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ELECTROKINETIC PHENOMENA IN FLUID
SATURATED POROUS MEDIA

by Joseph Neev

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science, Physics.

Golden, Colorado

Date 10/17/84

Signed: Joseph Neev
Joseph Neev

Approved: F.R. Yeatts
Dr. F.R. Yeatts,
Thesis Advisor

Golden, Colorado

10/17/84

F.D. Schowengerdt
Dr. Franklin D. Schowengerdt
Head,
Department of Physics

ABSTRACT

Electrokinetic phenomena owe their existence to an electric double layer formed at a solid-liquid interface. Because of this electric double layer mechanical disturbances are coupled to electric potential fluctuations. In this thesis the theory of electrokinetic phenomena is combined with Biot's treatment of the mechanical properties of fluid saturated porous media, to construct a general theoretical description of the electromechanical response of such systems. The new formulation includes Biot's mechanical dissipation effects, as well as electrical dissipation arising from finite fluid conductivity. It yields a set of field equations which can be solved exactly to describe the composite's particles displacements and electric potential. In the steady state limit the theory reproduces the electrokinetic expressions of steady state flow. The results predicted by this theory were found to be in good agreement with available field and laboratory observations. This new understanding of the physical properties of fluid saturated porous media may be a helpful, practical tool in the fields of geophysical exploration, reservoir management, civil engineering and others.

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LIST OF SYMBOLS

$A \equiv \lambda$	a Lamé' coefficient
\bar{B}	magnetic induction vector
b	Biot's dissipation coefficient
D	dissipation function
d	pore diameter
$\bar{E} =$	electric field vector
e_{ij}	strain in the solid
e.m.f.	electromotive force
f	frequency
f_c	characteristic frequency
f_t	transition frequency
g	electric conductivity
$H = P + R + 2Q$	Biot's elastic coefficient
i	$\sqrt{-1}$
\bar{J}	total current density
K	bulk permeability
k	specific permeability
$L = T - u$	Lagrangian density
N	Lamé' coefficients representing shear modulus
P	hydrostatic fluid pressure
$p = A + 2N$	Biot's elastic coefficient
Q	Biot's elastic coupling coefficient

$R=S/\epsilon$	Biot's fluid elastic coefficient
$S=-\beta P$	a fluid pressure on the aggregate
T	kinetic energy density function
U_i	a component of the average fluid displacement vector
u_i	a component of the solid displacement vector
$V=(v/V_c)^2$	the square of the non-dimensional wave velocity
V_c	Biot's characteristic velocity
v	wave velocity
W	the potential energy per volume
x	field points
β	the effective porosity
γ_{ij}	Biot's non-dimensional dynamic coefficient ($i, j=1, 2$)
ϵ	electric permittivity
ϵ	dilatation in the fluid
ζ	zeta potential
η	a generalized coordinate
κ	dielectric constant
μ	fluid viscosity
μ'	magnetic permeability
ν	kinematic viscosity
π	pi
ρ	mass density
ρ_{ij}	Biot's mass coefficients ($i, j=1, 2$)

σ_{ij}	Biot's non-dimensional elastic coefficients ($i, j=1, 2$)
σ	charge density
σ^e	equilibrium charge per pore's volume
σ_f	fluid charge per pore's volume
σ_s	solid charge per pore's volume
σ_n	(net) charge per pore's volume
τ_{ij}	a symmetric tensor, and represents a component of the total stress on a unit volume of the composite
ϕ	electric potential
ψ	electric double layer potential
ω	angular frequency
$\omega_c = b/\rho$	Biot's mechanical characteristic frequency
$\omega_p = g/\epsilon = \tau_c^{-1}$	the dielectric characteristic frequency (equal to the inverse of the material's electric time constant)

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I. INTRODUCTION

Electric effects associated with mechanical vibrations in the soil were discovered during geophysical measurements in the 1930's and were subsequently followed by several papers (Blau and Statham 1936) reporting experimental verifications and investigations as to the suspected origin of the phenomena. These effects were originally given the name "seismoelectric effects of the first and second kinds". The seismoelectric effect of the first kind (also known as "the seismic-electric" effect or "the J-effect") was discovered by Blau and Statham (1936) and was explained by Thompson (1939) as a voltage caused by the variation of earth resistivity with elastic deformation.

