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COLLOID ELECTROHYDRODYNAMICS*

This brief extracted review presents the recent development in basic and applied science and engineering of finely dispersed particles and related systems in general, but more profound and in-depth treatise are related to the liquid–liquid finely dispersed systems, i.e. emulsions and double emulsions. Twenty-five years ago, the idea, at first very foggy, came out from the pilot plant experiments related to the extraction of uranium from wet phosphoric acid. In particular the solution of the entrainment problems, breaking of emulsions/double emulsions, as the succession of the extraction and stripping operations/processes, was performed. In this pilot plant, secondary liquid–liquid phase separation loop was designed and carried out. The loop consisted of a lamellar coalescer and four flotation cells in series. Central equipment in the loop, relevant to this investigation, was the lamellar coalescer. The phase separation in this equipment is based on the action of external forces of mechanical and/or electrical origin, while adhesive processes at the inclined filling plates occur. Since many of related processes, e.g. adhesive processes, rupture processes and coalescence, were not very well understood, deeper research of these events and phenomena was a real scientific challenge.

Over the last decade, the biggest advances in physics, physical chemistry, and biochemistry have come from thinking smaller. This research takes an interdisciplinary approach to the elucidation of the momentum transfer phenomenon as well as the electron transfer phenomenon, at well-characterized developed, both rigid and deformable liquid–liquid interfaces. The considered scales are micro, nano and atto, using various theoretical approaches. Micro-scales may cover more or less classical chemical engineering insight, while nano- and atto-scales focus on modern molecular and atomic engineering.

This brief review consist of six parts that were experimentally and theoretically driven over the last twenty-five years; this work was presented in 55 selected references either as authors books, book chapters, scientific papers, lectures, congress and conference presentations. A general part contain a new classification of finely dispersed systems based on entities, then particular part, presents a historical review and motivation, giving short description of a developed pilot plant for solvent extraction of uranium, and the solution of the inevitable, undesirable, entrainment problems that occur during the extraction operations/processes. Further on, the central part presents a new theory of electroviscoelasticity using

a developed model of liquids; three possible mathematical formalisms have been derived and discussed related to this physical formalism. In addition, a new idea related to the probably possible discussion of the problems in the theoretical and experimental status of decoherence is mentioned. Finally, the implications and/or applications of the presented, both, theoretical and experimental issues are discussed considering the two philosophical breakpoints introduced in the general part [1–160].

GENERAL – CLASSIFICATION OF FINELY DISPERSED SYSTEMS [1]

Classification based on scales

Macro- and micro-scale

Classical chemical engineering has been intensively developed during a last century. Theoretical backgrounds of momentum, mass, energy balances and equilibrium states are commonly used as well as chemical thermodynamics and kinetics. Physical and mathematical formalisms are related to heat, mass, and momentum transfer phenomena as well as on homogeneous and heterogeneous catalysis. Entire object models, continuum models, and constrained continuum models are frequently used for the description of the events, and for equipment designing. Usual, principal, equipment are reactors, tanks and columns. Output is, generally, demonstrated as conventional products, precision products, chemistry (solutions), and biochemistry.

Nano-scale

Molecular engineering nowadays still suffers substantial development. Beside heat, mass, and momen-

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tum transfer phenomena, commonly used in classical chemical engineering, it is necessary to introduce electron transfer phenomenon. Description of the events is based on molecular mechanics, molecular orbits, and electrodynamics. Principal tools and equipment are micro-reactors, membrane systems, micro-analytical sensors and micro-electronic devices. Output is, generally, demonstrated as molecules, chemistry (solutions), and biochemistry.

Atto-scale

Atto-engineering, already more than a whole century, is in permanent and almost infinite development. Theoretical background is related to the surface physics and chemistry, quantum and wave mechanics, and quantum electrodynamics. Discrete models and constrained discrete models are convenient for description of related events. Tools and equipment are nano- and atto-dispersions and beams (demonstrations, ions, phonons, infons, photons and electrons), ultra-thin films and membranes, fullerenes and bucky-tubules, Langmuir–Blodgett systems, molecular machines, nano-electronic devices, various beam generators. Output is, generally, demonstrated as finely dispersed particles (plasma, fluosol–fog, fluosol–smoke, foam, emulsion, suspension, metal, vesicle and dispersoid).

Further possible classifications

Example given, related to the geometry: surface continuums, line continuums and point discontinuums. Related to the forces of interaction: electrostatic, van der Waals, solvation and steric. Related to the physico-chemical processes: diffusion, sorption, catalysis, membrane. Finally, here presented classification is based on *entities*, and may be considered as *the first philosophical breakpoint!*

Entities

An entity can be defined as the smallest indivisible element of matter that is related to the particular transfer phenomena. Hence, the entity can be either differential element of mass/demon, or an ion, or a phonon as quantum of acoustic energy, or an infon as quantum of information, or a photon, or an electron.

A possible approach is proposed to the general formulation of the links between the basic characteristics, levels of approximation and levels of abstraction related to the existence of finely dispersed systems, **DS**. At first, for the reason of simpler and easier physical and mathematical modeling, it is convenient to introduce the terms: homo-aggregate (phases in the same state of aggregation, **HOA**) and hetero-aggregate (phases in a more than one state of aggregation, **HEA**). Now the matrix presentation of finely dispersed systems is given by:

$$(\mathbf{DS})^{ij} = (\mathbf{HOA})\delta^{ij} + (\mathbf{HEA})\varphi^{ij} \quad (1)$$

where i and j refer to the particular finely dispersed system position, *i.e.* when $i = j$ than diagonal positions correspond to the homo-aggregate finely dispersed systems (plasmas, emulsions and dispersoids, respectively), and when $i \neq j$ than tangential positions correspond to the hetero-aggregate systems (fluosols/fog, fluosols/smoke, foam, suspension, metal, and vesicle, respectively). Furthermore, the interfaces may be deformable, **D**, and rigid, **R**, that is presented in Table 1.

Table 1. A new classification of finely dispersed systems (Course NTU, Ref. [155], pp. 7)

Dispersed phase	Dispersion medium		
	Gas	Liquid	Solid
Gas	Plasma D	Foam D	Metal R
Liquid	Fluosol/fog D	Emulsion D	Vesicle D
Solid	Fluosol/smoke R	Suspension R	Dispersoid R

Now, related to the levels of abstraction and approximation it is possible to distinguish continuum models (the phases considered as a continuum, *i.e.* without discontinuities inside entire phase, homogeneous, and isotropic) and discrete models (the phases considered according to the Born–Oppenheimer approximation: entities and nucleus/CTE motions are considered separately). Continuum models are convenient for micro-scale description (entire object models), *e.g.* conventional products, precision products, chemistry/solutions and biochemistry, while discrete models are convenient for either nano-scale description (molecular mechanics, molecular orbits), *e.g.* chemistry/solutions, biochemistry, molecular engineering and/or atto-scale description (quantum electrodynamics), *e.g.* molecular engineering, atto-engineering. Since the interfaces in finely dispersed systems are very developed, it is sensible to consider the discrete models approach for description of a related events.

