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Edison revisited: Electro mechanical effects in wet porous materials

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Abstract. Edison discovered that the coefficient of friction between a metallic plate and a porous material moistened with a dilute electrolyte could be modulated by an electric field. In experiments on the same kind of contacts (clays or chalks on carbon or metals) but without continuous tangential relative motion we measure two electro-mechanical effects at frequencies of the order of 10 kHz. An alternating field induces an alternating normal force between the porous material and the conducting base. The force is lagging by $\pi/2$ *versus* the field. A forced normal relative motion induces through the contact a current nearly in phase with the motion. For an explanation we start from Helmholtz theory of stationary electrophoretic phenomena. We present a model in which liquid motions obey the Helmholtz laws. It explains decently the phase relations between causes and effects, and approximately the values of the effects. In optical experiments on contacts between a wet clay and the transparent conducting coating of a glass plate we measure in the frequency range $1-100$ kHz a modulation of reflecting power induced by an alternating potential. The decrease of reflecting power is lagging by an angle close to $\pi/2$ behind the field. We think the modulation observed is induced by a modulation of the amount of liquid in the film present between glass and clay. In friction experiments this alternating liquid lubrication acting exclusively at the very places where friction occurs may have significant effect.

PACS. 47.55.Mh Flows through porous media – 82.45.+z Electrochemistry and electrophoresis – 46.30.Pa Friction, wear, adherence, hardness, mechanical contacts, and tribology

Introduction

In 1875 Edison was trying to invent a device able to transduce electric signals into mechanical motion without having recourse to the electromagnetic systems heavily patented by Bell for telephone applications.

He discovered [1–4] that the coefficient of friction between a foil of blotting paper damped with various dilute electrolytes and a metallic plate could be modulated by an electrical tension applied through the paper with the help of a second electrode fixed to the back of the paper. When the paper and its back electrode are in continuous tangential motion relatively to the metallic base plate, the friction force is sensitive to an electrical tension applied between electrodes.

A phone transmitter was developed in which the paper was replaced by a cylindrical piece of chalk put into rotation by a metallic axis acting as one electrode. The second electrode, a metallic plate pressed against the chalk by a static normal force of a few pounds transmitted the tangential friction force to the earpiece membrane.

To hear something the customer had to act on a winch to obtain after mechanical transmission involving a worm a small peripheral velocity of the chalk. It is said by witnesses [4] that similar enlarged devices could be operated as deafening loud-speakers.

According to Edison the acoustical energy was essentially supplied by the mechanical device producing the tangential motion and not by the modulating electrical energy input.

The effect discovered by Edison has been studied in many works. Some were done in his time [5]; others are more recent [6].

The present work is not focused on these friction effects. We investigate other properties of contacts between a wet porous material and a conducting solid. We shall refer to them as Edison contacts.

1 The Edison experiment

We repeated the Edison experiment using maybe a different kind of blotting paper but at first with the electrolyte PO_4HNa_2 he recommended. The device is described in Figure 1. It mainly consists of a twenty centimeters long cylinder B mechanically fixed in its middle. On the mirror M a collimated light beam is reflected. Any torsional motion of the bar deflects the reflected beam. A photocell split in four quadrants measures the deflections

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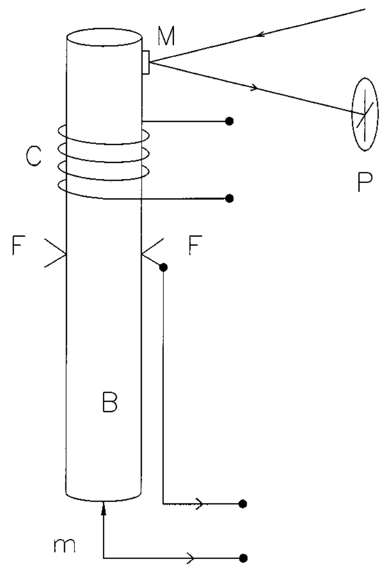

Fig. 1. Experimental device. B: cylindrical bar acting as a resonator. FF: Mechanical fixation. C: Coil for eventual magnetostrictive excitation. M: Mirror. P: Photocell with four quadrants. m: microphonic contact for oscillations measurements.

and determines the plane in which it moves. The microphonic electrical contact m has a resistance mainly sensitive to longitudinal motions (dilatation-contraction) but is also sensitive to torsional motions. On a steel cylinder we use the contact of a tellurium crystal.