The seismoelectric effect of the second kind (also known as "the E-effect" and less widely known as "the electroseismic effect") is characterized by an electrical potential generated within the earth by the passage of seismic waves. This electric potential manifests itself before the arrival of the seismic waves at the surface of the ground, in contrast with the effect of the first kind. Please note that much confusion exists in the literature over this nomenclature and caution must be exercised when one tries to determine what physical phenomenon is actually

being discussed. Zablocki and Keller (1961), for example, discussed in a 1961 paper electric potential variations associated with seismic wave propagation, and refer to the phenomenon in its entirety as "the seismic-electric effect". Martner and Sparks (1959), on the other hand, classified "the seismic-electric effect" as was done above (i.e., as the equivalent of the J-effect). The nomenclature confusion corresponds to lack of ability to clearly distinguish what mechanism or mechanisms give rise to the electro-seismic coupling phenomena and under what field conditions one mechanism dominates over the other.

To avoid further confusion I shall use hereafter the term "E-effect" when referring to all electrical phenomena associated with the generation of new potentials due to electrochemical effects at fluid-solid interfaces. The term "J-effect" will be reserved to fluctuation in existing potentials due to mechanically induced changes of the rocks specific resistivity. Other mechanisms such as pressure variation at the electrode's surface or a piezoelectric effect will not be considered in this thesis.

The seismoelectric effect of the second kind was first reported by Ivanov (1939) who named it "the E-effect" to distinguish it from the already known J-effect mentioned above. In the 1940's and 1950's, Ivanov published further

experimental results alleging that this effect can be caused by an electrofiltration phenomenon in moist soils. Frenkel (1944) was the first to present a mathematical treatment of this hypothesis based on Helmholtz theory of filtration potentials (also known as Helmholtz double layer theory). Bukhnikoshvili and Prangishvili (1956) reported on some field experiments which resulted in failure to observe the electroseismic effect.

Martner and Sparks (1959) reported on a different experiment in which an electrical signal was generated at the instant seismic waves intersected the base of the weathered layer. However, ambiguity existed as to whether the electrical signal was derived from a change in resistivity near the boundary and a consequent disturbance of existing potentials, (i.e., a J-effect mechanism), or from some boundary dependent mechanism which generates new potentials (i.e., an E-effect mechanism).

Zablocki and Keller (1961) reported on a study of "seismic-electric voltages developed by high-energy seismic waves". Their measurements were performed 3 to 5 miles away from an underground nuclear detonation of an equivalent of 5,000 tons of TNT. They proceeded to compare their results to voltage measurements obtained during the explosion of 500 tons of chemical explosive at 3.5 miles away from the

detonation point. The electric signal magnitudes due to the chemical explosion were on the order of a millivolt while the recorded signals from the nuclear detonation were an order of magnitude larger (i.e. about 10 mv). Zablocki (1966) reported on other large underground nuclear tests in which low frequency electrical transients were observed at the instant of detonation. The transients, reportedly, were so large in the vicinity of the shot chamber, that quantitative measurements of resistivity changes would have been extremely difficult. The potential, however, was interpreted by Zablocki (1966) to be predominantly magneto-hydrodynamic in origin, and similar effects were not observed with the small chemical explosives also used in this study.

Long and Rivers (1975) attempted to measure the electro-seismic response under field conditions in coastal plain sediments near Gordon, Ga. They reported that, "the magnitude of the voltage changes caused by an electroseismic response measured at the surface by a Wenner array with 9-m electrode spacing was 100 to 300 mv per mm/sec of vertical particle velocity at 15 Hz. The response correlated most strongly with the Rayleigh wave. Correlation with other compressional phases were also observed. A correlation with shear-wave arrivals was not confirmed." They also reported on field tests resulting in a 0.015 percent change in

resistivity of coarse sand for elastic dilatation in the Rayleigh wave corresponding to a strain of magnitude 10^{-6} . They concluded that, "the use of exploration methods employing the electroseismic response would be limited by the depth limitations of the resistivity methods and the need for a more complicated array. However, a modified system might be designed for down-hole investigations." And also, that "although no physical processes which generate the electroseismic response were elucidated with the field tests, they are undoubtedly related to the condition of the water in the pore spaces and the state of the stress". Finally, they went on to remark that "although general influence of seismic disturbances on electric potentials and resistivity was established in any measurement of the stress dependencies of resistivity in the field, the causative factors cannot be separated easily" (Long and Rivers, 1975).

In this thesis I will attempt to present a comprehensive theoretical treatment of the physical nature of what was designated by Ivanov "the seismoelectric effect of the second kind" or "the E-effect". Such a theory, I hope, will create better understanding of the generating mechanism behind this effect, and will thus help in distinguishing the physical manifestation of the E-effect in field measurements from other causative factors. This, in turn, may make the

E-effect more useful in geophysical exploration as well as in other science and engineering applications.