Hierarchy of entities

Figure 1a shows a stereographic projection/mapping from Riemann sphere, *i.e.* Figure 1b shows a “hierarchy” of entities, which have to be understood as a limit value of the ratio u_0/Z (withdrawn from magnetic Reynolds criteria ($Re_m = 4\pi l G u_0 / c^2$), where the conductivity G is expressed as a reciprocal of viscosity/impedance Z ($G = 1/Z$), l is the path length that an entity “override”, u_0 is the characteristic velocity, and c is the velocity of light).

In general, S corresponds to the slow system/superfluid, and F corresponds to the fast system/superconductor; now, it is possible to propose that all real dynamic systems are situated between these limits. Also, it seems sensible to think about the further structure of entities, *the second philosophical breakpoint*, *e.g.* the basic entity can be understood as an energetic ellipsoid shown in Figure 1c (based on the model of electron following

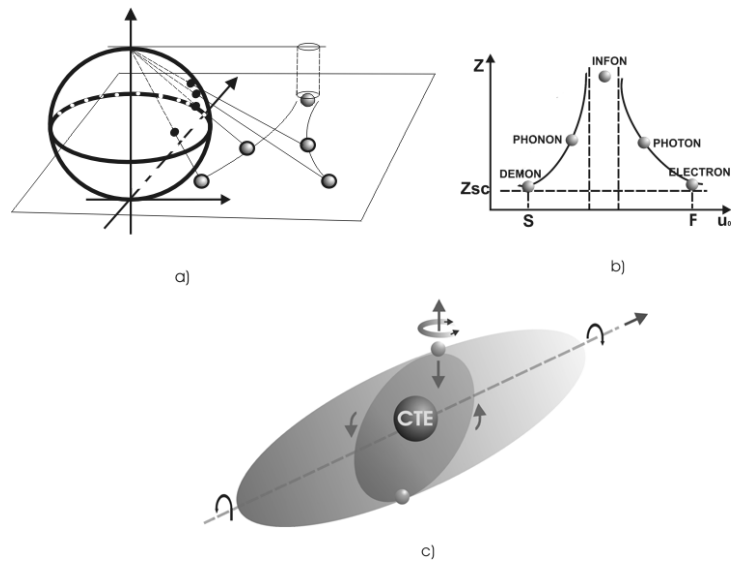


Figure 1. a) A stereographic projection/mapping from Riemann sphere; b) hierarchy of entities, correlation viscosity/impedance-characteristic velocity, S-slow/demon (superfluid) and F-fast/electron (superconductor); c) entity as an energetic ellipsoid (at the same time macroscopic and microscopic), CTE – center of total energy, motions (translation, rotation, vibration, precession, angle rotation). From reference 1, p. 20, courtesy of CRC Press/Taylor & Francis.

Maxwell–Dirac isomorphism/MDI: electron is an entity at the same time quantum-mechanical/microscopic, $N = -2$ and electrodynamic/macroscopic, $N = 3$) [1,153].

PARTICULAR – HISTORICAL REVIEW AND MOTIVATION

The work was initiated in an attempt to apply electro-mechanical principles for the elucidation of the secondary liquid–liquid phase separation problems, methods, equipment and/or plant conception. In solvent extraction operations during the generation of a polydispersed systems, some kind of the secondary liquid–liquid droplets, emulsions, or droplet-film structures, double emulsions, occur as an undesirable consequence. These droplets or droplet-film structures are small and stable,

therefore they are mechanically entrained by one of the primarily separated liquid phases. For the separation or breakage of simple or double emulsions, an additional force is needed. Figure 2 shows a drop size distribution and the critical diameters d_1 and d_2 , which correspond to the boundaries of the primary and the secondary separation, respectively [51].

The primary separation is determined by the physical processes of gravitational sedimentation and coalescence. Subsequently during the secondary separation of, e.g. the double emulsions, the processes of droplet-film rupture and coalescence occur in succession.

The aim of this work was development of a general and flexible methodology which may become a purposeful tool in solving the secondary liquid–liquid phase separation problems. The work also intended to

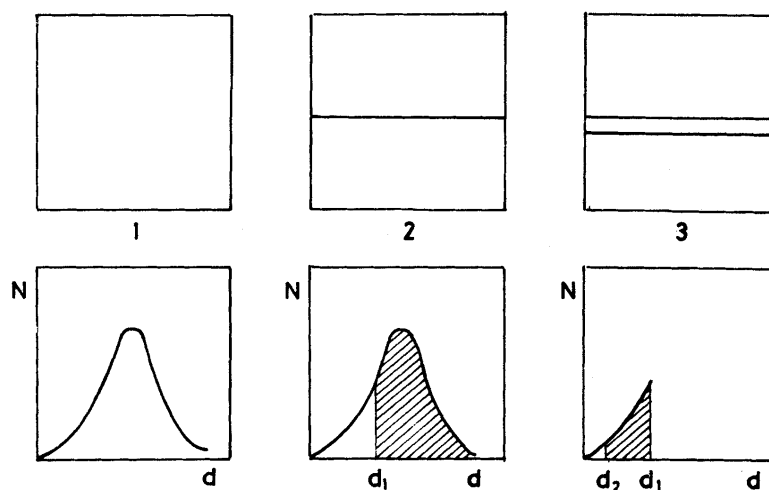
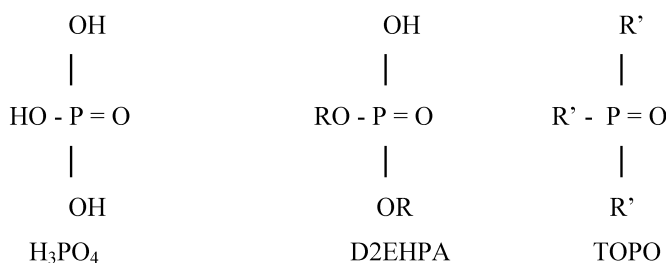


Figure 2. Drop-size distribution and critical diameters: 1) generation, 2) the primary separation and 3) the secondary separation.

perform the secondary liquid–liquid phase separation unit on a pilot plant scale, and to compare its efficiency with theoretical predictions and pilot plant scale experience.