The coil C is used to produce an oscillating magnetic field. In a ferromagnetic bar the longitudinal modes can be excited by ordinary magnetostriction. The torsional modes can also be excited by the skew effect discovered by Wiedemann [7]. Both kinds of modes have a high quality factor Q of the order of 10^4. We obtain Q from the measurement of the resonance lineshape. At the frequency of an eigenmode the system acts as a noiseless amplifier of gain Q for the detection of a periodic force.

The vibrations are excited with the Edison effect: a wet sheet of blotting paper backed by a thin sheet of an elastic alloy (1st electrode) is rubbed against the bar (2nd electrode) while an alternating tension at the frequency of the mode we want to excite is applied to the electrodes. The resistance of such an Edison contact was about 4 kΩ. For a torsional mode (fundamental T_1 at 8.4 kHz) we rub orthogonally to the bar axis ; for a longitudinal mode (fundamental L_1 at 13.4 kHz) we rub parallel to the axis. The average friction force associated to the tangential relative motion of velocity 5 cm s^{-1} was near 10^4 dynes (10^{-1}N). With an applied voltage of 15 V (peak value) at 8.4 kHz the modulated component of the force acting on T_1 was typically 20 dynes (2×10^{-4} N). The third harmonics (T_3 at 25.2 kHz and L_3 slightly below 40.2 kHz) could also be excited but with a smaller amplitude.

We have determined the phase relation existing between the induced tangential force modulating the average friction force and the applied voltage V. Setting by convention $V > 0$ when the porous paper is positive relatively to the bar we find the following result: the decrease of the friction force is in phase with $\int V\mathrm{d}t$, the time integral of V. Otherwise stated, the minimum of the friction force occurs when $\int V\mathrm{d}t$ is at its maximum.

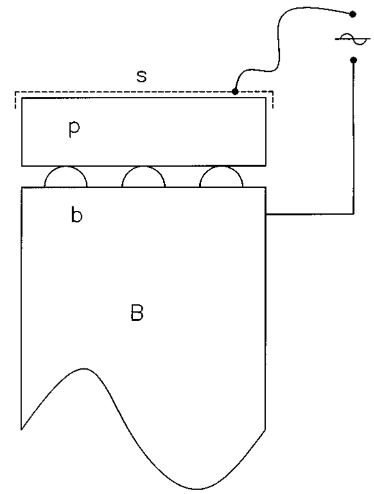

Fig. 2. Experimental details. B: top of the bar. b: three steel or carbon spheres 3 mm diameter. p: sample of porous material. s: silver paste electrode.

2 Electro mechanical effects related to normal motion

In the experiments to be described now, no tangential relative motion is imposed.

2.1 The device

The device of Figure 2 shows an enlarged view of the top of the bar B of Figure 1. An Edison contact is made between a piece of porous material p laying on three conducting balls b strongly fixed and electrically connected to the bar B. The second electrode on top of p is made of silver paste. In a previous study on the dynamical properties of dry "Hertzian" contacts we have shown, that near a longitudinal resonance frequency of the bar, the system behaves like a system of two coupled oscillators [8].

The frequencies of these two oscillators are respectively ν_L the longitudinal frequency of the free bar and ν_M the "mutual frequency" of resonance of relative motion of the object on the bar end supposedly fixed ($\nu_\mathrm{M} \simeq 2$ kHz for an objet weighting a few grams). Due to the presence of the object p the resonant frequency of the bar is pushed upwards by a few Hz because p does not move much and contributes more to the restoring force of the the bar mode than to its inertial mass. Effectively calling ξ the motion of the top of the bar and x the motion of the object center of mass, one finds that $-x\nu_\mathrm{L}^2$ equals $\xi\nu_\mathrm{M}^2$. Consequently the relative motion $\xi - x$ which is of interest in our experiments is close to ξ. In some experiments we have to deduce from measured values of ξ the force F which at resonance has produced this motion. Calling μ the mass which allows us to express the kinetic energy of the mode as $\mu\dot{\xi}^2/2$ the "restoring force" $\mu\omega^2\xi$ is equal to $2\pi QF$ where Q is the quality factor.