The object of the present thesis is, therefore, to construct a theory based on physical and chemical principles from the realms of colloid chemistry, continuum mechanics, electromagnetic theory and irreversible thermodynamics, which will extend Biot's (1956) treatment of elastic waves in fluid saturated porous media, by accounting for electrical effects associated with elastic deformation.

More recently, both theoretical treatments and field measurements were performed with respect to electrical effects associated with the flow of fluids into dilatant zones prior to earthquake occurrence. A theoretical model was constructed for diffusive flow of fluid by Dmowska et al. (1977). They pointed out that the difficulties in applying their model were due to the speculative nature of estimations of the global permeability, K , caused by different types of pores, cracks and fractures. Other difficulties arose from the liquid-vapor transition that takes place in the deeper parts of the crust. They therefore stated that "...it is probably safe to conclude, that the electrokinetic phenomena could accompany some very shallow earthquakes, although the exact determination of the magnitude of this phenomenon, assuming any rock permeability, would be

highly speculative."

Mizutani et al. (1976) based their predictions of the magnitude of the electric potential gradient associated with earthquakes on field measurements of the pore pressure gradient and applied it to existing treatments in physical chemistry literature of steady-state electrokinetic phenomena. They estimated electric potential gradient values of 10^{-4} up to 10^{-1} V/m. On the other hand, Sobolev et al. (1975) estimated much smaller values of the same parameters and arrived at electric field values as low as 10^{-5} to 10^{-6} V/m.

An important treatment and laboratory experiment verifying the usefulness of the electrokinetic effect in monitoring reservoirs fluid pressure was performed by Chandler (1981) for the zero-frequency limit. Chandler's experiment also showed that the use of the chemical double layer model coupled with Biot's treatment of acoustic wave propagation in fluid saturated media was justified and that his predictions showed good agreement with experimental values.

To conclude this survey of previous work on the effect of the electrokinetic phenomena on electrical measurements in the field, we must mention the extensive treatment given to the question of the influence of clay contamination and

electrolyte salinity on formation resistivity factor. The most extensive treatment of this aspect of electrokinetic phenomena was given by Winsauer and McCardell (1953). They presented a detailed model, based on an ionic double layer formation at the clay-electrolyte interface, which showed how electrical conductivity can be changed in response to variations in the electrochemical parameters.

It will be appropriate at this point to introduce some order in the various terms we have been using to describe the origin of the E-effect and agree upon a terminology appropriate to the electrochemical phenomena that we intend to investigate: As I have mentioned above, the electrochemical potentials of interest arise in response to mechanical disturbances and their effect on the ionic double layer at the solid-fluid interface. This type of electro-mechanical response, will, in turn, result in generation of the E-effect. Because the electrical signal has its origin in fluid motion induced by differential pressure, the phenomenon is often referred to in physical chemistry literature as "the electrokinetic effect". I therefore choose to adopt this terminology and shall henceforth refer to all electrical manifestations which find their origin at the ionic double layer and chemistry of interfaces, as "the electrokinetic phenomena".

In order to construct the desired theory of electrokinetic effects associated with acoustic wave propagation, the following steps will be taken in the course of this thesis: I shall begin, in Chapter II, with a review of Biot's theory of the elastic properties and acoustic wave propagation in fluid saturated porous media. Chapter III will introduce the fundamental concepts and principles of electrokinetic phenomena. It will also include a modern treatment of electrokinetic effects, from the point of view of irreversible thermodynamics and Onsager's reciprocity principle. In Chapter IV Biot's theory will be extended to include the electromechanical interaction and the system's field equations will be developed to their most general form. The Lagrange formalism method will then be presented to point more clearly to the physical origin of each and every term present in the field equations. In Chapter V I will show that these general field equations can be reduced, when steady state conditions are assumed, to the familiar set of equations describing steady state flow of fluid and charge (when the fluid component of the composite system is considered), and the familiar equilibrium conditions of elastostatic (when the solid phase is considered). In Chapter VI discussion and interpretation of the results will be offered, along with a discussion of the magnetic field in

the low frequency limit. Some of the possible applications of the theory will be discussed in this chapter too.

Lastly, I will have some concluding remarks in Chapter VII, where the overall scope of this thesis will be reviewed and possible future work will be discussed.

Please note that wherever the need arises, I will make use of the SI system of units.

II. BIOT'S THEORY

The summary presented in this section of the thesis is taken almost in its entirety from Biot's original work on the mechanics of deformation and acoustic propagation in porous media, presented in three papers (1956 I and II and 1961).

Please note that I often choose to express vector quantities in index notation and while doing so I conform with the Einstein summation convention. (In this convention, any index which is repeated in a single term indicates summation over that index for the entire range of values.)

