself alongside the other chain: A"doublechain" has formed (Fig. 2c). Formed in this manner, one can observe, after some time of effect of the alternating field, formations of 3 - 4 - 5 chains alongside each other.

This process shows definitely, that the directing and arranging power is only in the globul calottes of the particles turned toward the electrodes.

One observes rapidly rotating whirls at the electrodes (with weak amplification) the criteria of an "electroosmosis in the alternating field", as described by O. Blueh[6]. Under the influence of the field an electroosmosis will occur along the walls of the capillaries. However, since the capillaries (at least in part) are closed by the electrodes, a constant flow in one direction is not possible, and a retroflow along the capillary walls must occur. Thus the reversal points of the current directions are at the electrodes. For a detailed explanation of

this appearance we refer to the works of O. Blueh. Thus completely circular whirls of particles caught in the moving fluid were observed at the electrodes when the connected alternating potential had a certain height. With gradual lowering of potential the velocity of the rotation decreased and the circular bands were pulled apart to long stretched ellipses.

As already mentioned, at disconnection of the field the chains fall apart again. With gradual lowering of the alternating potential the firm structure loosens more and more. The small particles weakly show the Brown movement again, but still remain in the structure of chains. At a reached threshhold value of the potential gradient complete disintegration takes place.

On the basis of the experimental findings and the theory of electrical double-coat (Helmholz - v. Smoluchowsky) in connection with the explanations of electroosmosis and the electrical cataphoresis from it, the effect of the string of pearl chain formation of the particles under the effect of an alternating field is explained quite naturally.

π The emulsion particle is surrounded by an electrical double-coat, of which one layer lies firmly, immovable in the surface layer of the particle. The other, opposite charged layer is represented by ions, which have a final, molecular dimension surpassing distance from the first. These ions thus lie in the movable, free-fluid area of the dispersion material. With the existance of a potential gradient the particles are moved on the basis of an electrical cataphoresis. They are brought into oscillation in the alternating field. That this movement can actually occur at the velocity of the alternation was shown in the observations of Cotton and Mouton[7] and later of O. Blueh[8]. Exposed to an alternating field, colloidal silver particles carry out an oscillating movement at the rhythm of the period of the field and appear to the observer as a line with definitely pronounced end points. (At the end points the velocity of the movement = 0.)

It should be mentioned, that this movement was observed only at the existence of a low frequency alternating field; higher frequencies have not yet been used for these measurements. With regard to the much greater dimension of the emulsion particles compared to the by O. Blueh observed silver particles and the therwith connected much greater friction and the much quicker successive reversal of the alternating field used, it is only natural, that the oscillating movement of the emulsion particles is not visible. The fact: the movement of the fluid on the basis of electroosmosis in the alternating field, does not enter into consideration, as we have seen, for the explanation of the appearance of chain formation, because the appearance occurs also, when no closed chamber is used and electroosmosis cannot occur. We make no error therefore, when we assume the fluid as immovable. In addition, it cannot be assumed, that the fluid coat around the particle follows its rapid vibrations. If the vibration amplitude of the particle is greater than the distance of the layers of the double coat, the negatively charged particle at the moment of the maximum of amplitude with its now free negative charge will surpass the positively charged layer of its double coat. With the release of the negative charge the appearance of a super charge at the positively charged of the held back outer layer of the double coat will follow. The vibrating particle over the exterior layer of its double coat effects an apparent pole reversal of the total structure: particle ± double coat in rhythm of frequency. Two particles, standing below each other in the field, since they are subjected to the apparent pole reversal in the same sense and same rhythm, will always turn to the opposite pole and attract each other.

Proceeding from this conception of chain formation, there must obviously be a threshhold value of the connected alternating potential, where the arrangement of particles to chains no longer takes place. The threshhold value is reached when the achieved work through the field is no longer sufficient to

offer the oscillation of the particles a large enough amplitude to bring the free negative charge above that of the outer layer of the double coat. The work necessary to offer the particle an amplitude in its oscillation which is greater than the distance of the layers of the double coat, is composed of the work against the power of the surrounding fluid to the vibrating particle and the work, which is necessary to shift the layers of the - thought of condenser-double coat with their distance against one another. Aside from the dependency of the size of the amplitude on the double coat potential of the particles with a constant field, we are mainly interested: whether the effect of chain formation depends on the frequency with constant field strength.