2.2 The materials

As porous solids we used clays and chalks. We tried three kinds of clays: the white kaolin; the green clay you find in drugstores to be wrapped around sore ankles; white clay coming from China with the "Pottery Workshop" a toy for children and parents.

Starting from the powder, we mix a paste with water and form the desired shape. After baking an hour at 500 °C we get a highly porous structure strong enough to stay solid when impregnated with electrolytes. The saturation with water brings a 25% relative increase of weight.

Among chalks we tried natural chalk CO_3Ca (white rectangular bars of old schools) or compressed SO_4Ca (round bars of modern schools). For electrolytes we tried PO_4HNa_2, NO_3Ag, $CuCl_2$, KOH with concentrations 0.1 N to 0.01 N. For base electrodes we tried Pt and C to avoid an eventual chemical reaction, silver with NO_3Ag, copper with $CuCl_2$ and different steel. With all combinations of these elements we observed with similar amplitudes and phases, the two effects we now describe[1].

2.3 The effects

In each experiment we observe two effects corresponding to the two directions in which energy exchange can take place between its mechanical and its electrical forms.

We call arbitrarily the "direct effect" the fact that a periodic voltage V applied through the porous material induces a periodic force on the top of the bar. This force is not in phase with the applied voltage but with its integral $\int V \mathrm{d}t$. When this time integral is positive a downward force acts on the bar.

There also exists an inverse effect: if a periodic motion ξ is imposed to the top of the bar by other means (magnetostriction or thermal excitation by a needle) a current $\dot{q}$ is induced in the porous material circuit. The current is almost in phase with ξ, a maximum of current flowing from base to porous material when the extension of the bar is at a maximum. In some experiments we observe a small advance ($\pi/7$ or $\pi/8$) of $\dot{q}$ over ξ.

In the experiments we describe here we were careful to apply only alternating voltages. Continuous voltages applied to the contacts bring lasting perturbations to the impedance of the circuit, to the electromechanical effects and even to the elastic stiffness of the contact.

An integrated flow of direct current amounting to 10^{-4} coulomb is enough for these perturbations to begin to appear. They are not the same for the two directions of the current. Direct currents being avoided, the evolution in time of the effects can be ascribed to water evaporation from the sample.

[1] Experiments on porous glasses show similar effects.