A. Stress-Strain Relations in a Fluid Saturated Porous Elastic Solid.

1. Stress

The net stress in a porous medium is assumed to be the stress in the solid skeleton modified by the pore fluid pressure, i.e.:

$$\tau_{ij}^T = \tau_{ij} + \delta_{ij}S \quad i, j = 1, 2, 3 \quad (2.1)$$

where τ_{ij}^T is a component of the total stress on a unit volume of the composite, (τ_{ij}^T is a symmetric tensor and

thus $\tau_{ij}^T = \tau_{ji}^T$), τ_{ij} is a component of the stress on the solid skeleton of the unit volume (note that the normal components, τ_{11} , τ_{22} and τ_{33} , are positive when the force on the solid is a tension), β is a fraction of pore area per unit cross section (if we consider a statistically isotropic porous material, β is also the effective porosity of the medium), $S = -\beta P$ is a fluid pressure on the aggregate and is proportional to the hydrostatic fluid pressure P . (Note that S is taken negative when the force acting on the fluid arises from a hydrostatic pressure.)

2. Strain

The strain in the solid is defined in the usual way

$$e_{ij} = \frac{1}{2} (u_{i,j} + u_{j,i}) \quad (2.2)$$

where u_i is a component of the displacement vector. The strain in the fluid is defined by the dilatation

$$e = U_{i,i}$$

where U_i is a component of the average fluid displacement vector.

3. Relations Between Stress and Strain in the Fluid-Solid Aggregate.

First let us disregard dissipative forces and assume that we are dealing with a conservative system which is in equilibrium at rest. Any deformation is thus a departure from a state of minimum potential energy. Thus, in a first approximation we can express the potential energy as a positive definite quadratic form. We can therefore establish a linear dependence of the seven stress components (τ_{ij} and S) on the seven strain components (e_{ij} and ϵ). In general the potential energy per unit volume is given by $W = \int dW = \int \tau_{ij} de_{ij}$ where dW is an inexact differential which represents the strain energy density. Thus

$$W = \frac{1}{2} \tau_{ij}^T e_{ij} = \frac{1}{2} (\tau_{ij} e_{ij} + \epsilon S) . \quad (2.3)$$

The stress-strain relations may now be expressed as

$$\tau_{ij} = \frac{\partial W}{\partial e_{ij}} \quad \text{and} \quad S = \frac{\partial W}{\partial \epsilon} . \quad (2.4)$$

Assuming statistical isotropy we have

$$W = \left(\frac{1}{2} A \delta_{ij} \delta_{kl} + N \delta_{ik} \delta_{jl} \right) e_{ij} e_{kl} + \frac{1}{2} R (U_{i,i})^2 + Q u_{i,i} U_{j,j} \quad (2.5)$$

and then from (2.4)

$$\tau_{ij} = 2Ne_{ij} + (Ae + Q\epsilon) \delta_{ij} \quad (2.6)$$

$$S = Qe + R\epsilon$$

where $e = e_{kk}$, $\epsilon = U_{e,e}$, the elastic coefficients, $A \equiv \lambda$, $N \equiv \mu$ are Lamé coefficients; N represents the shear modulus of the skeleton, R is a measure of the pressure one must apply to the fluid to force a certain volume of the fluid into the aggregate while the total volume of the fluid remains constant (this is seen when we set $e = 0$ and then, from (2.6), $R = S/\epsilon$. We can also see that R must be positive). Q is a constant which represents coupling between the volume change of the solid and the fluid phases, (indeed if we set $S = 0$ then from (2.6) $\epsilon = -\frac{Q}{R}e$. Since $e > 0$ means a decrease in the porosity, i.e. $\epsilon < 0$, Q must also be positive).

B. Equations of Motion.

1. Purely Elastic Waves.

Let us consider again a unit cube of the composite as a volume element. The element is assumed to be small relative

to the wavelength of the elastic waves, and large compared to the size of the pores. The limitation on the upper value of the frequencies of elastic waves which has been introduced will turn out to be irrelevant for most practical problems. Because of the general principle that a velocity field in compressible fluids approximates that of an incompressible fluid for obstacles which are small compared to the wavelength, our assumption on the relative size of wavelength and pores implies that the microscopic velocity pattern is the same as if the fluid were incompressible.

If we take the six average displacement components of the fluid and the solid (i.e., respectively, U_i and u_i ($i = 1, 2, 3$)) as our Lagrangian coordinates, the kinetic energy density is given by

$$2T = \rho_{11} \left[\frac{\partial u_i}{\partial t} \frac{\partial u_i}{\partial t} \right] + 2\rho_{12} \left[\frac{\partial u_i}{\partial t} \frac{\partial U_i}{\partial t} \right] + \rho_{22} \left[\frac{\partial U_i}{\partial t} \frac{\partial U_i}{\partial t} \right] \quad (2.7)$$

The coefficients ρ_{11} , ρ_{22} and ρ_{12} are mass coefficients presumed to be constant which take into account the fact that the relative flow of fluid through the pores is not uniform. We shall discuss the significance of these coefficients shortly.