The fundamental equation for the velocity v of a particle under influence of a field is:

$$v = B.K.$$

where B is the mobility, K the product charge density x exterior potential gradient. The size of mobility B for globular particles according to Stokes law is

$$\frac{1}{6\pi r \eta}$$

or a size dependent on the velocity. It is questionable, whether the expression for B is still usable, when the particle is exposed to constant acceleration with the validity of the law: $v = B.K.$ the relationship of amplitude and connected potential must be constant, even with a change in frequency v.

Whether the effect of chain formation is dependent on frequency had to be made a project of detailed investigation. The principle of the measurements was to determine whether the threshhold value of alternating potential, at which no chain formation takes place, remains constant with a change in frequency. In order to be independent from concentration, viscosity, degree of dispersal and dielectricity constants of the emulsion, the influence of alternating fields of

various frequencies on the particles always on one and the same preparation was observed. The threshhold value of effective potentials at the electrodes was obtained with a tube voltmeter in the ⁄ following connection:

The alternating potential occurring at the ends of the coupling spool K variably coupled with the generator circle G (simultaneous effective potential at the electrodes of the chamber) is pressed on the grid of the cathode tube (with high emission, Telefunk tube R. E. 97) of the tube voltmeter. On the grid lies in addition an equivalent potential E_o which is measured at the potentiometer P and is so regulated that, when the generator tube is not yet connected, the milliamperemeter l_A in the anode circle of the tube shows almost no current. The principle of the effect of the tube voltmeter is visible on hand of the static characteristic of the tube.

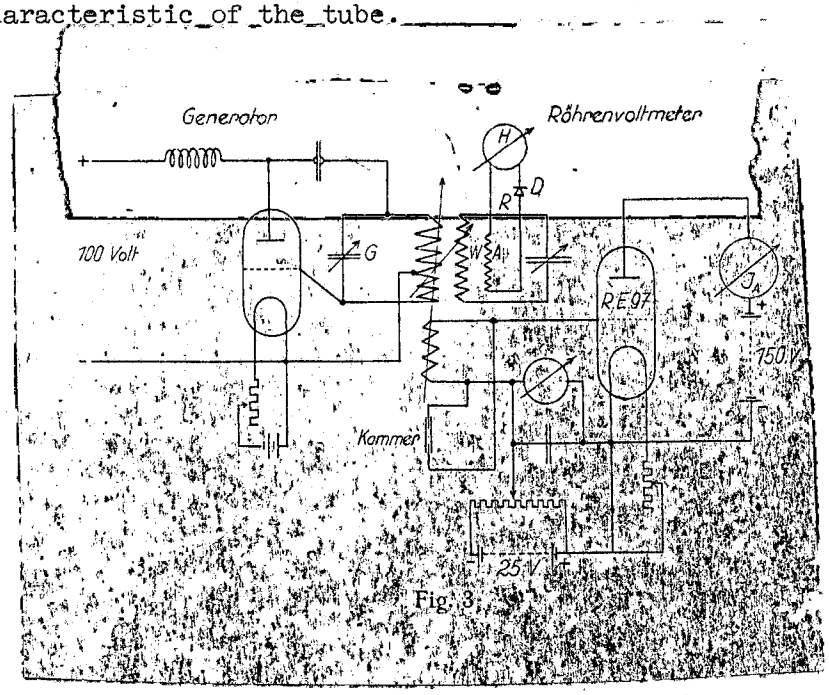

Fig. 3

The grid potentials are recorded on the abscissa, the belonging anode current values at constant heating and constant anode potential of the tube are on the ordinate. At E_o the anode current is almost = 0. At connection of the generator tube the grid is loaded in addition with the high frequency potential with the amplitude E_G, which swings around E_o. It corresponds to an anode current value I_A of the anode direct current (The tube in this connection acts in the same direction) which is read off at the milliamperemeter I_A. On hand of the

characteristic of the tube the size of the anode current is reversed I_A to E_G and thus can be assumed the effective potential on the electrodes of the chamber. The frequency v of the alternating potential is calculated from the wave length, which is determined with a gauged vibration circuit (W in the figure) couppled with the generator circuit G. When both circuits are in resonance, the high frequency indicator H in circuit R, consisting of the instrument, a crystal detector (D) and the coupling spool (A) shows a maximum current. The potential at the electrodes can be varied by looser or firmer coupling of the spool K with the generator circuit spool.