Successful prediction of a phase separation operation from any mathematical model requires determination of the necessary parameters of the system. These parameters can be determined through the use of theoretical correlations and/or experiments carried out on laboratory or pilot-plant scale. The reliability of determined parameters for use in the secondary liquid–liquid phase separation method selection and equipment design can be either questionable, fair and/or good. Good prediction of performance of phase separation units within a certain range of operating conditions require, very often, satisfaction of few contradicting conditions.



where R is: $\text{CH}_2\text{-CH}(\text{CH}_2)_3\text{CH}_3$ and R' is: $(\text{CH}_2)_7\text{CH}_3$
 $\begin{array}{c} | \\ \text{C}_2\text{H}_5 \end{array}$

The particular problem considered as the representative one, while developing the knowledge and data base, was mechanical entrainment of one liquid phase by the other in the solvent extraction operation. Experimental results obtained in the pilot-plant for uranium recovery from wet phosphoric acid were used as the comparable source [27–47]. In this pilot plant, the secondary liquid–liquid phase separation loop has also been realized [43–45,62]. The loop consisted of a lamellar coalescer

and four flotation cells in series. Central equipment in the loop, relevant to this investigation is the lamellar coalescer. The phase separation in this equipment is based on the acting forces of the mechanical and/or electrical origin while the adhesive processes at the inclined filling plates occur [1,48–52,153].

Pilot plant for uranium extraction from wet phosphoric acid

Description of the physicochemical system

The light continuous liquid was synergistic mixture 0.5 M (di-(2-ethylhexil)) phosphoric acid – 0.125 M trioctyl phosphin oxide in dearomatised kerosene (D2EHPA and TOPO manufactured by SNPE, France), and the heavy dispersed liquid was 5.6 M phosphoric acid. The structural presentation of the constituent liquids is:

Figure 3 shows measured variations of the relevant physical properties of the liquids with temperature.

Droplet-film structure: double emulsion

The secondary separation of the entrained light phase or the breaking of emulsion was examined in the pilot plant [27,28,62,153]. The schematic flow sheet of the selected operations, processes, and equipment is presented in Figure 4.

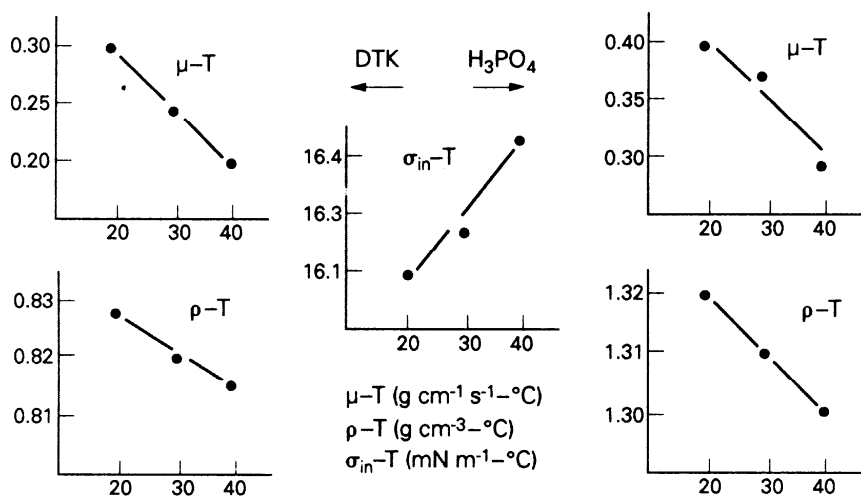


Figure 3. Measured variations of the relevant physical properties of the liquids with temperature, density, viscosity and interfacial tension.

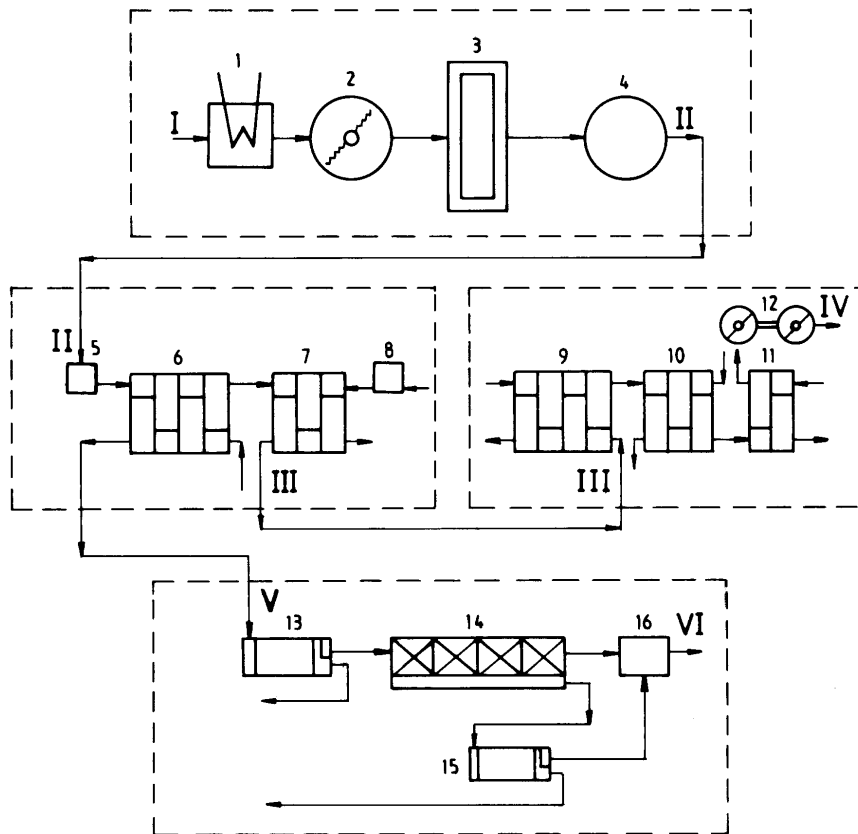


Figure 4. A schematic flow sheet of the selected operations, processes and equipment; 1 – cooler, 2 – thickener, 3 – vacuum filter, 4 – adsorption C, 5 – oxidation reactor, 6 – four M-S-E units, 7 – three M-S-S units, 8 – reduction reactor, 9 – four M-S-E units, 10 – three M-S-W units, 11 – two M-S-S units, 12 – two crystallizer units, 13 – lamellar coalescer, 14 – A-I-F cells, 15 – settler, 16 – raffinate tank.

In this pilot plant the light phase loop, relevant to this investigation [43,45,62,153] is shown in Figure 5.

The polydispersion was generated and the primary separation performed in a counter-current “pump-mix” mixer-settler battery 2 which was designed on the basis of

the laboratory batch and continuous studies [28,33,153].

Figure 6 shows *in situ* photograph of the particular droplet-film structures submerged into the droplet homophase continuum [1,11,38,62,153].