If q_i and Q_i are the total forces per unit volume acting (in the X_i - direction) on the solid and fluid respectively, Lagrange's equations give

$$\frac{\partial}{\partial t} \left(\frac{\partial T}{\partial u_i} \right) = \frac{\partial^2}{\partial t^2} (\rho_{11} u_i + \rho_{12} U_i) = q_i \quad (2.8a)$$

$$\frac{\partial}{\partial t} \left(\frac{\partial T}{\partial U_i} \right) = \frac{\partial^2}{\partial t^2} (\rho_{12} u_i + \rho_{22} U_i) = Q_i . \quad (2.8b)$$

Lagrange's formalism helps us understand the nature of the mass coefficients ρ_{11} , ρ_{22} and ρ_{12} : If $u_i = U_i$ there is no relative motion between the fluid and solid phases and the medium moves as a whole. Equation (2.7) then becomes

$$2T = (\rho_{11} + \rho_{22} + 2\rho_{12}) \dot{u}_i^2 \quad \text{with } \dot{u}_i \equiv \frac{du_i}{dt} .$$

We see that the sum of the mass coefficient has to be equal to the total mass density of the aggregate and we conclude

$$\rho = \rho_{11} + \rho_{22} + 2\rho_{12} .$$

We can write this quantity as a function of the porosity β and the mass density of the fluid ρ_f and solid ρ_s : The mass density of the solid and fluid per unit volume

of aggregate are, respectively

$$\rho_1 = (1-\beta) \rho_s \quad (2.10)$$

$$\rho_2 = \beta \rho_f .$$

Therefore, the total mass density of the aggregate is

$$\rho = \rho_1 + \rho_2 = \rho_s + \beta (\rho_f - \rho_s) . \quad (2.11)$$

The pressure difference in the fluid per unit length is

$$-P_{,i} = \rho_f \ddot{U}_i \quad (2.12)$$

or

$$-\beta P_{,i} = \rho_2 \ddot{U}_i .$$

The left hand side is the force Q_x acting on the fluid per unit volume. Thus, with (2.10) we may write

$$\rho_2 \ddot{U}_i = Q_i . \quad (2.12')$$

Since we consider the case where there is no relative motion between the liquid and solid phases (i.e. $u_i = U_i$), Equation (2.8a) becomes

$$(\rho_{12} + \rho_{22}) \ddot{U}_i = Q_i \quad . \quad (2.8'a)$$

Comparing Equation (2.12) and (2.8a) we conclude

$$\rho_{12} + \rho_{22} = \rho_2 \quad .$$

Combining this result with Equations (2.9) and (2.11) we also obtain $\rho_{11} + \rho_{12} = \rho_1$, we thus have

$$\rho_1 = \rho_{11} + \rho_{12} \quad (2.13)$$

$$\rho_2 = \rho_{22} + \rho_{12} \quad .$$

It can be seen, that the coefficient ρ_{12} represents a mass coupling parameter between the fluid and the solid phases. This becomes even more evident, by assuming that the motion of the fluid can be somehow restricted, i.e. $U_i = 0$; Equations (2.8) then become

$$\rho_{11} \ddot{u}_i = q_i \quad (2.8''a)$$

$$\rho_{12} \ddot{u}_i = Q_i \quad . \quad (2.8''b)$$

The second equation shows that when the solid is accelerated a force Q_i must be exerted on the fluid phase to prevent an average displacement of the latter. The parameter ρ_{12} that measures this effect is called "the coupling coefficient." We also note that since the force Q_i opposes the direction of acceleration of the solid \ddot{u}_i , we must have $\rho_{12} < 0$. In the case of no relative motion $q_i = \rho_{11} \ddot{u}_i$ in Equation (2.8a), (recall that q_i is the force exerted on the solid), thus, ρ_{11} represents the total effective mass density of the solid within the fluid. The total effective solid mass density ρ_{11} , must be equal to the mass density of the solid in the aggregate ρ_1 , plus an additional apparent-mass density ρ_a , due to the interaction with the fluid, i.e. $\rho_{11} = \rho_1 + \rho_a$. Thus, from (2.13) and the last result, we conclude that $\rho_{12} = -\rho_a$. (The nature of the mass coupling coefficient can become even clearer yet by considering a lumped parameters model. Please refer to Appendix B.)

