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ELECTRON AND MOMENTUM TRANSFER PHENOMENA AT DEVELOPED DEFORMABLE AND RIGID LIQUID-LIQUID INTERFACES

A new idea was applied for the elucidation of the electron and momentum transfer phenomena at both rigid and deformable interfaces in finely (micro, nano, atto) dispersed systems. The electroviscoelastic behavior of e.g., liquid/liquid interfaces (emulsions and double emulsions) is based on three forms of "instabilities"; these are rigid, elastic, and plastic. The events are understood as interactions between internal (immanent) and external (incident) periodical physical fields. Since the events at the interfaces of finely dispersed systems must be considered at the molecular, atomic, and/or entities level, it is inevitable to introduce the electron transfer phenomenon beside the classical heat, mass and momentum transfer phenomena commonly used in chemical engineering. Three possible mathematical formalisms have been derived related to this physical formalism, i.e. to the developed theory of electroviscoelasticity. The first is tension tensor model, where the normal and tangential forces are considered, only in mathematical formalism, regardless to their origin (mechanical and/or electrical). The second is van der Pol derivative model. Finally, the third model comprise an effort to generalize the previous van der Pol differential equations, both, linear and nonlinear; the ordinary time derivatives and integrals are now replaced by corresponding fractional-order time derivatives and integrals of order $p < 1$. Both, the presented model and theory can facilitate the understanding of entrainment problems in solvent extraction, developed interfaces in colloid and interface science, chemical and biological sensors, electro analytical methods, biology/biomedicine (hematology, genetics and electroneuro-physiology).

Key words: Electron transfer phenomena, Electrified liquid-liquid interfaces, Finely dispersed systems, Electroviscoelasticity, Emulsions.

Over the last decade the biggest advances in physics, physical chemistry and bio-chemistry 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 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. In this context, "atomic engineering" recalls the ancient idea of the interplay of particles that are small, indivisible and integer [Greek ($\alpha\tau\omicron\mu\omicron$)] [1]. In the recent scientific literature, terms such as nano-science and nanotechnology, functional artificial nano-architectures, nano-systems and molecular machinery, once considered merely futuristic, have become focuses of attention [1].

This paper presents a brief overview of the topic divided into two main parts: general, developing a new classification of finely dispersed systems based on entities, and particular, discussing electron and

momentum transfer phenomena at liquid-liquid interfaces.

GENERAL – CLASSIFICATION OF FINELY DISPERSED SYSTEMS

Classification based on scales [1] – Macro and micro scale

Classical chemical engineering was developed intensively during the 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 to homogeneous and heterogeneous catalysis. Entire object models, continuum models and constrained continuum models are frequently used for the description of events and for equipment design. Reactors, tanks and columns are the usual principal equipment. The output is, generally, demonstrated as conventional products, precision products, chemistry (solutions) and biochemistry.

Nano scale

Molecular engineering nowadays is still undergoing substantial development. Beside heat, mass and momentum transfer phenomena, commonly used in classical chemical engineering, it is necessary to

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introduce the electron transfer phenomenon. The description of events is based on molecular mechanics, molecular orbits and electrodynamics. The principal tools and equipment are micro-reactors, membrane systems, micro analytical sensors and micro-electronic devices. The output is, generally, demonstrated as molecules, chemistry (solutions) and biochemistry.

Atto scale

Atto-engineering is in permanent and almost infinite development for already more than a whole century. The theoretical background is related to surface physics and chemistry, quantum and wave mechanics, and quantum electrodynamics. Discrete models and constrained discrete models are convenient for the description of related events. The tools and equipment are nano and atto dispersions and beams (demons, 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. The output is, generally, demonstrated as finely dispersed particles (plasma, fluosol-fog, fluosol-smoke, foam, emulsion, suspension, metal, vesicle, dispersoid).

Further possible classifications

Examples given, related to geometry: surface continuums, line continuums and point discontinuums. Related to forces of interaction: electrostatic, van der Waals, solvation and steric. Related to physical – chemical processes: diffusion, sorption, catalysis, membrane. Finally, the classification presented here 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 a differential element of mass/demon, or an ion, or a phonon as a quantum of acoustic energy, or an infon as a quantum of information, or a photon or an electron [1,2].

A possible approach is proposed to the general formulation of the links between the basic characteristics, the levels of approximation and the levels of abstraction related to the existence of finely dispersed systems/**DS** [3]. 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 more than one state of aggregation/**HEA**). Now the matrix presentation of finely dispersed systems is given by

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

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

Table 1. A new classification of finely dispersed systems

DM* DP*	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

DP* – Dispersed Phase; DM* – Dispersion Medium; D – Deformable Interfaces; R – Rigid Interfaces.

Related to the levels of abstraction and approximation, it is now possible to distinguish continuum models (the phases considered as a continuum i.e. without discontinuities inside the 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, 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 model approach for the description of related events [4]. For easier understanding it is convenient to consult, among others, e.g. [5–16].