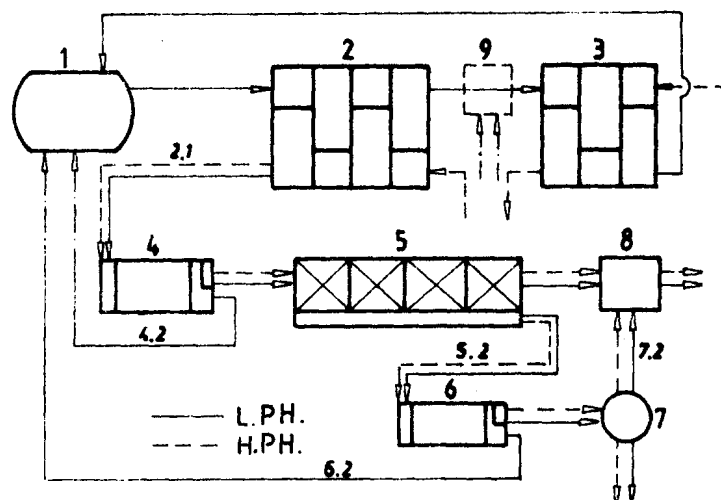


Figure 5. The light phase loop; 1 – the light phase tank, 2 – the mixer-settler extraction units, 3 – the mixer-settler reduction stripping units, 4 – the lamellar coalescer – central unit, 5 – the flotation units, 6 – the settler unit, 7 – the adsorption column unit, 8 – the raffinate tank, 9 – the light phase collector tank.

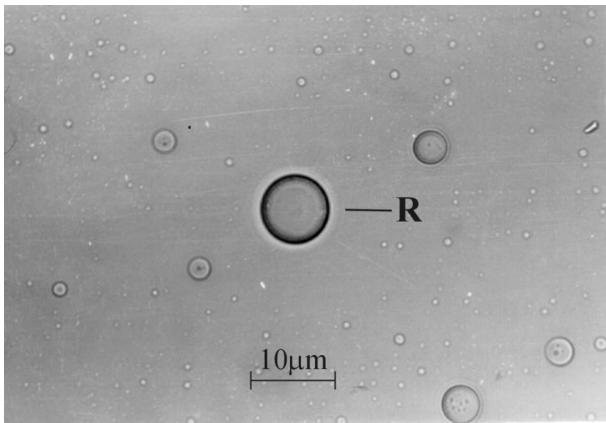


Figure 6. *In situ* photograph of the examined liquid-liquid droplet-film structure submerged into the droplet homophase continuum.

The entrained light phase in the form of the double emulsion was lead into the lamellar coalescer 4, as it is shown in Figure 5. Further on, the raffinate was lead through four air induced flotation units 5 (Denver A 5 type). The flotation overflow was split in the settler 6 and the heavy phase fraction was lead into the adsorption column 7 filled with activated carbon. Since the separated light phase contained some uranium, collected output was lead back into the reductive stripping units 3.

The physical processes that occur in the lamellar coalescer, *i.e.* at its inclined plates, are presented in Figure 7.

COLLOID ELECTROHYDRODYNAMICS: THEORY AND MODELING

Physical formalism – classical approach and a new approach

Following a classical deterministic approach, the phases that constitute a multiphase dispersed system are

assumed to be a continuum, *i.e.* without discontinuities inside the entire phase, that is considered homogenous and isotropic [1,153]. Therefore, the basic laws, *e.g.* conservation of mass, first and second Cauchy’s laws of motion, first and second laws of thermodynamics, are applicable.

According to the classical approach, the behavior of liquid-liquid interfaces in finely dispersed systems is based on an interrelation between three forms of “instabilities”. These are sedimentation, flocculation/coagulation, and coalescence. These events can be understood as a kind of interaction between the liquid phases involved [16,17].

Furthermore, the forces responsible for sedimentation and flocculation are gravity and van der Waals forces of attraction, respectively, and the forces responsible for coalescence are not well known, although some suggestions have been made recently [1,153].

A new, deterministic approach discusses the behavior of liquid-liquid interfaces in finely dispersed systems as an interrelation between three other forms of “instabilities”. These are rigid, elastic, and plastic [1,11,153]. Figure 8 shows the events that are understood as interactions between the internal/immanent and the external/incident periodical physical fields. Since both electric/electromagnetic and mechanical physical fields are present in a droplet, they are considered as immanent or internal, whereas ultrasonic, temperature, or any other applied periodical physical fields are considered as incident or external. Hereafter, the rigid form of instability comprises the possibility of two-way disturbance spreading, or dynamic equilibrium. This form of instability, when all forces involved are in equilibrium, permits a two-way disturbance spreading (propagation or transfer) of entities either by tunneling (low energy dissipation and occurrence probability) or by induction (medium or high energy dissipation and occurrence probability). A classical particle or system could

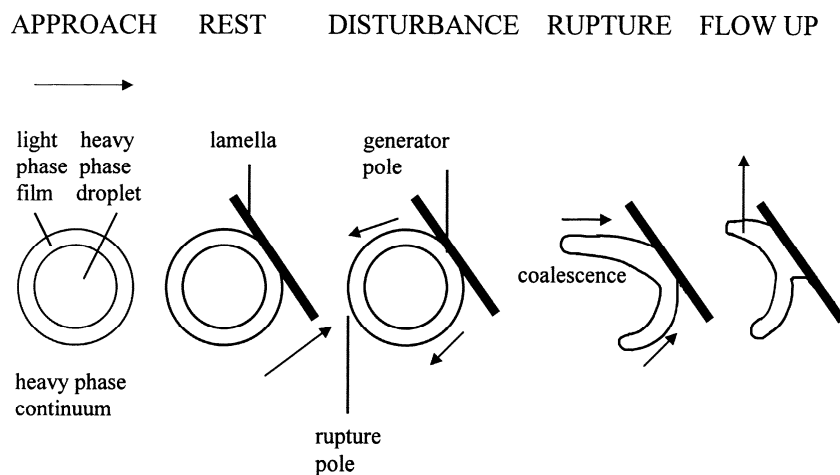


Figure 7. *The physical model of the processes during the secondary separation of the double emulsion on an inclined plate.*

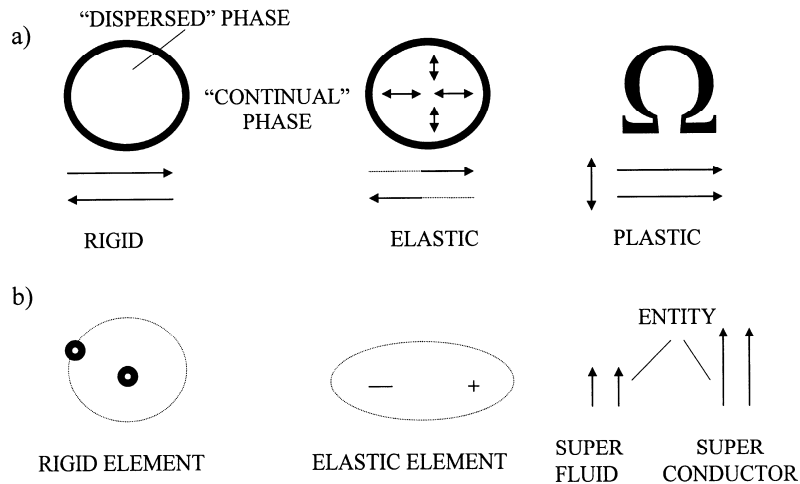


Figure 8. A new approach; a) "instabilities", rigid, elastic, plastic; b) the constructive elements of phases.

not penetrate region in which its energy would be negative, that is, barrier regions in which the potential energy is greater than the system energy. In the real world, however, a wave function of significant amplitude may extend into and beyond such region. If the wave function extends into another region of positive energy, then the barrier is crossed with some probability; this process is termed tunneling (since the barrier is penetrated rather than climbed). The elastic form of instability comprises the possibility of reversible disturbance spreading, with or without hysteresis. Finally, the plastic form of instability comprises the possibility of irreversible disturbance spreading with a low or high intensity of influence between two entities. Entity is the smallest indivisible element of matter that is related to the particular transfer phenomena. The entity can be either differential element of mass/demon, or phonon as quanta of acoustic energy, or infon as quanta of information, or photon, or electron.