Thethreshhold value was determined as follows: The alternating potential with known frequency is changed by variation of the coupling of spool K with spool G, so long, until two observed, closely neighbored particles of known size not longer attract each other, or at somewhat firm coupling (higher exterior potential) attraction of particles again occurs. Then, after change in frequency of the same particles if possible, the threshhold value of the potential is determined.

This measurement method while not too exact, does show the result very well, that the effect of chain formation is independent of frequency, at least in the area of the frequencies I used.

A few measurement results follow:

Emulsion I. Elektrodenabstand = 0,15 cm.

Frequenz	Schwellenwert d. Sp. Volt
$2 \cdot 10^4$	0,5
$5 \cdot 10^4$	0,5
$1 \cdot 10^5$	0,45
$5 \cdot 10^5$	0,45
$2 \cdot 10^6$	0,5

Emulsion II. Elektrodenabstand = 0,77 cm.

$2 \cdot 10^4$	8,0
$5 \cdot 10^4$	7,8
$1 \cdot 10^5$	8,2
$5 \cdot 10^5$	7,6
$2 \cdot 10^6$	8,5

Emulsion III. Elektrodenabstand = 0,35 cm.

$2 \cdot 10^4$	1,4
$5 \cdot 10^4$	1,2
$1 \cdot 10^5$	1,0
$5 \cdot 10^5$	1,5
$2 \cdot 10^6$	1,8

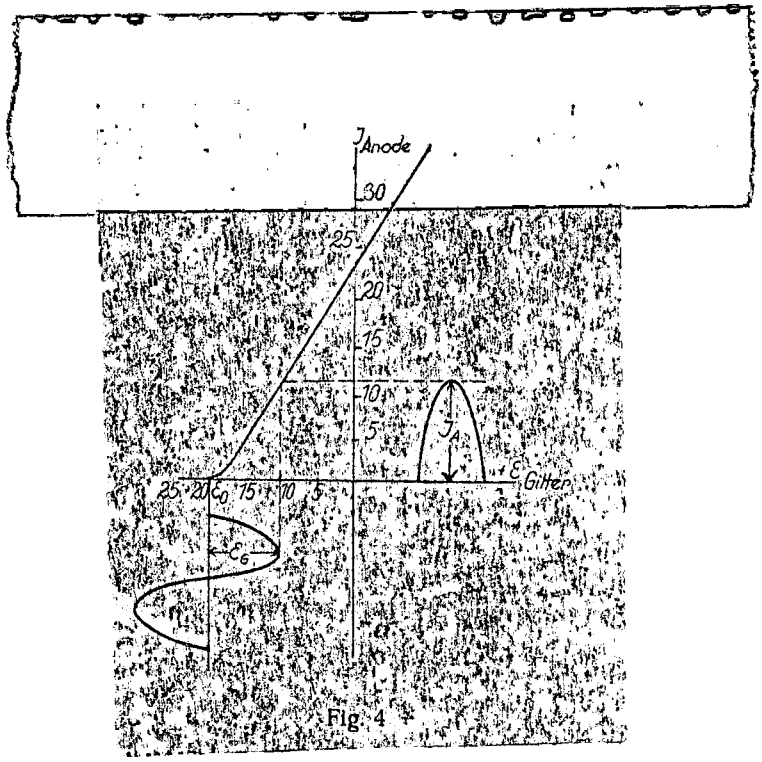

Fig. 4

Summary.

1. The by Thomson discovered effect of string of pearl chain formation of particles in the saturated air of a steamed iron light arc under the influence of a magnet was observed also in emulsion particles under the effect of an alternating field.

2. The mechanics of chain formation, especially the formation of multi chains is described.

3. An explanation of the appearance is given on the basis of a double-coat theory: the vibrating particle above the outer layer of its double coat effects an apparent pole exchange of the total structure: particle + double coat in the rhythm of frequency of the field. Two particles, one below the other, in the field, since they are exposed to the same rhythm and in the same sense to the apparent pole exchange, will always turn to the opposite pole and attract one another.

4. The question, is the chain formation dependent on the frequency of the field? was made a project of detailed investigation. The principle of measurements and the measurement method is described. The measurement results showed, that the effect of chain formation is independent of the frequency of the alternating field.