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Directed Ion Transport as Virtual Cause of Some Facilitated Friction–Lubrication Mechanism Prevailing in Articular Cartilage: A Hypothesis

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Abstract Based on certain characteristics of the acid–base quasi-equilibria and on structural properties of the synovial inhomogeneous fluid in a model articular cartilage (mAC), we try to hypothesize on its facilitated friction–lubrication mechanism. We opt for a scenario that under departure from the acid–base, pH-dependent equilibrium, directed transport of protons (H^+) is plausible, leading to a certain synergistic kinetic–thermodynamic pathway of the system as a whole. It can be viewed in such a way that protons, and virtually, other ions such as OH^-; Ca^{2+}, may pass through the (intra)micellar, possibly elongated spaces, playing their roles as if they were transported along temporarily formed ion (mainly, H^+) transmembrane channels. Such a hypothetical scenario would thoroughly contribute to some electrostatics-aided, interstitial (synovial) biofluid pressurization, often reported by experimentalists as the appropriate mechanism of facilitating the lubrication in a real articular cartilage (rAC) in microrheological conditions, encountered in articulating joints of mammals.

Keywords Joint lubrication (general) · Dynamic modeling · Human joint hydrodynamics · Rheology · Viscosity

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1 Introduction

The lubrication of interfaces in the articulating joints of mammals is conceptualized as being facilitated by a microscopic layer of surface-active phospholipids (SAPL—the solid lubricant "additive"), pressurized microscopic layer of fluid that is believed to be supplied from within the loaded/deforming matrices of contacting articular cartilage, some chemical elements and macromolecules such as hyaluronic acid. In this study, we wish to present the hypothesis that this joint biolubrication system performs its physiological functions by assuming the chemical configuration of reverse micelles. This hypothesis is then tested by developing and solving (in a sketchy way) the equations of a theoretical model of lubrication mechanics which also incorporates tribochemical components of rheological and anomalous chemical reaction nature.

Several analogues and theories of joint lubrication in mammals have been proposed [1]. However, in this short communication, we will focus on those involving the basic principle of tribochemistry such as that of Hills [2], in which it was proposed that the SAPL form two opposing adsorbed monolayers on the biosurfaces of contacting articular cartilages between which a layer of synovial fluid is dispersed during function or loading of the joint. This explanation of boundary lubrication seems to be based on the monomolecular adsorption principle of Hardy [3]. In this hypothesis study, we argue that this monolayer concept, which also requires that the surface of the operating molecular structures are hydrophobic, cannot explain fully the ultralow static-friction coefficient of the order of 10^{-3} or less, that is known to occur in the joint during motion. Furthermore, the seemingly oversimplified analogue of joint lubrication presented in the monolayer approach ignores completely the well-known fact that under load

SAPL preferentially form multilayered mesostructures that are characterized by a distinct bilayer architecture or reverse (inverse) micelles [4]. Of special importance is the possibility that if reverse micelles formation is involved in the lubrication process, then the quasi-static friction effect can be replaced by a roll-over one, leading to a more representative explanation of how the ultralow friction in the joint is achieved. Moreover, specific pores-involving structural configurations may temporarily emerge in the synovial fluid, being in general quite a complex system [1–3].

2 Dissipative Dynamical System Beyond Acid–Base Equilibrium: Basic Motivation and Sketchy Mathematical Formulation

Following the above physical concepts of cartilage–cartilage lubrication [1–4], it is plausible to develop a mathematical model which is based on two fundamental assumptions namely, that:

(i) the dynamics of the friction–lubrication events can be described by an anomalous (first-order) chemical reaction occurring in the micelle-forming environment; these dynamics, while carefully examined over the duration of an external load, express a slowly varying (in-time) non-homogeneity of the synovial viscoelastic interlayer [1–3];
(ii) the dynamics are assumed to operate in a fully rheological context [4] in which the interlayer viscosity appears to be also slowly (and, inverse powerly) decreasing function of external-load duration time.