Hierarchy of entities

Figure 1.a shows a stereographic projection/map-ping from a Riemann sphere, Fig. 1.b. shows a "hierarchy" of entities, which must be understood as a lim 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 the viscosity/impedance Z ($G = 1/Z$), l is the path length that an entity "overrides", 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. It is now possible to propose that all real dynamic systems are situated between these limits. Also, it seems sensible to think about the further

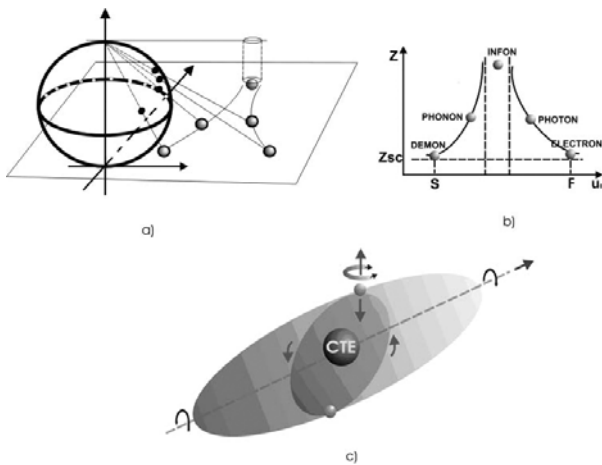


Figure 1.a. – The first philosophical breakpoint – a stereographic projection/mapping from a Riemann sphere; b. – hierarchy of entities, correlation viscosity/impedance–characteristic velocity, S–slow/demon (super fluid) and F–fast/electron (superconductor); c. – The second philosophical breakpoint – 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 Ref 1 p. 20, courtesy of CRC Press/Taylor & Francis.

structure of entities, the second philosophical breakpoint e.g., the basic entity can be understood as an energetic ellipsoid shown in Figure 1.c. (based on the model of electron following Maxwell–Dirac Isomorphism/MDI: an electron is an entity at the same time quantum–mechanical/microscopic $N=-2$ and electro–dynamic/macroscopic $N=3$). Now, a spatio–temporal, five dimensional existence of an entity/e.g., electron may be presented by the equation $[(x-a)^2 + (y-b)^2 + (z-d)^2 - (ct-e)^2 - ({}^kN_0\omega_N-f)^2 = 0]$, where kN_0 is the factor of spatio–temporal synergy (cm s), and ω_N is the isotropic angle rotation (s^{-1}) [17].

PARTICULAR – LIQUID/LIQUID INTERFACES

Physical formalism – structure – mechanism – dynamics

If a liquid–liquid interface, e.g. emulsion or double emulsion, is taken as a central and representative ($i=j=2$) finely dispersed system, it is possible to propose a theory of electroviscoelasticity [1–4, 18–23] based on a new constitutive model of liquids. Thus, hydrodynamic and electrodynamic motions are considered in the presence of both potential (elastic forces) and non–potential (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

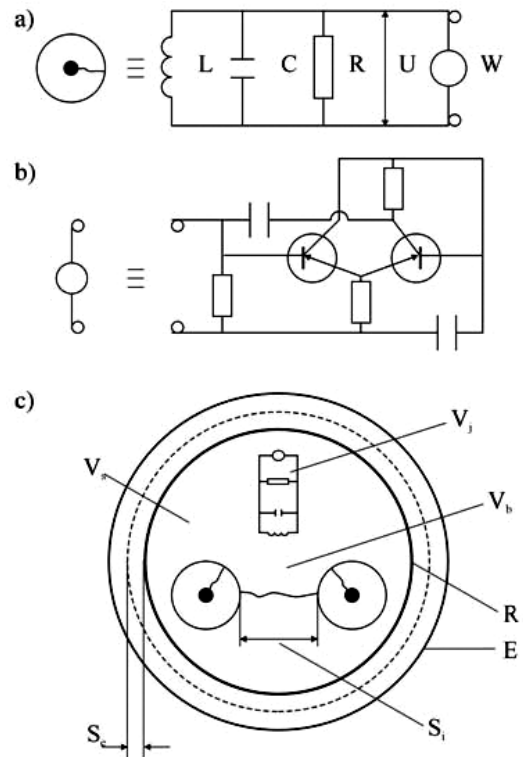


Figure 2. A graphical interpretation of the structural model: a. the electrical and mechanical analogue of the micro–collective/cluster, b. the equivalent circuit for the emitter coupled oscillator, c. the macro–collective/clusters – a schematic cross section of the droplet and its characteristics (V_j – structural volumes/clusters, V_s – excluded surface volumes/interspaces, V_b – excluded bulk volumes/interspaces, S_i – internal separation/inter–oscillator distance, S_e – external separation, R – rigidity droplet boundary, E – elasticity droplet boundary)

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.