Now, a disperse system consists of two phases, "continuous" and "dispersed". The continuous phase is modeled as an infinitely large number of harmonic electromechanical oscillators with low strength interactions among them. Furthermore, the dispersed phase is a macrocollective consisting of a finite number of microcollectives/harmonic electromechanical oscillators (clusters) with strong interactions between them. The cluster can be defined as the smallest repetitive unit that has a character of integrity. Clusters appear in a micro- and nano-dispersed systems. The microcollective consists of the following elements: rigid elements (atoms or molecules), the elastic elements (dipoles or ions that may be recombined), and entities (as the smallest elements) [1,11,153].

Structure – mechanism – dynamics

If the liquid–liquid interface, *e.g.* emulsion or double emulsion, is taken as a central and representative ($i = j = 2$,

Table 1) finely dispersed system it is possible to propose a theory of electroviscoelasticity based on a new constitutive model of liquids [1,8,11,40,41,153]. Thus, a hydrodynamic and electrodynamic motions are considered in the presence of both potential (elastic forces) and nonpotential (resistance forces) fields. The elastic forces are gravitational, buoyancy, and electrostatic/electrodynamic (Lorentz), and the resistance forces are continuum resistance/viscosity and electrical resistance/impedance. The principles of conservation of momentum, energy, mass, and charge are used to define the state of a real fluid system quantitatively. In addition to the conservation equations, which are insufficient to define the system uniquely, statements on the material behavior are also required; these statements are termed constitutive relations, *e.g.* Newton's law, Fourier's law, Fick's law, and Ohm's law.

Now, the droplet or droplet-film structure is considered as a macroscopic system with internal structure determined by the way the molecules (ions) are tuned (structured) into the primary components of a cluster configuration. At first, during the droplet formation and/or destruction periods, it may be assumed that the electrical analogue consists of a number of serial equivalent circuits; after rearrangement or coupling at resonant/characteristic frequency a probable equivalent circuit is shown in Figures 9a and 9b. Electrical analogue, Figure 9a, consists of passive elements (R , L , and C), and an active element (emitter-coupled oscillator, W). Further on, the emitter-coupled oscillator is represented by the equivalent circuit as shown in Figure 9b. Figure 9c shows the electrical (oscillators) and/or mechanical (structural volumes V_j) analogues when they are coupled to each other, *e.g.* in the droplet. Hence, the droplet consists of a finite number of structural volumes or spaces/electromechanical oscillators (clusters), V_j , a finite number of excluded surface volumes or interspaces, V_s ,

and of a finite number of excluded bulk volumes or interspaces, V_b . Furthermore, the interoscillator/cluster distance or internal separation, S_i , represents the equilibrium of all forces involved (electrostatic, solvation, van der Waals and steric). The external separation, S_e , is introduced as a permitted distance when the droplet is in interaction with any external periodical physical field. The rigid droplet boundary, R , presents a form of droplet instability when all forces involved are in equilibrium. Nevertheless, two-way disturbance spreading (propagation or transfer) of entities occur, either by tunneling mechanism (low energy dissipation and occurrence probability) or by induction mechanism (medium or high energy dissipation and occurrence probability). The elastic droplet boundary, E , represents a form of droplet instability when equilibrium of all forces involved is disturbed by the action of any external periodical physical field, but the droplet still exists as a dispersed phase. In the region between the rigid and elastic droplet boundaries, a reversible disturbance spreading occurs with or without hysteresis. After the elastic droplet boundary, the plastic form of droplet instability takes place, then electromechanical oscillators/clusters do not exist any more and the beams of entities or atto-clusters appear. Atto-clusters are the entities that appear in the atto-dispersed systems. In this region one-way propagation of entities occurs.

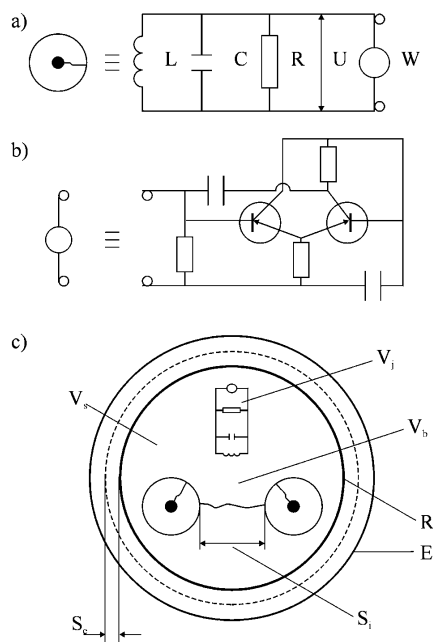


Figure 9. Graphical interpretation of the structural model: a) electrical and mechanical analog of the micro-collective/cluster; b) equivalent circuit for the emitter coupled oscillator; c) the macro-collective: a schematic cross-section of the droplet and its characteristics (V_j – structural volumes/clusters; V_s – excluded surface volumes/interspaces; V_b – excluded bulk volumes/interspaces; S_i – internal separation; S_e – external separation; R – rigidity droplet boundary; E – elasticity droplet boundary).

Mathematical formalisms - tension tensor model

Now, using the presented propositions and electro-mechanical analogies, an approach to non-Newtonian behaviors and to electroviscoelasticity is to be introduced. When the droplet is stopped, *e.g.* at an inclined plate in the lamellar coalescer, and when the droplet is in the state of “forced” levitation than the volume forces balance each other, and the surface forces alone will be considered [1,8,11,8,38–41,48–52,153]. It is assumed that the surface forces are, for the general case that includes the electroviscoelastic fluids, composed of interaction terms expressed by:

$$dF_s^i = T^{ij} dA_j \tag{2}$$

where the tensor T^{ij} is given by

$$T^{ij} = -\alpha_0 \delta^{ij} + \alpha_1 \delta^{ij} + \alpha_2 \zeta^{ij} + \alpha_3 \zeta_k^i \zeta^{kj} \tag{3}$$

and T^{ij} is composed of two tensors, δ^{ij} is Kronecker symbol, and ζ^{ij} is the stretching tensor. In the first and second isotropic tensors the $\alpha_0 = \alpha_0(\rho, U)$ and $\alpha_1(\rho, U)$ are the potentiostatic pressures, where U represents hydrostatic or electrostatic potential. Now, the general equilibrium condition may be derived from Eq. (3), and may be expressed by:

$$\tau = \frac{-\alpha_0 + \alpha_1 + \alpha_2 \left(\frac{\sigma}{d} \right) + \alpha_3 \left(\frac{\sigma}{d} \right)}{2(\alpha_2 + \alpha_3)} \tag{4}$$

where τ is the tangential stress. Note that for dispersed systems consisting of, or behaving as Newtonian fluids, $\alpha_3 = \alpha_3(\rho, U)$ is equal to zero.