Typically under steady state, or even, static conditions, a thermodynamic quasi-equilibrium situation exists in the joint where the articular surface, a biosurface, is in equilibrium with both the fluid expressed from within the cartilage matrices and the synovial fluid. Thus, the biolubriction mechanism between two phospholipid bilayers on cartilage, the surfaces of which have been studied for decades appears to be a challenge in resolving this problem of practical interest [5]. What continues, for example, to be poorly understood about joints are the tissue and molecular interactions processes which are highly specialized in structure and function. Concerning synovial fluid components namely the glycoprotein lubricin, hyaluronan held by proteoglycans, and phospholipid molecules participating in frictionless biolubrication [6]. The biolubrication of surfaces is not only determined by the solvent (water) as a lubricant, but also by the additives as ions and macromolecular components, and certainly by the pH-sensitive acid–base equilibria in the system [7]. The hydration of ions and macromolecules in a polyelectrolyte takes place between two phospholipid charged bilayered surfaces of the real articular cartilage (rAC). The two normal articular bilayer phospholipidic surfaces are very hydrophilic and perform in accordance with all the characteristics of the core of reverse micelles [7]. The lipid bilayer membranes are 6–10 nm thick and act as barriers to the diffusion of polar solutes, whereas the embedded proteins and cholesterol provide the pathways for the charge core of reverse micelle that is capable of (i) organizing water molecules and ions on articular surfaces, (ii) play an essential role in stabilization of charged particles and elimination of flocculation, (iii) allow polyelectrolyte molecules, electrostatically attach to hydrophilic surface of a phospholipid, to maintain a double layer made up of electrostatic charges at the interface of contacting rAC, (iv) cause the selective transfer of certain molecular substances through the lipid barrier, and (v) allow for the mechanical transfer of information from the extracellular matrix into the interior of the cell [8].

In turn, the dynamic conditions to satisfy incorporate non-equilibrium thermodynamics [9] which is triggered by the application and movement of loads (pressures), and which includes quasi-periodic behavior [9], lasting sometimes over relatively long periods of time, dissipative mechanisms associated with the formation of the structure of the lubricant [10], etc. In order to describe the dynamic conditions, a new biolubrication model with capacity beyond the Hills–Hardy concepts [1–3] which can account for wear in a mechano-chemical process is required. Such a model will also incorporate the age-dependent characteristic of the synovial fluid which can be included in the form of electrical repulsive mechanism in accordance with Roberts [11]. Furthermore, we argue that such a model will be based on hydrophilic lubrication [7] rather than the hydrophobic mechanism proposed by Hills [12].

2.1 Conceptual Non-equilibrium Thermodynamics Model—Tribochemistry of Biofilm Formation and Destruction

2.1.1 A Physical Stage Before Applying a Hydrostatic Pressure

According to our understanding of the dynamics of the rAC, now transferred to the construction of the mAC, that we would like to propose, the articulation space essentially consists of two bilayers, upper and lower (u-Bi and l-Bi, respectively) plus an interlayer, in which Lubricin (L), as well as Hyaluronan (HA) molecules, and water (H_2O) dipoles, etc., are dispersed. Essentially, the u-Bi and l-Bi consist of H_2O in its dissociated state [7] and SAPL in an elongated (swollen) state [10]. The L-s include a certain content of SAPL too. Both Bi-s are viewed as double layers

(say, of Stern type [7]), in which the outer monolayer is amenable to some structural changes, whereas the inner monolayer is electrostatically "pinned" to its corresponding biosurface. The changes are mainly assumed to be defects, i.e., the creation of a SAPL-lacking hole (with on average two H_2O molecules surrounding the SAPL molecule in its elongated state) as well as, those taking place after applying a pressure (load), leading to the annihilation of the hole by two L-s, involving just one H_2O molecule, perhaps engaging mutually the L-s in, let us say, a "wedding" pair. Notice that any annihilation–creation event may contain H_2O in its dissociated state. Other ions, such as OH^-; Ca^{2+}, for example, i.e., mostly those coming from the presence of salts in the system also contribute to the characteristics of the structured (also, multilayered) complex fluid [7].

2.1.2 *A Physical Stage After Applying a Hydrostatic Pressure*

According to [10], when pressurized the elongated SAPL-s present in the monolayer are squeezed, with each of them carrying automatically two H_2O molecules away, on average. An excess of H_2O in the interlayer gives rise to internal pressure actions resulting in backflow of L-s, with each carrying on average one molecule of water back into the upper monolayer, thereby substituting the previously desorbed and water-carrying SAPL, such that the hole annihilation effect would prevail.

This ability of the bilayer to undergo partial destruction, (since the first layer of the adsorbed bilayer is assumed to be undisturbed) owing to relatively strong electrostatic effect, makes it possible to maintain articular space fluid with dispersed SAPL molecules. We argue that these dispersed molecular units have the capacity to aggregate under an applied pressure due to the minimization of their surface energies to form micelles. In this respect, in the inter-articular fluid layer, this aggregation of SAPL will result in them becoming partially hydrophobic and orientating their hydrophilic heads inwards and exposing their tails outwards. In this condition, the relatively smooth surfaces created by the SAPL aggregates, namely reverse micelles, mostly, are altogether capable of facilitating sliding motion on the (laterally shifted) surfaces of the lower and upper contacting articular cartilage. Because of this capacity to organize or aggregate themselves, the SAPL in their reverse micelles form are capable of both load carriage and facilitation of the low friction that is associated with the mammalian joint [1, 13]. The conceptual basis of joint lubrication stated above will be formalized below within the framework of an autonomous dynamical system (1)–(3) and its principal structure–property microrheological characteristics (7) and (8).