The droplet or droplet–film structure is now considered as a macroscopic system with an 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 the resonant/characteristic frequency a probable equivalent circuit is shown in Fig. 2.a and b. The electrical analogue, Fig. 2.a, consists of passive elements (R , L , and C) and an active element (emitter–coupled oscillator W). The emitter–coupled oscillator is represented by an equivalent circuit as shown in Fig. 2.b. Figure 2.c 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/electro–mechanical 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 the forces involved (electrostatic, solvation, van der Waals and steric) [1-4]. 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 the forces involved are in equilibrium. Nevertheless, the two-way disturbance spreading (propagation or transfer) of entities occurs, either by the tunneling mechanism (low energy dissipation and occurrence probability) or by the induction mechanism (medium or high energy dissipation and occurrence probability). The elastic droplet boundary E represents a form of droplet instability when the equilibrium of all the 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, reversible disturbance spreading occurs with or without hysteresis. After the elastic droplet boundary, the plastic form of droplet instability takes place, then electro-mechanical oscillators/clusters do not exist any more and beams of entities or atto-clusters appear. Atto-clusters are the entities that appear in atto-dispersed systems. In this region the one-way propagation of entities occurs.

Mathematical formalisms –Tension Tensor Model

Using the presented propositions and electro-mechanical analogies, an approach to non-Newtonian behaviors and to electroviscoelasticity is now introduced. When equation (2) is applied to the droplet when it is stopped, e.g., as a result of an interaction with some periodical physical field, the term on the left-hand side becomes equal to zero.

$$\rho \frac{D\tilde{u}}{Dt} = \sum_i \tilde{F}_i (dx dy dz) + D\tilde{F}_s \tag{2}$$

Furthermore, if the droplet is in the state of "forced" levitation, and the volume forces balance each other, then the volume force term is also equal to zero [1-3,24,25]. It is assumed that the surface forces are, for the general case that includes electroviscoelastic fluids, composed of interaction terms expressed by

$$d\tilde{F}_s = \tilde{T}^{ij} d\tilde{A} \tag{3}$$

where the tensor \tilde{T}^{ij} is given by

$$\tilde{T}^{ij} = -\alpha_0 \delta^{ij} + \alpha_1 \delta^{ij} + \alpha_2 \zeta_5^{ij} + \alpha_3 \zeta_k^i \zeta^{kj} \tag{4}$$

where \tilde{T}^{ij} is composed of four tensors, δ^{ij} is the Kronecker symbol, and ζ_5^{ij} is the tension tensor, and $\zeta^{ik}\zeta^{kj}$ is the tension coupling tensor. In the first isotropic tensor the potentiostatic pressure $\alpha_0 = \alpha_0(\rho, U)$ is domi-

nant and the contribution of the other elements is neglected. Here U represents the hydrostatic or electrostatic potential. In the second isotropic tensor, the resistance $\alpha_1 = \alpha_1(\rho, U)$ is dominant and the contribution of the other elements is neglected. In the third tension tensor, its normal elements $\alpha_2\sigma$ are due to interfacial tensions and the tangential elements $\alpha_2\tau$ are presumed to be of the same origin as the dominant physical field involved. In the fourth tension coupling tensor, there are normal, $\alpha_3\sigma^i_k$, and $\alpha_3\sigma^{kj}$ elements and tangential $\alpha_3\tau^i_k$ and $\alpha_3\tau^{kj}$ elements that are attributed to the first two dominant periodical physical fields involved. The general equilibrium condition for the dispersed system with two periodical physical fields involved may be derived from Eq. (4) and expressed by

$$\tau_d = \frac{-\alpha_0 + \alpha_1 + \alpha_2 \left(\frac{\sigma}{d}\right) + \alpha_3 \left(\frac{\alpha}{d}\right)}{2(\alpha_2 + \alpha_3)} \tag{5}$$

where τ_d are the tangential elements of the same origin as those of the dominant periodical physical field involved. Figure 3 shows the schematic equilibrium of the surface forces at any point of a stopped droplet-film structure while in interaction with some periodical physical field [25]. 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

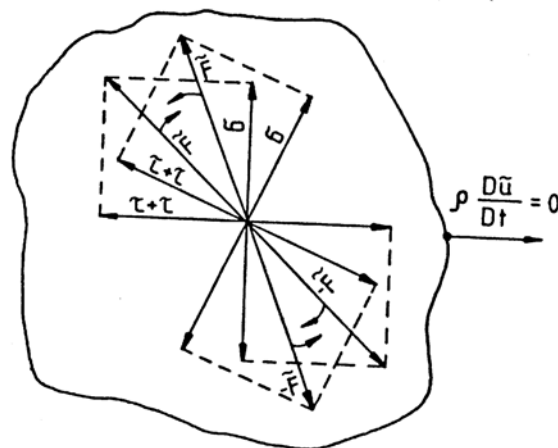


Figure 3. Balance of surface forces at any point of a stopped droplet-film structure while in interaction with a periodical physical field (a two dimensional projection), F represents the projection of the resultant surface forces vector in three N dimensional configuration space, τ stands for the tangential and σ for the normal components, Reprinted from ref 25, p.438, with permission from Academic Press.

$$\tau_v = \mu_0 \frac{du}{dx} + \mu_1 \frac{d^2u}{dx^2} + \mu_2 \left(\frac{du}{dx}\right)^2 \tag{6}$$