The coupling coefficient ρ_{12} is, therefore, the same as the apparent mass density ρ_a with an additional change of sign. We can now interpret Biot's Dynamic Coefficients in terms of the composite mass densities and write

$$\rho_{11} = \rho_1 + \rho_a$$

$$\rho_{22} = \rho_2 + \rho_a \quad (2.13')$$

$$\rho_{12} = -\rho_a$$

If we require that the kinetic energy is of a positive definite quadratic form, we get additional conditions on the dynamic coefficients: $\rho_{11} > 0$ and $\rho_{11} \rho_{22} - \rho_{12}^2 > 0$. We also note that ρ_1 , ρ_2 and ρ_a are positive by their physical nature.

The generalized forces on the solid and fluid phases can be represented in terms of the stresses, respectively

$$q_i = \tau_{ij,j} \quad (2.14)$$

$$Q_i = S_{,i}$$

Thus, from Equation (2.8) we have (for the general case)

$$\tau_{ij,j} = \frac{\partial^2}{\partial t^2} (\rho_{11} u_i + \rho_{12} U_i) \quad (2.15)$$

$$S_{,i} = \frac{\partial^2}{\partial t^2} (\rho_{12} u_i + \rho_{22} U_i)$$

Note also that, because of the coupling coefficient, an acceleration of the solid without average motion of the fluid produces a pressure gradient in the fluid.

2. Waves With Dissipation.

Before concluding this section let us briefly consider Biot's treatment of the equation of motion in a fluid saturated porous medium when dissipation effects are introduced. Biot's approach to the formalism of the problem of mechanical dissipation will give us a helpful hint in our attempt to incorporate electrokinetic phenomena into his theory.

Biot divides the propagation of mechanical waves in a fluid saturated porous medium into two types according to the kind of microscopic motion of the fluid in the pores. If the fluid motion is a Poiseuille type of motion (which means that its Reynolds number does not exceed a certain critical value), friction forces have a dominating role over inertia forces and, in this case, the pressure gradient exerted on the fluid is simply related to the average velocity of the fluid through a real constant coefficient in Darcy's law

$$\bar{\nabla}P = b\dot{\bar{u}} \quad (2.16)$$

where $b = \mu/k$; μ is the fluid viscosity and k is Darcy's coefficient of permeability. Thus b is a real constant, that depends on the viscosity and permeability which characterize the medium. (It is worth noting here, that for a porous medium the coefficient b becomes, $b = \beta^2 \frac{\mu}{K}$ where β is the effective porosity and $K = \beta k$.) If, on the other hand, the Reynolds number of the relative flow exceeds the characteristic value, the assumption of Poiseuille flow does not hold, inertia forces become important, and the coefficient b becomes complex.

The assumption of Poiseuille flow also breaks down when we exceed a certain transition frequency f_t which depends on the kinematic viscosity of the fluid and on the size of the pores. The transition frequency is defined by the relation

$$f_t = \pi v / 4d^2 \quad (2.17)$$

where $v = \mu/\rho_f$ is the kinetic viscosity, d is the pore diameter and ρ_f is the fluid density. For a porous material saturated by water at 15°C we find $f_t = 100$ Hz for $d = 10^{-4}$ m and $f_t = 10^4$ Hz for $d = 10^{-5}$ m.

Biot showed that all the results obtained from his treatment of the low frequency range are preserved in the theory of the high frequency waves, if we multiply the coefficient b in Darcy's law by a complex factor $F(k)$ which takes into account pore geometry and the medium sinuosity. We shall use this simplifying result, avoiding the complex theory which leads to it, and concentrate on reviewing Biot's results for the low-frequency range while keeping in mind that all the results are also applicable to the high frequency range under the modification suggested above.

If we accept the assumption of a Poiseuille flow, the microscopic flow pattern inside the pores is uniquely determined by the six generalized velocities \dot{u}_i , \dot{U}_i . Kinetic energy, again, depends only on \dot{u}_i and \dot{U}_i . Dissipation depends only on the relative motion between fluid and solid $(\dot{u}_i - \dot{U}_i)$.

To allow for the use of Lagrange's formalism we introduce the dissipation function concept. We may write this function in a homogeneous quadratic form with the six generalized velocities:

$$2D = b(\dot{u}_i - \dot{U}_i)(\dot{u}_i - \dot{U}_i) . \quad (2.18)$$

Note that the dissipation function D , vanishes when \dot{U}_i approaches \dot{u}_i .