2.2 Quantitative Model of the Biolubrication Mechanism

Given the above, articular cartilage can be described a complex fluid-based load processing and lubrication layer which mostly loses efficiency with age roughly in the same manner as a car's shock absorber after frequent and extensive use. Consequently, the surface tribochemical functional characteristics of the tissue can be modeled in terms of a dynamic mechano-chemical system that includes a dissipation mechanism as developed in Ref. [9]. This will involve monolayer dynamics which can be described mathematically by Eq. 1 of Ref. [9], which is well-known in surface physics and is an analog of Smirnov's equation, cf. [9] and Refs. therein.

In this present formulation, the SAPL concentration ρ, is included as a function of time t, so that this Smirnov-type equation [9] reads:

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = b_{\mathrm{S}} + c\rho - \delta\rho^2 \tag{1}$$

where $b_s \equiv b_s[\phi]$ is the external concentration source of lipids that are responsible for exchange of matter with the monolayer, as described in Ref. [7]. The coupling between ρ and ϕ is assumed for the purpose of the present study to be linear in a similar manner to that of Ref. [9], in accordance with the local number-conservation law, which we argue also holds for our SAPL–water system. Therefore, $b_s[\phi] = a + \beta\phi$, in a similar manner to the variation of $e_s = e_s[\rho]$ in Ref. [9], now transferred to a similar first-order ordinary differential equation [10] of the form

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = e_{\mathrm{S}} + N_{\mathrm{HA}}K[1-\phi], \tag{2}$$

with $e_s \equiv e_s[\rho] = e + f\rho$. Equation 2 reflects adequately the first-order kinetics of micelles formations [10].

Realize that ϕ denotes the concentration of micelles at time t. In a way similar to that followed in Ref. [9], a and e are designated as independent free-source SAPL-production parameters, with the sources at the surface and in the bulk, respectively. The parameters, β and f, represent the main (system) coupling parameters, where the coupling is thought of as acting between all surface and bulk SAPL-production sources in the system, including both internal and external (supplying) sources. N_{HA} stands for the number of HA molecules—they are assumed, because of their affinity to water, to facilitate the reverse-micellar formations. Finally, c and δ are quantitatively responsible for the creation–annihilation mechanism to work in a competitive manner, depending on whether the former is greater than the latter, or vice versa (note that the creation–annihilation sources in Eq. 1 are of opposite signs). Certainly, $\phi_{\mathrm{nM}} + \phi = 1$, where the quantity indexed by nM corresponds to the SAPL

concentration (or, probability of finding a SAPL) in a non-micellar state. This also means that preferentially only the concentration of SAPL in the micelles, ϕ and possibly the concentration of SAPL included in L-s contribute to the overall dynamics of the tissue model, with other contributors, such as HA-s, etc. (see above) playing a secondary role, thus being (almost) not included formally in the mAC dynamics so described.

The ϕ obeys the generalized Avrami–Kolmogorov (AK) phase-change kinetics [10], thus resulting in Eq. 2, wherein the most interesting aspect, or equivalently, the most essential novelty of our modeling, is concerned with the new time kernel, $K \equiv K(t)$, contributing to behaviors that were not represented in the formulation contained before, cf. [9], and Eqs. 13–15 therein. It is because it includes not only the subtleties of time changes of the viscosity in the interlayer, pertaining to the synovial biofluid as the rheological entity, but also anticipates the inhomogeneities formed during the process, emerging due to SAPL aggregation and reverse micelles' creation in the interlayer, while also including the possibility of the micelles varying in geometry (geometrical thermodynamics) to round, spherical or not, in a manner similar to the development in Ref. [10] (see Refs. therein), within the otherwise standard AK phase-change conceptual framework.

Thus, in this present work, by completing, similarly as in Ref. [9] the system (1) and (2) with the third equation, as follows,

$$\frac{\mathrm{d}K}{\mathrm{d}t} = \mathrm{Const.}K \times [\kappa - \kappa^{-1}] \tag{3}$$

we propose the following autonomous system of ordinary autonomous differential equations (ODEs), Eqs. 1–3, with its characteristic function $\kappa \equiv \kappa(t) = [K(t)/\mathrm{const.}]^{-1/\mathrm{h}} - 1$, to describe the overall friction–lubrication dynamics in the mAC in terms of suitable phase–space $\{\rho, \phi, K\}$ relationships involved in the tribo-lubrication and fluid pressure characteristics [14] in the inter-articular space during joint loading.