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 ohm, capacitive, and inductive components, will be correlated with the tangential tensions of electrical origin τ_e , as follows:

$$\tau_e = Z_0 \frac{d\phi_e}{dt} + Z_1 \frac{d^2\phi_e}{dt^2} + Z_2 \left(\frac{d\phi_e}{dt}\right)^2 \tag{7}$$

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

A more detailed discussion about the derivation of these equations can be found in Refs. [5,9,13,16,25–30].

van der Pol integer order derivative model

The postulated assumptions for an electrical analogue are the following:

1. The droplet is a macro system (a collective of particles) consisting of structural elements that may be considered as electro–mechanical oscillators.
2. Droplets as micro collectives undergo tuning or coupling processes and so build the droplet as a macro collective.
3. 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 electro–mechanical oscillators is based on electromechanical and electrodynamic principles. At first, during droplet formation it is possible that the serial analog circuits are more probable, but later, as a consequence of tuning and coupling processes, 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 4 presents the resultant equivalent electrical circuit, rearranged under the influence of an applied physical field, such as an antenna output circuit [1,2,25].

A non–linear integral–differential equation of the van der Pol type represents the initial electromagnetic oscillation

$$C \frac{dU}{dt} + \left(\frac{U}{R} - \alpha U\right) + \gamma U^3 + \frac{1}{L} \int U dt = 0 \tag{8}$$

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 ohm resistance (resistance of the energy transformation, electromagnetic into the mechanical or damping resistance), t is time; α and γ are constants determining

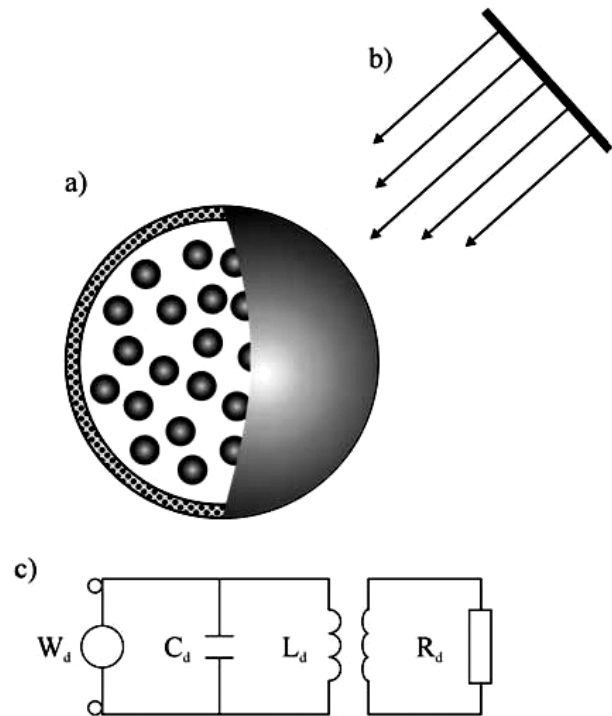


Figure 4. The structural model of electroviscoelasticity: a. the rigid droplet, b. the incident periodical physical field, c. the equivalent electrical circuit W_d represents the emitter–coupled oscillator, C_d , L_d , and R_d are the capacitive, inductive and resistive elements of the equivalent electrical circuit, respectively. Subscript d is related to the particular diameter of the droplet under consideration. "From ref 2. p. 854, courtesy of Marcel Dekker, Inc.

the linear and non–linear 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 the amplitude $A_0 = [(\alpha-1)/R/3\gamma/4]^{0.5}$.

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 oscillations of the "continuum" particle (molecule surrounding the droplet or droplet–film structure), which can be represented by the particular integral

$$C \frac{dU}{dt} + \left(\frac{1}{R} - \alpha\right) U + \gamma U^3 + \frac{1}{L} \int U dt = -2A_n \cos \omega t \tag{9}$$

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

$$C \frac{dU}{dt} + \left(\frac{1}{R} - \alpha\right) U + \frac{1}{L} \int U dt + \gamma U^3 = i(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(j\omega t) A_n(\omega) d\omega \tag{10}$$

where $i(t)$ is the noise current and $A_n(\omega)$ is the spectral distribution of the noise current as a function of frequency [1,2].

In the case of non-linear oscillators, however, the problem of determining of noise output is complicated by the fact that the output is fed back into the system, thus modifying the effective noise input in a complicated manner [1,2]. The noise output appears as an induced anisotropic effect.

van der Pol fractional order derivative model – linearized

In an effort to generalize the previous equation the ordinary time derivative and integral were now replaced by the corresponding fractional-order time derivative and same as integral of the order $p < 1$ [33–42]. Fractional derivatives provide an excellent instrument for the description of memory and hereditary properties of various materials and processes. This is the main advantage of fractional derivatives in comparison with classical integer-order models, in which such effects are in fact neglected. Here, the capacitive and inductive elements, using fractional-orders $p \in (0,1)$, enable the formation of a fractional differential equation, i.e. a more flexible or general model of liquid-liquid interface behaviour. A differ-integral form using the Riemann–Liouville definition is given by

$${}^0D_t^p [U(t)] = \frac{d^p U}{dt^p} = \frac{1}{\Gamma(1-p)} \frac{d}{dt} \int_0^t \frac{U(\tau)}{(t-\tau)^p} d\tau, \quad 0 < p < 1 \tag{11}$$