The processes of formation/destruction of the droplet or droplet-film structure are non-linear. Furthermore, the viscosity coefficients, μ_i ($i = 0,1,2$), where each consists of bulk, shear, and tensile components, when correlated to the tangential tensions of mechanical origin, τ_v , can be written as:

$$\tau_v = \mu_0 \frac{du}{dx} + \mu_1 \frac{d^2u}{dx^2} + \mu_2 \left(\frac{du}{dx} \right)^2 \tag{5}$$

where u is the velocity and x is one of the space coordinates.

Using the electrical analog, the impedance coefficients, Z_i ($i = 0,1,2$), where each consists of ohmic, capacitive, and inductive components, will be correlated with the tangential tensions of electrical origin, τ_e , as follows:

$$\tau_e = Z_0 \frac{d\phi_e}{dt} + Z_1 \frac{d^2\phi_e}{dt^2} + Z_2 \left(\frac{d\phi_e}{dt} \right)^2 \tag{6}$$

where ϕ_e is the electron flux density, and t is the time coordinate.

Van der Pol integer order derivative model

Postulated assumptions for an Electrical analogue:

1. The droplet is a macro-system (collective of particles) consisting of structural elements that may be considered as electromechanical oscillators.

2. Droplets as micro-collectives undergo tuning or coupling processes, and thus build the droplet as a macro-collective.

3. The external physical fields (temperature, ultrasonic, electromagnetic, or any other periodic) cause the excitation of a macro system through the excitation of micro-systems at the resonant/characteristic frequency, where elastic and/or plastic deformations may occur.

Hence, the study of the electromechanical oscillators is based on electromechanical and electrodynamic principles. At first, during the droplet formation it is possible that the serial analog circuits are more probable, but later, as a consequence of tuning and coupling processes the parallel circuitry become dominant. Also, since the transfer of entities by tunneling (although with low energy dissipation) is much less probable it is sensible to consider the transfer of entities by induction (medium or high energy dissipation). Figure 10 presents the resultant equivalent electrical circuit, rearranged under the influence of an applied physical field, such as an antenna output circuit.

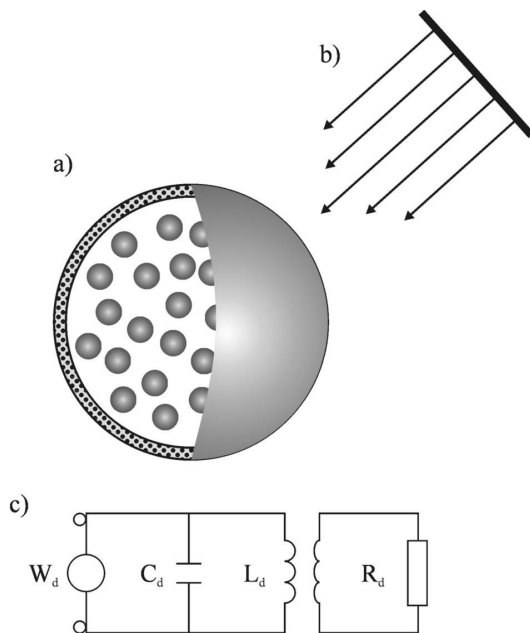


Figure 10. Definition sketch for understanding the theory of electroviscoelasticity: a) rigid droplet; b) incident physical field, e.g. electromagnetic; c) equivalent electrical circuit-antenna output circuit. W_d represents the emitter-coupled oscillator, C_d , L_d and R_d are capacitive, inductive, and resistive elements of the equivalent electrical circuit, respectively. Subscript d is related to the particular diameter of the droplet under consideration. Courtesy of Marcel Dekker, Inc. (From references [1] and [11]).

A nonlinear integral-differential equation of the van der Pol type represents the initial electromagnetic oscillation:

$$C \frac{dU}{dt} + \left(\frac{U}{R} - \alpha U \right) + \gamma U^3 + \frac{1}{L} \int U dt = 0 \tag{7}$$

where U is the overall potential difference at the junction point of the spherical capacitor C and the plate, L is the inductance caused by the potential difference, and R is the ohmic resistance (resistance of the energy transformation, electromagnetic into the mechanical or damping resistance), t is the time; α and γ are the constants determining the linear and nonlinear parts of the characteristic current and potential curves. U_0 , the primary steady-state solution of this equation, is a sinusoid of frequency close to $\omega_0 = 1/(LC)^{0.5}$ and amplitude $A_0 = [(\alpha - 1)/R/3\gamma]^0.5$.

The noise in this system, due to linear amplification of the source noise (the electromagnetic force assumed to be the incident external force, which initiates the mechanical disturbance), causes the oscillations of the “continuum” particle (molecule surrounding the droplet or droplet-film structure), which can be represented by the particular integral:

$$C \frac{dU}{dt} + \left(\frac{1}{R} - \alpha \right) U + \gamma U^3 + \frac{1}{L} \int U dt = -2A_n \cos \omega t \tag{8}$$

where ω is the frequency of the incident oscillations.

Finally, considering the droplet or droplet-film structure formation, “breathing”, and/or destruction processes, and taking into account all the noise frequency components, which are included in the driving force, the corresponding equation is given by:

$$\begin{aligned} C \frac{dU}{dt} + \left(\frac{1}{R} - \alpha \right) U + \frac{1}{L} \int U dt + \gamma U^3 &= i(t) = \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(j\omega t) A_n(\omega) d\omega \end{aligned} \tag{9}$$

where $i(t)$ is the noise current and $A_n(\omega)$ is the spectral distribution of the noise current as a function of frequency.

In the case of nonlinear oscillators, however, the problem of determining of the noise output is complicated by the fact that the output is fed back into the system thus modifying in a complicated manner the effective noise input. The noise output appears as an induced anisotropic effect.