The only essential difference when compared with the analysis carried out previously in Ref. [9] is that the third equation of the system is more complex, giving rise to some new friction–lubrication sub-effects, especially to zero [9] and non-zero (this is the novelty!) stationary states, responsible for quick or slow decays of the SAPL-created micelles in the system, respectively. Furthermore, the most interesting correlation with regard to the earlier model developed for the 'tribo-polimerization' process which also involves dissipation mechanism, is that the temporal characteristics of micelles formation can be qualitatively elucidated by means of a probability of system return, P_{ret}, namely that the longer the 'cycles' of micelles' appearance/disappearance take, the less probable its return to the origin such that the relation $P_{\mathrm{ret}} \sim t^{-\frac{d_S}{2}}$ quite firmly applies [9, 10]. The principal structure–property parameter, d_S, named the spectral (Random Walk) dimension [9] appears to be, under the condition $K(t)\mathrm{d}V_n/\mathrm{d}t \rightarrow$ const. (V_n—the volume of a micellar nucleus [10]), an informative parameter too. In this case our newly developed model, it is also related to the mechanical behaviors of the SAPL in their squeezed, mixed, and elongated (swollen) biomacromolecular states, characterized by the corresponding (mechanical) exponents, γ, where $\gamma = 1/3;\ 1/2;\ 3/5$, respectively [10], involved in the De Gennes–Taupin type scaling formulae. Note formally, that: (i) the function κ above includes another exponent, h, obeying $h = 1-(d_S/2)$ [9]; (ii) by a simple analytical inspection it is easy to show that the ODEs system (1–3) can be obtained in such a least-dissipation autonomous (closed) form only if $h = 3\gamma-1$. Otherwise, it can be exclusively derived in its explicit time-dependent form, thus going easily out of control both mathematically and physically [9]. Thus, the relation $h = 3\gamma-1$ entails the overall friction–lubrication system to be in the least-dissipation regime of utmost effectiveness. In such a regime, entropy production revealed by the well-known Gibbs principle goes to minimum, keeping always the system dynamics out of equilibrium though sometimes really close to it, i.e., toward maximum entropy equilibrium statistical–mechanical condition.

The temporal behavior, represented by system of equations (1)–(3) can be explored mainly in a numerical way, cf. [9], leaving the system as proven to be quasi-periodic, which suits very well the specifics of on-rAC (and, on-mAC) based dynamics of friction and lubrication, which are also observed to be quasi-periodic, owing to their rest–activity periods, distributed often in a stochastic manner but sometimes expressing also some (almost) deterministic regularities [15]. This short communication is, however, not intended to explore this behavior, leaving some flavor of such an exploration to [9] again, because some similarities are expected while performing it (also, a very limiting analytical examination, whenever possible, is consequently omitted).

3 Anomalous Random-walk Approach and its Contribution Toward Lowering the Suffered Friction Effect, Comparison with Experimental Findings

To proceed further, we wish to explore the more microscopic than mesoscopic (see the preceding section) behavior of the mAC, with the hope that it helps elucidate some interstitial fluid pressurization effects in any rAC [14, 15].

First, from the above it follows that to have ODEs system (1)–(3) virtually at work, that is, in its least-

dissipative autonomous form, cf. [16] and Refs. therein, we have to accept its basic dynamic constraint, namely

$$3\gamma + (d_S/2) = 2 \tag{4}$$

which truly reflects its synergistic structure–property relationship (S–PR), where the 'structure' is given a microscopic contraction–elongation mechanical property [10], γ, while the 'property' implies a Random Walk (RW) type transport of the ions along the so designed porous-wet structure, composed of SAPL-s. The spectral (or, fracton) dimension of the process, d_S, can be, by means of a (A–O, Alexander–Orbach) conjecture [9], interconnected with two other parameters, the apparent fractal dimension of the SAPL in a given state, as well as the trajectory (geometrical) dimension of the RW along a SAPL, d_F and d_{RW}, respectively, by means of the A–O type formula [9], $d_S = 2d_F/d_{RW}$. It ultimately results in having Eq. 4 rewritten as

$$3\gamma + (d_F/d_{RW}) = 2, \tag{5}$$

yielding finally the desired S–PR.