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

So, in that way one can obtain a linear fractional differential equation with zero initial conditions as follows:

$$C_0 D_t^p [U(t)] + \left(\frac{1}{R} - \alpha\right) U + \frac{1}{L} {}^0D_t^p [U(t)] = i(t) \tag{12}$$

Using the Laplace transformation of (12) leads to

$$G(s) = \frac{U(s)}{i(s)} = \frac{1}{Cs^p + 1/Ls^p + (1/R - \alpha)} = \frac{s^p}{Cs^{2p} + (1/R - \alpha)s^p + 1/L} \tag{13}$$

or

$$G(s) = s^p G_3(s), \quad G_3(s) = \frac{1}{as^{2p} + bs^p + c}, \quad a = C, \quad b = (1/R - \alpha), \quad c = 1/L \tag{14}$$

Further, $G_3(s)$ has the form

$$G_3(s) = \frac{1}{as^{2p} + bs^p + c} = \frac{1}{c} \frac{cs^{-p}}{as^{2p-p} + b} \frac{1}{1 + \frac{cs^{-p}}{as^{2p-p} + b}} = \frac{1}{c} \sum_{k=0}^{\infty} (-1)^k \left(\frac{c}{a}\right)^{k+1} \frac{s^{-p(k+1)}}{(s^{2p-p} + b/a)^{k+1}} \tag{15}$$

The term-by-term inversion, based on the general expansion theorem for the Laplace transform [34] and using (appendix A) produces

$$G_3(t) = \frac{1}{a} \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \left(\frac{c}{a}\right)^k t^{2p(k+1)-1} E_{2p-p, 2p+pk}^{(k)} \left(\frac{b}{a} t^{2p-p}\right) = \frac{1}{a} \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \left(\frac{c}{a}\right)^k t^{2p(k+1)-1} E_{p, 2p+pk}^{(k)} \left(\frac{b}{a} t^p\right) \tag{16}$$

where $E_{\lambda, \mu}(z)$ is the Mittag-Leffler function in two parameters (see Appendix A) and its k -th derivative is given by

$$E_{\lambda, \mu}^{(k)}(t) = \frac{d^k}{dt^k} E_{\lambda, \mu}(t) = \sum_{j=0}^{\infty} \frac{(j+k)! t^j}{j! \Gamma(\lambda j + \lambda k + \mu)}, \quad k = 0, 1, 2, \dots \tag{17}$$

The inverse Laplace transform of $G(s)$ is the fractional Greenfunction:

$$G(t) = {}^0D_t^p [G_3(t)] = \frac{d^p G_3(t)}{dt^p} \tag{18}$$

where the fractional derivative of $G_3(t)$ (18) is evaluated with the help of (11). Finally, this allows an explicit representation (appendix B) of the solution:

$$U(t) = \int_0^t G(t-\tau) i(\tau) d\tau \tag{19}$$

Again, the initial electromagnetic oscillation is represented by a differential equation, Eq. (8), and when the non-linear terms are omitted and/or canceled, the first step, i.e. a homogeneous solution may be obtained using a numerical calculation derived from the Grunwald definition [23], as shown in Fig. 5.

The calculation was performed for the following parameters:

$$\alpha = 0.9995; U_0 = 15 \text{ mV}; p = 0.95; T = 0.001 \text{ s.}$$

Further on, considering Eq. (11) i.e. a non-homogenous solution is obtained and presented in Fig. 6.

The obtained result appears as a band because the input (cos) is of the fractional order; and the output is in a damped oscillatory mode of high frequencies!

The calculation was performed for the parameters [where the derivative of $\cos(\omega_0 t)$ is also fractional, of the order r]:

$$\alpha = 0.95; U_0 = 15 \text{ mV}; p = 0.95; T = 0.01 \text{ s};$$

$$A_n = 0,05 \text{ nm}; \cos(\omega_0 t) = d^r/dt^r (\sin \omega_0 t).$$

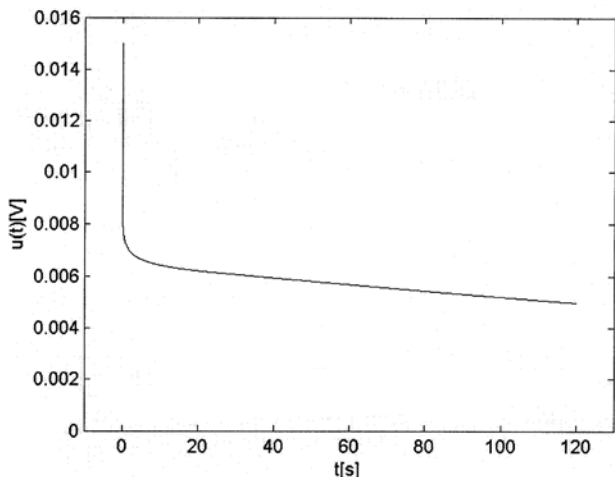


Figure 5. Calculated solution, linearized Eq. (8), homogeneous solution; $\alpha = 0.9995$; $U_0 = 15 \text{ mV}$; $p = 0.95$; $T = 0.001 \text{ s}$