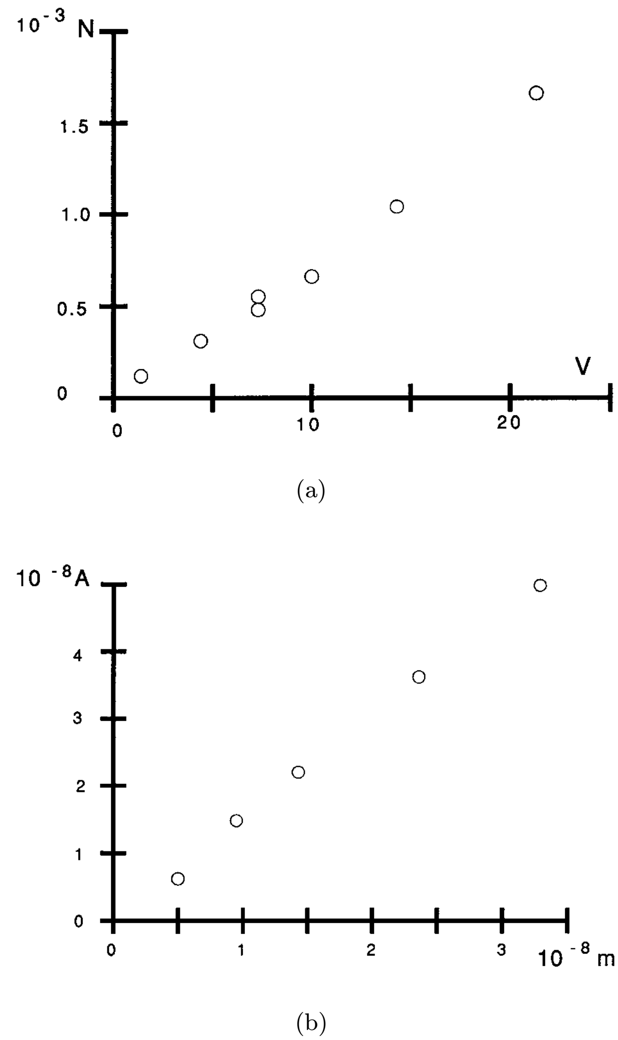

Fig. 3. Experimental results on electro-mechanical effects kaolin baked at 500 °C one hour laying on steel balls. (a) *Direct effect.* Abscissas: applied voltage in volts (peak values); ordinates: oscillating force acting on the bar in Newtons $\times 10^{-3}$. (b) *Inverse effect.* Abscissas: amplitudes of oscillations excited by magnetostriction in units of 10^{-8} meters. Ordinates: current induced through the porous material in units of 10^{-8} A.

For a sample of weight 8 g having absorbed 2 g of electrolyte the initial evaporation rate is of the order of 1 mg per minute.

Figures 3a and 3b show the amplitude of the direct and inverse effects at the frequency 13.4 kHz. The kaolin plate of 8 g lays on three steel balls of diameter 3 mm. The electrolyte is PO_4HNa_2 0.01 N. The upper limit of the range of linearity of the direct effect could not be determined, the saturation of the position detector occurring first. The impedance of the porous circuit element was a pure resistance of 80 kΩ.

For the direct effect, we find from the measurements relative to three similar contacts working in parallel that for one contact

$$\frac{F}{V} = 2.26 \times 10^{-5}\ \mathrm{N(volt)^{-1}}\ \text{or}\ 6.77 \times 10^{2}\ \text{e.s.u.}$$

Since in fact F follows $\int V \mathrm{d}t$ it is of interest to calculate

$$\frac{\omega F}{V} = 1.90\ \mathrm{Newton(volt)^{-1}s^{-1}}.$$

For the inverse effect on each contact

$$\frac{\dot{q}}{\xi} = 0.50\ \mathrm{Am^{-1}}\ \text{or}\ 1.5 \times 10^{7}\ \text{e.s.u.}$$

A systematic error in the scale of ξ measurements would have opposite effects on the two calculated coefficients.

For other electro-mechanical effects, electro-capillarity and piezo-electricity, Lippmann [9,10] has shown that for the sake of free energy conservation one could expect in reversible processes reciprocity relations of the kind.

$$\left(\frac{\partial F}{\partial V}\right)_{\xi} = -\left(\frac{\partial q}{\partial \xi}\right)_{V}. \tag{1}$$

For instance in electro-capillary effects F is surface tension and ξ is surface area. Here we can compare $\omega F/V = 1.90$ to $\dot{q}/\xi = 0.50\ \mathrm{Am^{-1}}$.

The respective signs are normal: an upward motion ξ induces a current raising V towards positive values and a positive V induces a downward force *opposing* the upward motion ξ.

But a factor 3.8 in favour of the direct effect spoils an eventual reciprocity relation.

3 A tentative explanation

There are two well-known mechanical effects of electrostatic cause occurring in electrolytes near a solid surface. The electro-capillary effects first investigated by Lippmann [9] and later studied by Helmholtz [11]. The electrophoretic effects occurring in porous material with insulating walls (*cf.* many references in [12–14]). The electro-capillary effect shows up only on specific metal-electrolyte combinations. The electrophoretic effects are present in every porous material with any electrolyte. We observe the same "universality" for the electro-mechanical effects described here and we shall try and account for the observed facts with an "electrophoretic" model.

3.1 Helmholtz theory

Inside a pore of insulating walls filled with an electrolyte Helmholtz [12] supposed the existence of an electrical double layer. Some of the charges staying on the liquid side can move along with the liquid while the opposite layer in stuck to the wall. The excess charges in the liquid (usually positive) are close to the wall [13,14].

Two effects take place which we describe in the case of straight cylindrical pores.