Let us imagine, what seems plausible to be taken for granted in the above emphasized least-dissipation (mechanical structure versus transport property) regime, $\gamma = (h + 1)/3$, that transport of the ions after a load goes via possibly effective geometrical routes. It comes out from both, the formulation of system (1)–(3) as least-dissipative [16], cf. [9], and Refs. therein, as well as from the fact that the ion transport is also facilitated by electrostatics [11], so that $d_F \approx 1$ is reasonable to demand fairly, because the transport should go along possibly the shortest, straight microtrajectories (as if it was within temporarily formed 'nanotubes'), certainly along the SAPL-s, perhaps forming their micellar cores in a more or less piecewise manner. This is as if it was performed along microscopic inter-micellar, or sometimes intra-micellar nanopores, created temporarily by the complex system under study, that could resemble ion (proton) channels to some extent [13, 17]. Such physically motivated assumption gives the S–PR, Eq. 5, in a slightly simpler form

$$3\gamma + (1/d_{RW}) \approx 2, \tag{6}$$

which enables us to get, for the three distinguished mechanical states, $\gamma = 1/3;\ 1/2;\ 3/5$, the RW exponents: $d_{RW} = 1;\ 2;\ 5$, for the vigorous, "intermediate" (Gaussian) and slow random walkers [9], respectively, primarily the protons, being the lightest, i.e., much prone to undergo an adequate action after the external-load (by a brute external force/load) being applied.

Note that from the hydrodynamic point of view, the squeezed state appears naturally after external-load's action, and also naturally, the RW is becoming vigorous, thus supplying the system with enough (directional) kinetic energy, E_{kin}, which automatically increases the system's momentum, P, since for each individual ion of mass m, the well-known relation $E_{kin} = P^2/2m$ virtually applies. Certainly, the total momentum contributes univocally to the pressure of the mAC, thus in the $\gamma = 1/3$ state by increasing it strikingly due to the presence of the vigorous RW for which the broad "avenues" or passages are most open (note again that the overall rationale presented entails hydrodynamics to some extent). A probable primary mechanism could be that they are open for the proton (H^+) permeation through the SAPL membranes formed, because the SAPL-s, while getting squeezed, liberate the protons by breaking the hydrogen bonds by which the protons are attached to the temporarily formed transmembrane water pores. This revealed microscopic mechanism may contribute to explain the (electrostatics-enhanced [11]) interstitial fluid pressurization as the main factor contributing to facilitate friction–lubrication process in rAC, herein rationalized formally by its more ideal (abstracted) counterpart, abbreviated consequently by mAC throughout the paper. One may also say, when embarking on the ion-channel analogy [18], that the (pressure-induced [10]) channel is open in the $\gamma = 1/3$ state, neither open nor close in the $\gamma = 1/2$ state, or finally, definitely closed (or, inactivated?) in the $\gamma = 3/5$ state, that is supposed to be the (acid–base) quasi-equilibrium state [7, 13]. Since the structure of the complex synovial fluid, both in mAC and rAC, changes systematically over time, suffering additionally from many loads applied, a certain degradation as well as aging effect can also be anticipated as associated with the biolubrication effect. Therefore, an analogy, readily based on non-Markovianity of the open–close dynamics of the ion channel [19], attributed to a flickering behavior of the channel walls' constituents, presumably destroying the hydrogen bonds, is also very plausible to occur—this is in excellent accord with all the our rationale presented herein.

It is then only a matter of solving Eq. 3, which yields asymptotically some algebraic function in time, as well as of applying an (extended) Einstein–Smoluchowski (ES) fluctuation–dissipation formula [4, 9, 10],

$$\eta(t) = k_B T/D(t), \tag{7}$$

wherein $D(t) = d/dt < r^2(t) >$, and $< r^2(t) = Ct^{2/d_{RW}}$ (with another constant, C [9]) in order to estimate the dynamic time-dependent viscosity of the system. Thus, the viscosity given in terms of the (extended, means here: explicitly time-dependent) ES formula, behaves in accordance to the inverse power of time. Bear in mind that this quantity is proportional to the interstitial fluid pressure, cf. [14, 15].

The dynamic friction coefficient $f(t)$ of the mAC during a load of duration t is naturally proposed to be