Lagrange's equations with the dissipation function are now of the form

$$\frac{\partial}{\partial t} \left(\frac{\partial T}{\partial \dot{u}_i} \right) + \frac{\partial D}{\partial \dot{u}_i} = q_i \quad (2.19)$$

$$\frac{\partial}{\partial t} \left(\frac{\partial T}{\partial \dot{U}_i} \right) + \frac{\partial D}{\partial \dot{U}_i} = Q_i$$

Thus, upon substitution of D and T we have the six equations of motion:

$$\frac{\partial^2}{\partial t^2} (\rho_{11} u_i + \rho_{12} U_i) + b \frac{\partial}{\partial t} (u_i - U_i) = q_i \quad (2.20)$$

$$\frac{\partial^2}{\partial t^2} (\rho_{12} u_i + \rho_{22} U_i) - b \frac{\partial}{\partial t} (u_i - U_i) = Q_i$$

substituting, as before, $q_i = \tau_{ij,j}$ and $Q_i = S_{,i}$ and using Hooke's law to express the stresses in terms of the strains we have

$$N\bar{v}^2 \ddot{\bar{u}} + \bar{v} [(N+\lambda)e + Q\epsilon] = (\rho_{11} \ddot{\bar{u}} + \rho_{12} \ddot{\bar{U}}) + b(\dot{\bar{u}} - \dot{\bar{U}}) \quad (2.21)$$

$$\bar{v}(Qe + Re) = (\rho_{12} \ddot{\bar{u}} + \rho_{22} \ddot{\bar{U}}) - b(\dot{\bar{u}} - \dot{\bar{U}}) .$$

When the equation for the purely elastic case (Equation (2.15)), or the equation for motion with mechanical dissipation (Equation (2.19)) is solved for plane waves, it is found that there is one rotational wave and two dilatational waves propagating in the medium. The two dilatational waves correspond to fast and slow velocities of the symmetric and antisymmetric modes of particle displacement amplitudes. The additional wave velocity is to be expected on physical grounds, since coupled oscillation causes the single frequency of oscillation to split into two characteristic frequencies. For further discussion of this please refer to Appendix B.

An interesting result is the possible existence of a wave such that no relative motion occurs between the fluid and solid (i.e. $u_i = U_i$). This situation occurs if a certain "dynamic compatibility" relation is satisfied between the elastic and dynamic constants. In this case the wave oscillating in the symmetrical mode (i.e. the one with in-phase particle displacements), will propagate with a velocity of $V_1 = \sqrt{H/\rho}$. The wave with the antisymmetrical mode will propagate with a lower velocity V_2 . This is a case where dissipation due to fluid friction will disappear.

Biot found from the solution of Equations (2.21) that in the case of the rotational waves the phase velocity

increases slightly with frequency, f , while the absorption coefficient is proportional to the square of the frequency. In the limit of zero frequency, the rotational wave remains propagatory and approaches a reference velocity $V_r = \sqrt{N/\rho}$ which is the velocity when there is no relative shearing motion between fluid and solid. At the limit of zero frequency the rotational wave velocity is proportional to the square of the frequency. Note also that since shear motion involves no elastic coupling, Biot arrives at only one shear wave velocity, the same result as the one obtained for a single component homogeneous medium (subject, of course to modification by the inertial coupling coefficient ρ_{12}).

Biot's two dilatational waves were denoted as waves of the first and second kind. The waves of the second kind are highly attenuated and their propagation is closely analogous to heat conduction. The dispersion of the waves of the first kind was found to be practically negligible, with a phase velocity increasing or decreasing with frequency, depending on the mechanical parameters. The absorption coefficient of the waves of the first kind was found to be proportional to the square of the frequency just as for the rotational waves. As dynamic compatibility is approached dispersion and attenuation of the waves of the first kind

tend to vanish. The attenuation of this wave may therefore vary widely for materials of similar composition, and may be larger or smaller than the attenuation of the rotational waves.

In the zero frequency limit the wave of the first kind approaches a reference velocity V_c like f^2 . V_c is the velocity of a dilatational wave in the aggregate when $e = \epsilon$, i.e. when the dynamic compatibility relation is satisfied and there is no relative motion between the solid and the fluid. In this limit the wave of the second kind becomes diffusive and its phase velocity approaches zero like the square root of the frequency. In the quasistatic limit, when inertial terms are neglected, only the slow/diffusive wave (the wave of the second kind) survives.