3.1.1 Inverse effect

Let us consider a velocity profile $u(r) = u_0(1 - r^2\alpha^{-2})$ induced along a cylindrical tube of radius α; r is the distance from the axis. Let us put $N = \alpha - r$. For small N:

$$u(N) = \frac{2u_0}{\alpha}N. \tag{2}$$

Using the Poisson relation between electric density and potential one has after integration on the circle orthogonal to the radius an expression of the current:

$$\dot{q}_1 = -u_0 \int_0^{\alpha} N \frac{\partial^2 \varphi}{\partial N^2} \mathrm{d}N = u_0(\varphi_0 - \varphi_\alpha) \tag{3}$$

$\varphi_0 - \varphi_\alpha$ is the potential difference between the axis of the tube and the wall.

In the stationary conditions the relation between u_0 and the pressure gradient which induces it is

$$u_0 = \frac{\partial P}{\partial z}\frac{\alpha^2}{4\eta} \tag{4}$$

where η is the viscosity.

If the forces inducing u_0 are suddenly cancelled the kinetic energy is dissipated by viscosity with a time constant τ:

$$\tau^{-1} = \frac{2\eta}{\rho\alpha^2} \tag{5}$$

ρ is the density. If the pores is small the relaxation is fast. For instance, if $\alpha = 10^{-4}$ cm, $\tau^{-1} = 2 \times 10^{6}\ \mathrm{s^{-1}}$.

3.1.2 Direct effect

A field E along the pore induces a flow of liquid. The acceleration equation is

$$\rho\frac{\partial u}{\partial t} = \eta\frac{\partial^2 u}{\partial N^2} - \frac{E}{4\pi}\frac{\partial^2 \varphi}{\partial N^2}. \tag{6}$$

In the stationary case, Helmholtz leads to the conclusion that φ and u have the same shape flat in the middle and dropping sharply at the walls.

$$u_0 = \frac{E}{4\pi\eta}(\varphi_0 - \varphi_\alpha). \tag{7}$$

The spatial distribution of the charges in the liquid does not appear in equation (7) any more than in equation (3) for the inverse effect.

There remains $\varphi_0 - \varphi_\alpha$ a potential difference of 1 or 2 V determined by the nature of the walls and of the electrolyte. With a field E of 1 V cm^{-1}, the velocity u_0 is in the micron s^{-1} range. The spatial extension D

of the positive charges in the liquid determines the range over which φ and u rise near the wall. This extension has been discussed by Stern *et al.* [13,14]. It is larger for dilute solutions but in most cases $D \leq 10$ Å.

This quantity plays a part in the kinetics. Close to the wall the rate of viscous dissipation of energy per unit volume will be $\eta u_0^2 D^{-2}$. So, at least initially, the relaxation rate indicated in equation (5) is multiplied by the large factor αD^{-1}.

3.2 Application to our experiments

The phase relationships observed between causes and effects show the way. In the direct effect the force is in phase with the time integral of E.

According to equation (7) the velocity u_0 goes with E. The force is in phase with the integral of u_0 which is proportional to the amount of fluid having flown through a cross-section of the pore and eventually its mouth.

Consequently one can guess that this alternating liquid flow builds an alternating variation of pressure at the contact points. In the inverse effect the current $\dot{q}$ is in phase with ξ the motion of the bar.

From equation (3) $\dot{q}$ is proportional to u_0 which in turn needs a pressure gradient to exist (Eq. (4)).

Consequently it is likely that variations of pressure in phase with ξ are induced by the bar motion near the pore estuaries.

We see the narrow space between a porous sample and the base as a "pressure chamber" in which pressure is modulated either by injecting more liquid (direct effect) or by reducing the volume (inverse effect). The observed phase relationships suggest that the leaks at the edges are not significant. To test in a negative way the value of this model we tried as a conducting base a piece of highly porous tantalum. The effects were very small in these conditions. Effectively the model requires an impervious base.

To go further into quantitative analysis some knowledge of the porous structure would be welcome. We should know the transverse size of the pores and the kind of lattice they form inside the samples.

Visual observation with a Nomarsky microscope of high magnification shows a mosaic landscape. The edges of the small "stones" appear coloured in green and red like stained glass. The material being completely white as a whole (kaolin) it may be inferred that some elements (the holes or the walls?) are not much larger than the visible light wave length.