$$f(t) \simeq 1/K(t), \tag{8}$$

thus being an inverse of the tribo-micellization kernel function of the mAC, *K(t)* is solely given above by means of Eq. 3. This proposal is justified due to the fact that an external load may cause the hydrogen bonds, keeping the protons (and possibly, other cations, e.g., OH^-) within the structured-water containing SAPL membrane [20, 13], to break when a brute force, i.e., a heavy external load becomes effective [20]. It is then easy to recover, at least in a qualitative way, some experimental curves by Ateshian et al. [14], displaying the dynamic microrheological behavior of our system in a $\{\eta(t), f(t)\}$ plane, for the given time interval t (a detailed fitting of the curves displayed in Fig. 5 of Ref. [14] is left for another study, but the algebraic behavior in time, displayed in the $\{\eta(t), f(t)\}$ plane looks similar to experimental curves provided by Fig. 5 in Ref. [14]). It is noteworthy to underline that the model hypothetically presents both functions as algebraic functions of time (power laws), which is excellent for a simple fitting procedure to be applied. A more realistic fitting can be done by departing from the $d_F \approx 1$ most effective behavior, that is, by relaxing the (straight) ion-channel/nanotube (quite oversimplified) assumption employed so far, which is by the way fairly idealized toward materializing the conceptual purpose of this work. An additional option appears to be to scan [surely, according to the constraints (5)–(6)] over γ and d_{RW} exponents' values in order to reproduce well step-by-step the more realistic temporal behavior in the $\{\eta(t), f(t)\}$ experimental plane, tightly comparable to that presented in Ref. [14]. In general, a far more sophisticated though not entirely coming-from-first-principles approach, pointing to the very subtleties of the uncovered microrheology, associated with its underlying, and very relevant time scale, could prospectively go by replacing Eq. 3 by its fractional $2/d_{RW}$-counterpart, consult insightfully [21], and Refs. therein.

At this point, it would be appropriate to make a comment on as-yet proposed boundary lubrication mechanisms manifesting in synovial joints, especially based on an extensive survey of methods and concepts collected and discussed thoroughly in [20, 22].

From this discussion it follows clearly that there is a quite substantial lack of a reliable microscopic mechanism of the biolubrication under consideration. The more and more refined, both experimental and theoretical rheological studies, typically based on more macroscopic (i.e., viewed in classical, say Coulomb–Amontons and/or continuum fluid-mechanics approach) [6, 14] than microscopic, supposedly water-entailing [23] concepts of friction-and-adhesion mechanisms, have not yet arrived at a consistent and conclusive picture of the microscopic, possibly least-dissipative mechanism of the biolubrication in the joints. They express, however, not only a vital interest in solving this problem, but also in our opinion, they also show up some well-approaching tendencies toward a satisfactory solution to the joint biolubrication problem. To be more concrete, let us offer a microrheological, represented by our $\{\eta(t), f(t)\}$ context, and experimentally motivated rationale (say, toward designing a suitable experiment), supporting well to some quite sufficient extent the above statement.

Namely, in the presented hypothesis study, there is of course still an ample place for testing the hypothesis developed. We wish to figure out very much that it would be possible when looking at the experimental setups and methods applied recently [20, 5, 14, 15]. The experimental test would roughly rest on applying the surface force balance (SFB) device [20], or possibly, a comparable experimental equipment based on the surface forces apparatus (SFA), in general [5, 14]. Let us focus on the SFB apparatus that is able to measure the friction–adhesion effects with high precision, i.e., down to resolutions of about nanometer fractions. Typically, an applied force as a function of the separation between two opposing, surfactant-coated surfaces is measured by the SFB. These nonlinear force–separation relations are well correlated in this ex-vivo experiment with the multiple interference spectra (and, the fringes types) of the heat-filtered white light [20].

First, let us focus on what can be measured. We are of the opinion, that, while based on our hypothetical study, the time-dependent quantities, defined by Eqs. 7 and 8 could be a legitimate approach (or, some other, related characteristics in the frequency domain) to obtaining the corresponding Fourier transforms. In the former, while performing a cyclic (normal) load-on and load-off experiment, such as the one reminiscent of that depicted in Fig. 2 of Ref. [22] (but first more in favor of the normal load, with possible shear avoidance, cf. [14]), one could provide the corresponding force–distance plots as a function of the experiment's duration, starting from the separation of a few hundreds of nanometers (distinctly above the asperity, or micelle diameter), while squeezing and relaxing (viz. returning from the squeezed state) periodically the synovial fluid layer dispersed between mica cylinders [20].

Next, by detecting the related changes in the light interference (optical) spectra, assuming that the viscosity of the synovial fluid of interest is properly estimated before, one could at least provide the relative changes in viscosity of the confined fluid in the course of time, as expressed in Eq. 7. Another option could be to measure the viscosity changes with respect to the known value of water viscosity in standard conditions. Yes, indeed, by proposing such an alternative way, we would like to stress very much, consistently with [20, 22], the importance of water as an extremely effective biolubrication agent. What