Recent development

Van der Pol fractional order derivative model – linearized

In an effort to generalize Eqs. (7) and (8), the ordinary time derivatives and integrals are now replaced with corresponding fractional-order time derivatives and

integrals [1,13,15,136–145,153]. Here, the capacitive and inductive elements, using fractional-order $p < 2$ ($p = n - \delta$, $n = 1, 2, \delta \ll 1$) enable formation of the fractional differential equation, *i.e.* more flexible or general model of liquid–liquid interfaces behaviour. Now, a differ-integral form using Riemann–Liouville definition is given by:

$${}_0D_t^p[U(t)] = \frac{d^p U}{dt^p} = \frac{1}{\Gamma(1-p)} \frac{d}{dt} \int_0^t \frac{U(\tau)}{(t-\tau)^p} d\tau, \quad 0 < p < 1 \quad (10)$$

$${}_0D_t^{-p}[U(t)] = \frac{1}{\Gamma(p)} \int_0^t \frac{U(\tau)}{(t-\tau)^{1-p}} d\tau, \quad p > 0$$

Further on, a linear fractional differential equation with zeros initial conditions is obtained:

$$C_0 D_t^p[U(t)] + \left(\frac{1}{R} - \alpha\right)U + \frac{1}{L} {}_0D_t^{-p}[U(t)] = i(t) \quad (11)$$

Further evaluation and calculation related to the solutions of the linearised, both homogeneous and non-homogeneous, fractional integro-differential equations is presented elsewhere [1,13,15,136–145,153].

In the case of nonhomogeneous solution obtained result appears as a band because the input (cos) is of the fractional order too; and output is in a damped oscillatory mode, of high frequencies!

Van der Pol fractional order derivative model – nonlinear case

Nonlinear fractional differential equations have received rather less attention in the literature, partly because many of the model equations proposed have been linear. Here, both cases a nonlinear homogenous ($i(t) = 0$) and nonhomogeneous ($i(t) \neq 0$) are considered. Equivalent nonlinear problem applying differentiation of Eq. (7) is presented by:

$$C \frac{d^2 U}{dt^2} + \left(\frac{1}{R} - \alpha + \mathcal{N}^3\right) \frac{dU}{dt} + \frac{1}{L} U = 0 \quad (12)$$

In an effort to generalize the previous equation fractional order, van der Pol equation becomes:

$${}_0D_t^{2p}U(t) = \frac{1}{C} \left(\frac{1}{R} - \alpha\right) {}_0D_t^p U(t) - \frac{3\gamma}{C} U(t) {}_0D_t^p U(t) - \frac{1}{CL} U(t) \quad (13)$$

Further evaluation and calculation related to the solutions of the nonlinear, both homogeneous and non-homogeneous, fractional integro-differential equations is presented elsewhere [1,13,15,136–145,153].

Experimental confirmation

Presented theoretical predictions including both physical and mathematical formalisms have been experimentally corroborated by means of the electrical inter-

facial potential (EIP) measurements, and by means of the nuclear magnetic resonance spectroscopy (NMR). The obtained experimental results were in good agreement with postulated theory [1,13,15,136–145,153].

PROBABLY POSSIBLE FURTHER DEVELOPMENT

Classical limit of quantum mechanics

This part will treat one important question of the classical limit of quantum mechanics, *i.e.* is a quantum mechanics applicable at macroscopic level? This question resulted during the research of complex systems by the end of the last century. According to the developed strategy, the proposition appeared is: if the macroscopic physical systems are only the special case of a quantum-mechanical systems (*e.g.* like in von Neumann's theory of the measurement problem) than it is possible to observe, under specified conditions, their quantum mechanical behavior [149,150].

The behavior of a droplet-film structure submerged into the droplet homophase or double emulsion, including its formation–existence–destruction states, described in this paper [1–153], will be considered as a close to the representative open macroscopic quantum system (OMQS) under the specified conditions. Hence, OMQS are quantum subsystems, *i.e.* open quantum systems that are in inevitable permanent interaction with other physical systems, which may be named environment [150]. Does the theory of electroviscoelasticity, here presented, may be useful in discussion and/or further elucidation related to the problems of the experimental and theoretical status of decoherence?

Some needed definitions [150]:

1. The choice of an OMQS has to be in accordance to the criteria that confirm its description by the motion equation in a “classical domain”.

2. It is convenient that the classical motion equation of the OMQS contain dissipative term.

3. The motion equation of the OMQS must be related, clearly and unequally, to the physical units whose values define distinguishable macroscopic states of the system.

4. The choice of a needed conditions for the following of the behavior of one OMQS have to be limited by the condition that some of the parameters values may correspond to the limit of the correspondence principle, *i.e.* the condition $n \rightarrow \infty$ is invalid.

5. It is convenient to consider, theoretically, the behavior of the chosen OMQS, and therefore to prepare possible predictions comparable with experimentally attainable situations.

The Leggett's Program:

These five points present a Leggett's task and basis for exploration of the macroscopic quantum phenomena

of the second kind, *i.e.* the confirmed quantum mechanical nature of the OMQS is related to these physical situations where the quantum effects are unequally linked to the macroscopically distinguishable states [149–152].

Suggested problem – the model

Finely dispersed system, emulsion/double emulsion, discussed in the paper, now will be considered as the composite system “droplet-film structure + droplet homophase (S + E)”. Equivalent electrical circuit of the composite system is presented in Figures 9a, 9b and 10c; the history of this system consists of the initial/formation, intermediate/transition, and final/rigid states.

Keeping in mind all the requirements, the needed definitions and Leggett’s program the model assumptions are [149–152]:

1. Every stationary state (initial, intermediate and final) is characterized by interaction in the composite system that is of the same kind – being able to give rise to the occurrence of decoherence with the cluster arrangements as the “pointer basis states”.

2. Nonstationary state is characterized by the change in the character of interaction in the composite system. The net effect takes the following “phases” each having its own characteristic time:

a) action of the external/incident physical field/formation of the droplet-film structure (producing the non-stationary state), taking time, measured using developed liquid-liquid contact cell (LLCC) [1,11,51,149,153], $t_{\text{ext}} = 125$ ms, Figure 11;

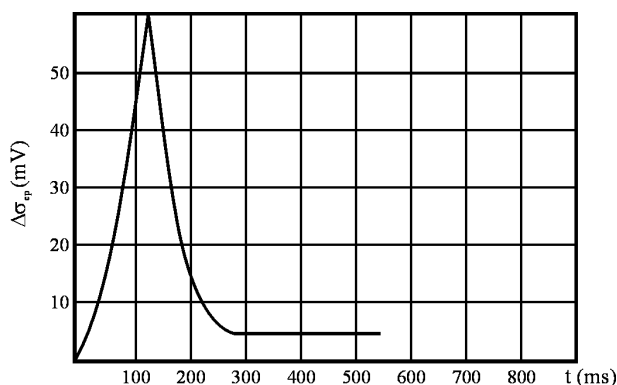


Figure 11. Measured variations of the EIP with time for the examined system phosphoric acid/D2EHPA-TOPO-kerosene at the spherical interface. Reprinted from reference [154] with permission from Academic Press.

b) transition/relaxation of the electroviscoelastic droplet-film structure into the rigid one (establishing the new, final stationary state), taking time, measured by LLCC, $t_{\text{relax}} = 8$ min, Figure 12;

c) decoherence process (in the final stationary state), taking time of the “decoherence time”, t_D .