The above equations are relative to one cylindrical pore. Let us define now the number of *connected* pores opening in a surface S at the contact

$$n = \gamma \frac{S}{\pi \alpha^2} \cdot \qquad (8)$$

From values of permeability of such materials [15] one can estimate $10^{-2} \leq \gamma \leq 10^{-1}$. Geometrical arguments suggest that γ cannot be much smaller than the porosity which is of the order of 10^{-1}. From equation (7) written for one pore we derive the depth of modulation of the amount of water having flown through S; calling E_0 the field near the contact:

$$q = \gamma S \frac{\varphi_0 - \varphi_\alpha}{4\pi\eta} \frac{E_0}{\omega} \cdot \qquad (9)$$

If we call ξ_0 the average height of the pressure chamber of area S, K the compressibility of water, the depth of modulation of pressure will be

$$P = \gamma K^{-1} \frac{\varphi_0 - \varphi_\alpha}{4\pi\eta\xi_0} \frac{E_0}{\omega} \qquad (10)$$

and the force of the direct effect will be this pressure multiplied by the contact area S.

For the inverse effect we get from equations (3, 4) the total current

$$\dot{q} = \gamma S \frac{\varphi_0 - \varphi_\alpha}{4\pi\eta} \left(\frac{\partial P}{\partial z}\right)_0 \qquad (11)$$

$(\frac{\partial P}{\partial z})_0$ being the pressure gradient near the contact in a direction normal to the base. Of course the pores are not directed along the normal; this point is altering the meaning of both equations (10, 11).

The pressure is modulated as $K^{-1}\xi\xi_0^{-1}$. Setting $(\frac{\partial P}{\partial z})_0 = \frac{P}{a_\mathrm{p}}$ one gets to account for the inverse effect

$$\dot{q} = \gamma S K^{-1} \frac{\varphi_0 - \varphi_\alpha}{4\pi\eta\xi_0} \frac{\xi}{a_\mathrm{p}} \cdot \qquad (12)$$

From equation (10), setting $E_0 = \frac{V}{a_\mathrm{v}}$ one obtains

$$\omega F = \gamma S K^{-1} \frac{\varphi_0 - \varphi_\alpha}{4\pi\eta\xi_0} \frac{V}{a_\mathrm{v}} \cdot \qquad (13)$$

In that equation setting $\gamma = 10^{-2}$, $S = 10^{-2}$ cm^2, $K^{-1} = 2 \times 10^{10}$ cgs, $\xi_0 = 10^{-3}$ cm, and from electrical resistance measurement $a_\mathrm{v} = 10^{-1}$ cm one gets reasonable agreement with the measured values of the forces observed in the direct effect.

A reciprocity relation similar to equation (1) would hold only if a_v in equation (13) was equal to a_p in equation (12). It would be the case if the surfaces of constant potential were also the surfaces of constant pressure. The quantity $\xi\dot{F}$ would then be equal to $V\dot{q}$ which would mean:

$$\left(\frac{\dot{F}}{V}\right)_\xi = \left(\frac{\dot{q}}{\xi}\right)_\mathrm{V} \cdot \qquad (14)$$

In a "plane condenser" geometry with straight pores of length L normal to a plane base and to a plane upper electrode one would get $a_\mathrm{p} = a_\mathrm{v} = L$.

This special situation could be realized with the use of porous silicon.

To reach the symmetrical equations (12, 13) we did not use *a priori* the Onsager's reciprocal relations which have been invoked for electrophoretic effects [16].

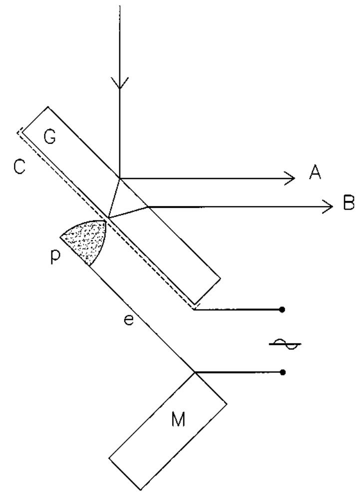

Fig. 4. Optical observation of an Edison contact. G: glass plate. C: conducting transparent coating. p: porous pencil-shaped material. e: elastic metallic sheet. M: supporting moving mechanics. Channel A: reference. Channel B: measure of reflected light intensity. Various lenses and diaphragms not shown.