distinguishes, however, our conception from those highlighted in [20, 22], and supported by explanations on the relations between structured and bulk water surrounding an amphiphile (a protein, for example) [23], appears to be that we rather advocate more strongly for water dissociation at thermodynamic equilibrium [7, 8], as well as for a certain plausible deterioration of water structure as a whole under respective confinement by means of breaking the hydrogen bonds [23]. This can occur as a consequence of an effective transport of protons applies ultimately [24]; or equivalently, when the system is in disequilibrium after applying a sufficient load to it. Then, according to Ref. [23], the hydrogen bonding, with its creation and annihilation events, is also related to the translational and/or rotational motions of the amphiphilic molecules per se. NMR-based relaxation spectra can reveal this hydrogen-bonding formation or breakage [23, 20]. One could also imagine that it could be done within the SFB (or, SFA [5]) method with proper labeling, a task being not a "mission impossible" for a biochemist, the constituents of the asperities in the joint's superficial tissue layer [20], called somehow by us micelles or amphiphilic aggregates [7, 10] of the synovial fluid's main surfactants and/or polyelectrolytes [20]. Thus, our view, involving in addition a presence of small ions, such as Na^+; Ca^{2+}, and the likes [7], does not entirely contradict but can be seen as complementary to, well as independent of the end-grafted polymers (De Gennes type) concept, wherein the brushes are adsorbed at both solid surfaces of a working joint [20]. Instead, we rather propose an external-load caused self-organization of the complex synovial multilayer into micelles, and possibly, other similar spatial hydrated nanoscale domains [10]. Certainly, the relaxation (correlational spectra, possibly of Kohlrausch–Williams–Watts anomalous type [9, 10]) spectra thus obtained in the course of the experiment's duration should reveal a mechanistic response of the soft system to the water action, in general, such as the Boltzmann type creep compliance, cf. the classic by Ferry quoted in Ref. [20] (again, another quite equivalent option would be to enter the dielectric relaxation spectroscopy, putatively of non-Debye proveniency). From them, for the methods see also Ref. [14] and Refs. therein, the time-dependent friction function can also be extracted, cf. Eq. 8, especially in its very relation to Eq. 3, the latter being soluble and virtually ready for a desired fitting to available experimental data.

4 Conclusions

By presenting our fairly hypothesized rationale, we have shown that with respect to this conceptual tribo-chemical lubrication mechanism uncovered, the formation and disintegration of reverse micelles may be seen to be pivotal to their super-lubricating role in an open thermodynamic system/condition. Consequently, the development of micelles/aggregates, and the channels (interspaces) they may form, would be a desirable factor to the physiological function of rAC/mAC [24], and especially in withstanding the effects of the usually heavy load imposed on the joint while facilitating frictional behavior at the same time. Conversely to their formation under load, when load is removed, the micelles, as temporary by-products of the thermodynamic system would "spontaneously" disappear, simply in accordance with the Kelvin–Laplace–Young law (an important exception toward structural biomatter gradients can also be proclaimed [25]), since the (internal) pressure of water within the micelles is large compared to that of the external water; while it is also possible for the dissolution of any micelle to occur as a consequence of traumatic loading [2, 3]. Therefore, a periodic friction–lubrication process [15, 9] associated ultimately with the creation–annihilation of ion tracks viz. nanochannels in the matrix during either short or long term joint function can be hypothesized to be a plausible mechanism contributing to the complex facilitation of mammalian joint motion.

Other than explaining the ultralow (dynamic) friction effect in the AC as a whole, the non-equilibrium thermodynamic model that has been formulated seems to provide quite a legitimate basis for the super-lubrication [15] of the entire joint and the role of the (reverse) micelles in this Ref. [26] since it is also capable of explaining additionally why the rolling-friction coefficient in the joint, due to (round) micelles' formation, is typically lower than its static counterpart.

Finally, this study suggests a probable mechanism of ultralow friction in the AC as being at first sight fairly attributable to the rather well-known proton-channeling mechanism (toward H^+ intra- and inter-micellar nanopores) [24], as well as fairly describable by the introduced microrheological context of the $\{\eta(t), f(t)\}$ friction–lubrication space, with Eqs. 7 and 8 involved. From our hypothesis, it follows that protons permeation is possible to occur since the sufficiently heavy external-load may change the critically pH- and temperature-dependent acid–base equilibrium [7, 13], this way inducing a transmembrane potential, urging to transport protons in a voltage-gated manner [24]. Thus, the interstitial fluid pressurization is ultimately carried out electromechanically, and can also be viewed in terms of protons (ions) permeation through the transmembrane micelles-containing inhomogeneous AC interlayers [14, 15, 18–21], no matter whether with this model or in reality [27].