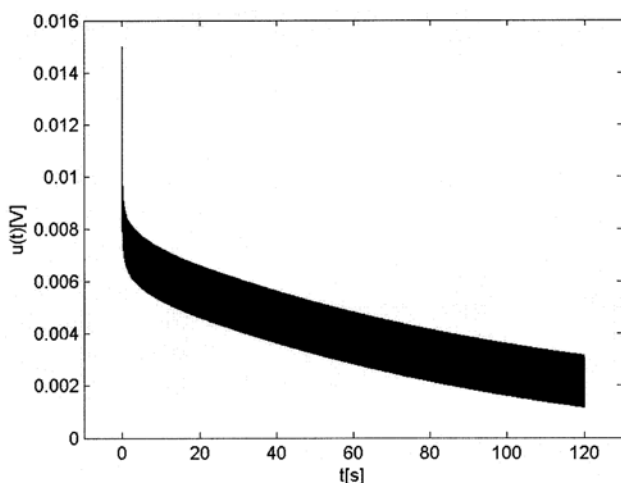


Figure 6. Calculated solution, linearized Eq. (9), non-homogeneous solution; $\alpha = 0.95$; $U_0 = 15 \text{ mV}$; $p = 0.95$; $T = 0.01 \text{ s}$; $A_n = 0.05 \text{ nm}$; $\cos(\omega t) = d^l/dt^l (\sin \omega t)$

Here the presented model is derived only for the linearized van der Pol equation, while the more realistic non-linear case will be the subject of a future paper. Numerical calculations must be performed using parallel data processing [1,23].

Numerical Methods for Non-linear Fractional Order Derivative Equations

In some cases for the numerical calculation of non-linear equations, one can use the fact that a fractional derivative is based on a convolution integral, the number of weights used in the numerical approximation to evaluate the fractional derivatives. Also, one can apply the predictor-corrector formula for the solution of systems of non-linear equations of lower order. This approach is based on rewriting the initial value problem as an equivalent fractional integral equation (Volterra integral equation).

$$x(t) = x_0 + \frac{1}{\Gamma(p)} \int_0^t f(s, x(s)) (t-s)^{p-1} ds, \quad (20)$$

One may then, introduce uniformly distributed grid points [1]. The next step is to find an approximation by the predictor-corrector approach. One can use the fractional Euler method for the predictor and for the corrector the product trapezoidal formula [34]. Also, it was desired to develop numerical schemes that are convergent, consistent, and stable, but these properties are not treated here.

EXPERIMENTAL CONFIRMATION

Presented theoretical predictions including both physical and mathematical formalisms were experimentally corroborated by means of electrical interfacial potential (EIP) measurements and by means of nuclear magnetic resonance spectroscopy (NMR). The obtained experimental results were in fair agreement with the postulated theory [1,2].

Description of the system

The heavy liquid was 5.6 M phosphoric acid, and the light liquid was the synergistic mixture of 0.5 M di (2-ethylhexyl) phosphoric acid (D2EHPA) and 0.125 M tri-n-octylphosphine oxide (TOPO) in dearomatized kerosene [1-4,24].

EIP Measurements

A method and apparatus were developed to volta-metrically monitor the change of the electrical interfacial potential (EIP) appearing during the formation of the electric double layer (EDL), while two-phase contact occurs [1,24]. Measurements of the EIP_i were performed during the processes of formation and transition of the electroviscoelastic sphere into a rigid sphere as shown in Figs. 7. and 8 [1,2,24].

Fig. 7 shows the measured change in the EIP appearing during the introduction of the heavy-phase

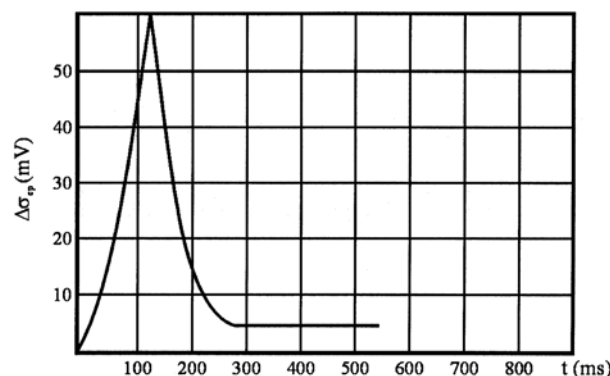


Figure 7. Measured variations of the electrical interfacial potential (EIP) with time for the system phosphoric acid/D2EHPA-TOPO-kerosene at a spherical interface