Therefore, the complete generation of the dispersed system/double emulsion takes overall time:

$$t_0 = t_{\text{ext}} + t_{\text{relax}} + t_D \quad (14)$$

Overall Hamiltonian of the composite system is:

$$H_{\text{overall}} = H_{\text{SO}} + H_{\text{EO}} + H_{\text{int}} \quad (15)$$

where

$$H_{\text{int}} = H_{\text{S+E}} \quad (16)$$

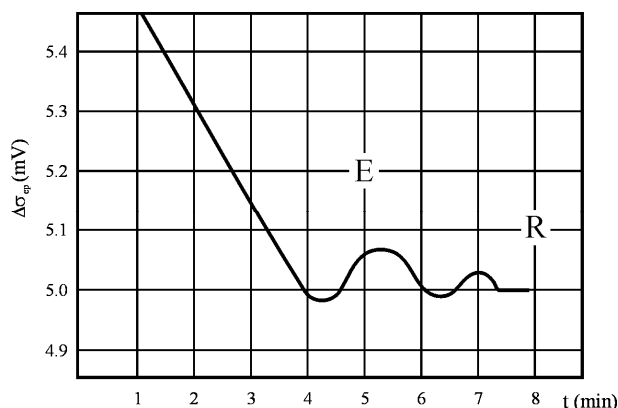


Figure 12. Measured spontaneous oscillations of the EIP during the “breathing” period; transformation of the electroviscoelastic sphere into the rigid sphere. Reprinted from reference [154] with permission from Academic Press.

Suggested experimental confirmation

Since the equivalent electrical circuit, Figure 9a, may be considered as a kind of Superconducting Quantum Interference Device (SQUID), probably, it may be possible to couple, (at resonant frequency, where all events occur) one adjusted, sensitive tunnel diode oscillator as one detector of Macroscopic Quantum Tunneling Effect (MQTE) [149].

IMPLICATIONS

Philosophical breakpoints

The first philosophical breakpoint

A theory of electroviscoelasticity using fractional approach constitutes a new interdisciplinary approach to colloid and interface science. Hence, 1-more degrees of freedom are in the model, 2-memory storage considerations and hereditary properties are included in the model, and 3-history impact to the present and future is in the game!

This theory and models discussed may facilitate the understanding of, *e.g.* entrainment problems in solvent extraction, very developed interfaces in colloid and interface science, chemical and biological sensors, electro-analytical methods, biology/biomedicine (hematology, genetics and electrophysiology).

Furthermore, both, the model and theory may be implemented in studies of structure; interface barriers/symmetries – surface (bilipid membrane cells, free bub-

bles of surfactants, Langmuir–Blodgett films) – line (genes, liquid crystals, microtubules) – point (fullerenes, micro-emulsions) and – overall (dry foams, polymer elastic and rigid foams).

The second philosophical breakpoint

Also, the further evaluation of the idea related to the entity understood as an energetic ellipsoid, based on the model of electron following Maxwell–Dirac Isomorphism (MDI) seems to be sensible. Such an approach, and consequent knowledge, may be implemented in the studies of, *e.g.* ionics, spintronics, fractional-quantum Hall effect-fluids, decoherence sensitivity, quantum computation, entities/quantum particles entanglement [1,11,153–160].

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IZVOD**KOLOIDNA ELEKTROHIDRODINAMIKA**Aleksandar M. Spasić¹, Mihailo P. Lazarević², Milan V. Mitrović³, Dimitrije N. Krstić³¹Institut za tehnologiju nuklearnih i drugih mineralnih sirovina, Departman za hemijsko inženjerstvo, Beograd, Srbija²Mašinski fakultet, Departman za mehaniku, Univerzitet u Beogradu, Beograd, Srbija³Tehnološko–metalurški fakultet, Katedre za hemijsko i metalurško inženjerstvo, Univerzitet u Beogradu, Beograd, Srbija

(Pregledni rad)

Kratak pregledni rad predstavlja novije rezultate razvoja osnovnih i primenjenih nauka i inženjerstva vezanih za fine disperzne čestice i sisteme u opštem smislu, a posebna pažnja je posvećena tečno–tečnim finim disperznim sistemima kao što su emulzije i dvostruke emulzije. Rad je nastao kao rezultat rešavanja problema zahvatanja jedne tečne faze drugom u pilot postrojenju za ekstrakciju uranijuma iz fosforne kiseline. Problem zahvatanja predstavlja razdvajanje emulzija i dvostrukih emulzija nastalih kao neželjena posledica uzastopnih operacija/procesa ekstrakcije i reekstrakcije. U pilot postrojenju je razvijena i realizovana sekcija za razdvajanje emulzija i dvostrukih emulzija; sekciju čini serijski vezan lamelarni koalescer, centralni uređaj za dalja istraživanja, i četiri flotacione ćelije. Razdvajanje emulzija/dvostrukih emulzija u lamelarnom koalesceru, na zakošenim talasastim perforiranim pločama ispune, zasniva se na akciji/učešću spoljnih sila mehaničkog i/ili električnog porekla. Kako mnogi od relevantnih procesa u toku razdvajanja, adhezija, pucanje, koalescencija, nisu bili dovoljno razjašnjeni dalja i dublja istraživanja ovih događaja i fenomena su predstavljali pravi naučni izazov. Upotrebnost vrednosti rezultata prikazanih istraživanja višestruko prevazilazi primarni cilj rešavanja problema zahvatanja u operacijama/procesima ekstrakcije tečno–tečno; tako neki od primera primene razvijene teorije elektroviskoelastičnosti, fizičkih i matematičkih modela mogu doprineti boljem razumevanju pojava/fenomena na razvijenim međupovršinama u naukama o koloidima, hemijskim i biološkim sensorima, elektroanalitičkim metodama, biologiji/biomedicini, (hematologiji, genetici, elektroneurofiziologiji). Dalje, razvijena teorija i modeli mogu koristiti izučavanju strukture međupovršinskih barijera/simetrija, površinskih (bilipidne membranske ćelije, mehurovi površinski aktivnih komponenata, Langmuir–Blodget filmovi), linijskih (geni, tečni kristali, mikrotubule), tačkastih (fulereni, mikroemulzije), svih zajedno (suve pene, elastične i rigidne polimerne pene). Na kraju, dalji razvoj nekih od ideja i pristupa, prikazanih u radu, može koristiti izučavanju, na primer klasičnog limita kvantne mehanike, eksperimentalnog i teorijskog statusa dekoherencije, otvorenih makroskopskih kvantnih sistema, makroskopskog kvantnog tunelovanja i umrežavanja kvantnih čestica/entiteta.

Ključne reči: Elektrohodinamika • Elektroviskoelastičnost • Nanoreologija • Tečno–tečne međupovršine • Fini disperzni sistemi • Emulzije • Dvostruke emulzije • Naelektrisane međupovršine

Key words: Electrohydrodynamics • Electroviscoelasticity • Nanorheology • Liquid–liquid interfaces • Finely dispersed systems • Emulsions • Double emulsions • Electrified interfaces