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References

1. Hills, B.A.: Role of surfactant in peritoneal dialysis. Perit. Dial. Int. **20**, 503–515 (2000)
2. Hills, B.A.: Boundary lubrication in-vivo. Proc. Inst. Mech. Eng. **214**, 83–94 (2000)
3. Hardy, W.B.: Collected Papers of Sir William Hardy. Cambridge University Press, Cambridge (1936)
4. Israelashvili, J.N.: Intermolecular and Surface Forces. Academic Press/Elsevier, Amsterdam (1991)
5. Hamrock, B.J., Schmid, S.R., Jacobson, B.O.: Fundamentals of Fluid Film Lubrication. Marcel Dekker, New York (2004)
6. Benz, M., Chen, N., Jay, G., Israelashvili, J.N.: Static forces, structure and flow properties of complex fluids in highly confined geometries. Ann. Biomed. Eng. **33**, 39–51 (2005)
7. Pawlak Z., Kotynska J., Figaszewski Z.A., Oloyede A., Gadomski A., Gudaniec A.: Impact of the charge density of phospholipid bilayers on lubrication of articular cartilage surfaces. J. Achiev. Mater. Manufact. Eng. **23**, 47–50 (2007); this is also available in Arch. Mater. Sci. Eng. **29**, 24–29 (2008), an extended version of this reference
8. Pasquali-Ronchetti, I., Quaglino, D., Mori, G., Bacchelli, B., Ghosh, P.: Hyaluronan–phospholipid interactions. J. Struct. Biol. **120**, 1–10 (1997)
9. Gadomski, A.: Description of the kinetics of a model tribopolymerization process. J. Math. Chem. **22**, 161–183 (1997)
10. Gadomski, A.: Stretched exponential kinetics of the pressure induced hydration of model lipid membranes. A possible scenario. J. Phys. II Fr. **6**, 1537–1546 (1996)
11. Roberts, A.D.: Role of electrical repulsive forces in synovial fluid. Nature **231**, 434–436 (1971)
12. Hills, B.A., Crawford, R.W.: Normal and prostatic synovial joints are lubricated by surface-active phospholipid. J. Arthoplasty **18**, 499–505 (2003)
13. Pawlak, Z., Crawford, R.W., Oloyede, A.: Hypothetical model of hydrophilic lubrication in synovial joints. Proc. AUSTRIB 2006, Brisbane/Australia, paper 233
14. Ateshian, G.A., Wang, H., Lai, W.M.: The role of interstitial fluid pressurization and surface porosities on the boundary friction of articular cartilage. J. Tribol. **120**, 241–248 (1998)
15. Zhu, Y., Granick, S.: Superlubricity: a paradox about confined fluids resolved. Phys. Rev. Lett. **93**, 096101/1–4 (2004)
16. Assenova, E., Kandeva, M.: Self-organization aspects in tribosystems. The Annals of the University "Dunarea de Jos" of Galati Fascicle VIII. Tribol. 25–28 (2003)
17. Perozo, E., Cortez, D.M., Sompornpisut, P., Kloda, A., Martinac, B.: Open channel structure of MscL and the gating mechanism of mechanosensitive channels. Nature **418**, 942–948 (2002)
18. Bezrukov, S.M., Winterhalter, M.: Examining noise source at the single-molecule level: 1/f noise of an open maltoporin channel. Phys. Rev. Lett. **85**, 202–205 (2000)
19. Siwy, Z., Fulinski, A.: Origin of $1/f^{\alpha}$ noise in membrane channel currents. Phys. Rev. Lett. **89**, 158101/1–4 (2002)
20. Klein, J.: Molecular mechanism of synovial joint lubrication. Proc. Inst. Mech. Eng. **220**, 691–710 (2006)
21. Metzler, R., Klafter, Y.: When translocation dynamics becomes anomalous. Biophys. J. **85**, 2776–2779 (2003)
22. Briscoe, W.H., Simon, T., Tiberg, F., Thomas, R.K., McGillivray, D.J., Klein, J.: Boundary lubrication under water. Nature **444**, 191–194 (2006)
23. Halle, B., Davidovic, M.: Biomolecular hydration: from water dynamics to hydrodynamics. Proc. Natl. Acad. USA **100**, 12135–12140 (2003)
24. Decoursey, D.E.: Voltage-gated proton channels and other proton transfer pathways. Physiol. Rev. **83**, 475–579 (2003)
25. Dell'Isola, F., Gouin, H., Seppecher, P.: Radius and surface tension of microscopic bubbles by second gradient theory. C R Acad. Sci. Paris **320**, 211–216 (1995)
26. Pawlak, Z.: Tribochemistry of Lubricating Oils. Elsevier, Amsterdam (2003)
27. Mouw, J.K., Imler, S.M., Levenston, M.E.: Ion-channel regulation of chondrocyte matrix synthesis in 3D culture under static and dynamic compression. Biomech. Model Mechanobiol. **6**, 33–41 (2007)