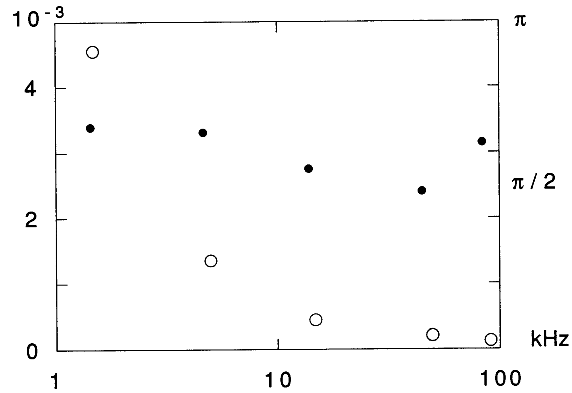

Fig. 5. Modulation of reflected light intensity. Porous material: clay baked at 500 °C damped with PO_4HNa_2 0.1 N. Voltage applied: 1.4 V. Abscissas: frequency in kHz. log scale. Ordinates: left hand scale circle points: amplitude of modulation of the reflected light divided by the decrease in reflected intensity induced by the contact of the clay tip in static position. Relative units 10^{-3}. Right hand scale: phase advance of signal *versus* tension, black points.

4 An optical experiment

Figure 4 shows a device designed to compare the respective reflecting power of the two faces of a glass plate. We use a glass of thickness 6 mm having on one side a transparent electrically conducting coating. A film of water put on this face divides the reflecting power in the experimental condition by a factor close to 4. With a force of about 2 g we apply on the conducting face the end tip of a pencil-shaped piece of clay damped with an electrolyte.

The presence of the wet clay tip reduces the amount of reflected light to 80% of its initial value in the dry state.

Experiments of translation of the beam spot relatively to the clay tip suggest a size of about 40 μm for the beam spot and 20 μm for the poorly reflecting area of contact of the clay tip. When an alternating voltage is applied between clay and coating the reflected light intensity is modulated.

The static decrease of reflected light due to application of the clay tip on the glass induced in our detecting device a signal of 60 mV. At each frequency we observe some amplitude of alternating electrical signal proportional to the reflected light modulation. We plot in Figure 5 these signals after division by 60 mV to obtain a dimensionless modulation depth.

The experiments previously described were limited to a few eigen frequencies of the resonating bar. In this optical experiment no resonance takes place and a continuous range of frequency can be scanned.

At low frequencies the modulation depth is of the order of 10^{-3}. Towards higher frequencies it goes down somewhat like ω^{-1}.

The phase shift between signal and applied tension stays approximately constant near 0.6π.

Consequently we can state: the decrease of reflecting power follows approximately $\int V \mathrm{d}t$ whose amplitude is $V\omega^{-1}$.

If the contact area is filled with liquid as we supposed for the electro-mechanical effects the reflected light modulation must be ascribed to an alternating spreading of the liquid at the edges of the contact area.

The approximate constancy of the phase shift between cause and effect shown in Figure 5 is related to an interesting point: the process involved follows the time integral of V up to 100 kHz. Its time constant must be smaller than 10^{-6} s.

5 Conclusion

We have found many reasons to think that at the contacts between a wet porous material and a conducting base the application of a field pushed and pulled a certain amount of liquid.

Let us consider again the original Edison effect which is a modulation of the friction force by an electric field. Qualitatively it seems sensible to explain a decrease of friction by an injection of lubricating fluid exactly at the place where friction takes place, an increase of friction occurring in the suction part of the cycle.

We can try and evaluate the amount of liquid involved. Let us use equation (9). Edison was interested in the audible frequency range; at equal voltage the volumes of liquid involved were 10 times larger than in our experiments at 13 kHz.

Using a transformer after his carbon microphone he could obtain a field of 30 V cm^{-1} at the porous contact.

From equation (9), choosing $\gamma = 10^{-2}$, our lower estimated limit, one finds that the amount of liquid oscillating is equal to the surface area S of the contact multiplied by a height of 0.5 Å.

It has been reported [17] that a height of 2.5 Å of an electrolyte can decrease dramatically the friction coefficient between two mica sheets.

More experiments are needed to prove that the same effect occurs in Edison contacts.

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