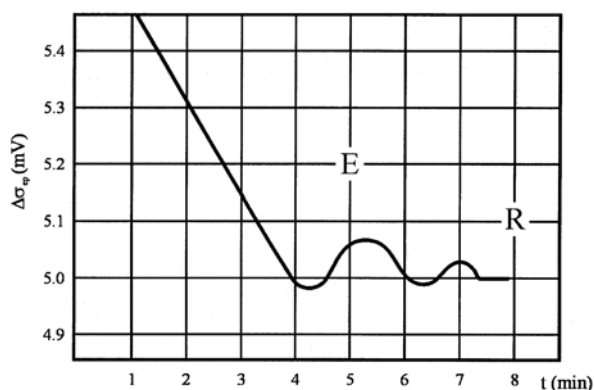


Figure 8. Measured spontaneous oscillations of the EIP during the "breathing" period; transformation of an electroviscoelastic sphere into a rigid sphere; memory storage process

droplet into the light-phase continuum [2]. It can be seen in the figure that an interfacial jump potential peak appears during the formation of the EDL. Thereafter, the EIP decreases to a constant value. The lowering of the EIP in absolute value during the flow is due to the participation of cations that form the dense part of the EDL. The anions are the counter-ions in the diffuse part. The redistribution of these anions and cations between the region close to the surface and the surface layers of the heavy-phase define the kinetics of the EIP [2, 18].

Figure 8 shows the measured spontaneous oscillations of the EIP during the "breathing" period. After the EIP jump, which is in the millivolt-millisecond scale, the EIP continues to oscillate in the parts of the millivolt-minute range. Its damped oscillatory mode is (probably) due to the hydrodynamic instability of the interfacial surface, as a consequence of the local gradients of the interfacial tension and density in the mutual saturation processes of liquids [2, 18]. The other relevant interpretation of the EIP spontaneous oscillations may be expressed as follows: the electroviscoelastic sphere undergoes the transformation into a rigid sphere. This transformation can be understood as a memory storage process.

³¹P NMR Measurements

In order to determine the resonant (characteristic) frequency, a NMR spectrometer was used as a reactor for the energetic analysis. The impedance Z at the resonant frequency ω_0 is equal to the resistance R . The resonant frequency of the electromechanical oscillator can be considered as a characteristic frequency within the vibro-rotational spectrum of the molecular complex that builds the droplet film structure [2]. Figure 9 shows ³¹P NMR spectrum of the examined droplet-film structure.

All the experiments were performed and all the spectra were acquired on a Bruker MSL 400 spectrometer with a 9.395 T magnet and at a ³¹P frequency of 161.924 MHz. The transmitter was set at a resonance frequency with the phosphoric acid standard

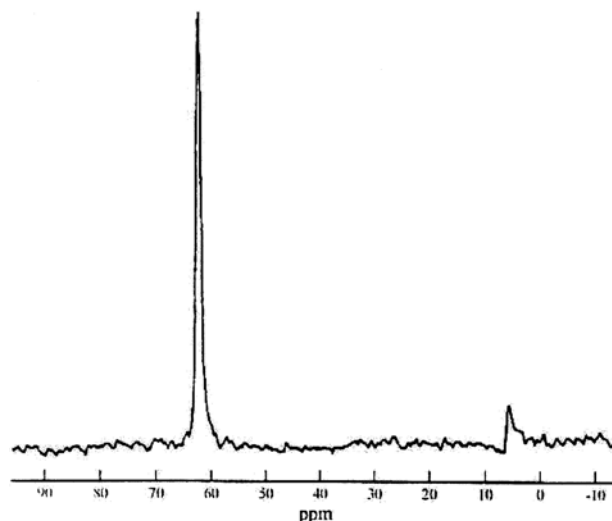


Figure 9. ³¹P NMR spectrum of D2EHPA-TOPO-kerosene sample (phosphoric acid standard solution, sweep width of 15000 Hz); the peak at 7 ppm corresponds to D2EHPA, and that at 62 ppm corresponds to TOPO.

solution, and a sweep width of 15000 Hz was employed. The swept region corresponded to the range between -10 and 90 ppm.

IMPLICATIONS

A theory of electroviscoelasticity using the 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 the 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, electroneurophysiology). Furthermore, both, the model and theory may be implemented in studies of structure; interface barriers/symmetries – surface (bilipid membrane cells, free bubbles of surfactants, Langmuir Blodgett films), – line (genes, liquid crystals, microtubules), – point (fullerenes, micro-emulsions) and – overall (dry foams, polymer elastic and rigid foams).

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APPENDIX

Appendix A

A two-parameter function of the Mittag-Leffler type is defined by the series expansion:

$$E_{\alpha,\beta}(z) = \sum_{k=0}^{\infty} \frac{z^k}{\Gamma(\alpha k + \beta)}, \quad (\alpha, \beta > 0). \tag{21}$$

The Mittag-Leffler function is a generalization of the exponential function e^z and the exponential function is a particular case of the Mittag-Leffler function. The relationship is expressed as

$$E_{1,1}(z) = \sum_{k=0}^{\infty} \frac{z^k}{\Gamma(k+1)} = \sum_{k=0}^{\infty} \frac{z^k}{k!} = e^z. \tag{22}$$

$$E_{1,m}(z) = \frac{1}{z^{m-1}} \left\{ e^z - \sum_{k=0}^{m-2} \frac{z^k}{k!} \right\}$$

A one-parameter function of the Mittag-Leffler type is:

$$E_{\alpha}(z) = \sum_{k=0}^{\infty} \frac{z^k}{\Gamma(\alpha k + 1)} \tag{23}$$

The Laplace transform of the Mittag-Leffler function in two parameters is

$$\int_0^{\infty} e^{-t} t^{\beta-1} E_{\alpha,\beta}(zt^{\alpha}) dt = \frac{1}{1-z}, \quad (|z| < 1) \tag{24}$$

and a pair of the Laplace transforms of the function $t^{\alpha k + \beta - 1} E_{\alpha,\beta}^{(k)}(\pm z t^{\alpha})$ is:

$$\int_0^{\infty} e^{-pt} t^{\alpha k + \beta - 1} E_{\alpha,\beta}^{(k)}(\pm a t^{\alpha}) dt = \frac{k! p^{\alpha - \beta}}{(p^{\alpha} \mp a)^{k+1}}, \tag{25}$$

(Re(p) > |a|^{1/α})

Appendix B

The solution of the initial-value problem for an ordinary fractional linear differential equation with constant coefficients using Green's function is presented. The consideration taken into account for the given differential equation under homogeneous initial conditions is $b_k = 0, k = 1, 2, \dots, n$:

$${}_a D_t^{\sigma_n} y(t) + \sum_{k=1}^{n-1} p_k(t) {}_a D_t^{\sigma_{n-k}} y(t) + p_n(t) y(t) = f(t) \tag{26}$$

$$\sigma_k = \sum_{j=1}^k \alpha_j, \quad 0 \leq \alpha_j \leq 1, \quad j = 1, 2, \dots, n$$

The analytical solution of the given problem takes the form [32]

$$y(t) = \int_0^t G(t, \tau) f(\tau) d\tau \tag{27}$$

where $G(t, \tau)$ is known as Green's function of equation (26). For fractional differential equations with constant coefficients this function is

$$G(t, \tau) = G(t - \tau) \tag{28}$$

and in such case the Green function can be obtained by the Laplace transform method. Therefore, the solution of linear fractional differential equations with constant coefficients reduces to determining the fractional Green function. Finally, for inhomogeneous initial conditions, the solution has the form:

$$y(t) = \sum_{k=1}^n b_k \psi_k(t) + \int_0^t G(t-\tau) f(\tau) d\tau, \tag{29}$$

$$b_k = [{}_0 D_t^{\sigma_k - 1} y(t)]_{t=0}$$

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IZVOD

FENOMENI PRENOSA ELEKTRONA I KOLIČINE KRETANJA NA RAZVIJENIM DEFORMABILNIM I RIGIDNIM MEĐUPOVRŠINAMA TEČNO-TEČNO

(Naučni rad)

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Primenjena je nova ideja za rasvetljavanje fenomena prenosa elektrona i količine kretanja na razvijenim, deformabilnim i rigidnim, međupovršinama u finim (mikro, nano, ato) disperznim sistemima. Ponašanje elektroviskoelastičnih fluida, na primer međupovršina tečno-tečno (emulzije, dvostruke emulzije) se predstavlja u tri stanja/"nestabilnost", rigidno, elastično i plastično. Relevantni događaji na međupovršinama se posmatraju kao interakcije unutrašnjih (imanentnih) i spoljašnjih (incidentnih) periodičnih fizičkih polja. Pored fenomena prenosa količine kretanja, toplote i mase, koji se koriste u hemijskom inženjerstvu, za posmatranja na nivou molekula, atoma i/ili entiteta neophodno je uvesti i fenomen prenosa elektrona. Za postularani fizički formalizam, teoriju elektroviskoelastičnosti, izvedena su tri matematička formalizma. U prvom modelu posmatra se delovanje normalnih i tangencijalnih sila, samo u matematičkom smislu, bez obzira na njihovo poreklo (mehaničko i/ili električno). Drugi model je integro-diferencijalna jednačina tipa van der Pol. Treći model predstavlja generalizaciju modela van der Pol za oba slučaja, linearni i nelinearni, integrali i diferencijali reda celih brojeva su zamenjeni integralima i diferencijalima reda izlomljenih brojeva. Predstavljeni modeli i teorija omogućavaju dublje razumevanje: problema zahvatanja u ekstrakciji tečno-tečno, događaja na razvijenim međupovršinama u nauci o koloidima i međupovršinama, hemijskih i biohemijskih senzora, elektroanalitičkih metoda, biologije/biomedicine (hematologije, genetike, elektroneurofiziologije).

Ključne reči: Fenomeni prenosa elektrona, Naelektrisane međupovršine tečno-tečno, Fini disperzni sistemi, Elektroviskoelastičnost, Emulzije.