Both rotational waves and the waves of the first kind exhibit a maximum value of attenuation per cycle when their frequencies approach the characteristic frequency f_c which depends on the kinematic viscosity of the fluid and the pore diameter. The characteristic frequency is introduced for convenience purposes and is defined by

$$f_c = \frac{b}{2\pi \rho_2} = \frac{b}{2\pi \rho (\gamma_{12} + \gamma_{22})} \quad (2.22)$$

where ρ is the mass density of the composite, $\gamma_{12} = \rho_{12}/\rho$

and $\gamma_{22} = \rho_{22}/\rho$ are the nondimensional dynamic coefficients and b was already defined for porous media. If, for example, we introduce the assumption that the pores behave like circular tubes of diameter d we may write $b = 32\mu\beta/d^2$ where d is the pore diameter. For this case it is found that f_c relates to the transition frequency f_t by $f_t/f_c = \frac{\pi^2}{64}$ and thus, if the assumption made on the shape of the pore is acceptable, we can approximate the transition frequency as $f_t \approx 0.154 f_c$. Note that the characteristic frequency depends only on the composite physical properties and thus, if these properties are known, the transition frequency for the above case can be predicted.

In the neighborhood of f_c the inertia and viscous terms are of the same order. As the frequency increases beyond f_c , a boundary layer develops where the velocities are out of phase. As the frequency becomes higher, this boundary layer becomes very thin. The viscous forces are then confined to this layer, and the microvelocity field in the major portion of the fluid is determined by potential flow and dominated by inertial terms. The friction force of the fluid on the solid becomes out of phase with the relative rate of flow and exhibits a frequency dependence which is represented by a complex quantity. In the very high frequency limit the behavior of the porous medium is as if

the fluid is completely free of viscosity. The phase velocities for this limit are the same as the phase velocities for the purely elastic case, i.e. they have a constant value which is determined by the elastic and dynamic coefficients of the material. In general we may say that the rotational wave and the wave of the first kind propagate mainly in the solid constituent of the medium but are modified by the fluid. The dilatational wave of the second kind propagates in the fluid but is modified by the presence of the solid phase.

All of the results mentioned above were summarized by Biot in a series of plots in his two papers on the low and high frequency ranges (Biot 1956). All plots were represented nondimensionally by referring to the characteristic frequency f_c . The characteristic frequency is thus seen to provide a natural frequency scale of the material, the nondimensional abscissa of the plots being the ratio f/f_c .

III. THE ELECTROKINETIC EFFECTS.

A. Historical Review

The phenomena referred to collectively as electrokinetic effects pertain to a liquid flow that occurs along a solid/liquid interface as a result of an applied potential gradient, and conversely to the potential developed when a liquid is made to flow past a solid surface. As early as 1808 it was noticed by Reuss (1809) that when a potential difference was maintained across a porous plug of wet clay or sand separating two portions of water, a flow of water occurred from one side of the plug to the other. This phenomenon, now known as electroosmosis, is almost always observed when an e.m.f. is applied to electrodes located on opposite sides of a porous diaphragm immersed in water or other ionic liquid. If the liquid flow is not restricted, it will continue as long as a potential difference is maintained; if the flow is restricted, a pressure will build up until it is sufficient to cause a back-flow through the diaphragm that exactly balances the electroosmotic flow. This pressure is known as "the electroosmotic pressure".

Quantitative measurements of electroosmotic flow were first made about 1850 by Wiedemann (1852), who found that equilibrium pressure is proportional to the applied voltage

and independent of dimensions of the diaphragm for a given system.

About ten years later, Quinke (1861) reasoned that because a porous object essentially consists of a mass of fine capillaries, electroosmosis should occur in a single capillary tube; this was indeed the case. Quinke was also the first to discover that when a liquid was forced to flow through a capillary tube or porous diaphragm, a potential difference was created; this is the converse of electroosmosis, and the e.m.f. developed is called "the streaming potential". Another discovery made by Quinke led to the first correct hypothesis as to the origin of the electrokinetic effects: He showed that the liquid flow in electroosmosis is not necessarily in the same direction as the current flow. These facts led to the hypothesis that the electrokinetic effects were caused by the presence of electrically charged layers of opposite sign at the solid liquid boundary. An applied voltage would therefore cause a relative displacement of the charged layers; the liquid, being free to move, thus flowed in a direction dependent on the sign of the charge it carried. This hypothesis also explained the streaming potential as a result of a charge displacement caused by the forced flow of liquid along the solid surface.

Another manifestation of the electrokinetic effect was investigated by Dorn (1880) who noted that when suspended particles are forced to move through a liquid in response to gravitation, a potential gradient is generated in the direction of movement. This phenomenon, variously called the Dorn effect, sedimentation potential, or migration potential, can also be qualitatively explained by the hypothesis mentioned above.

A theoretical treatment of the electric double layer dates from 1879 and the work of Helmholtz (1879), who suggested that formation of such a layer was of general occurrence at a phase boundary. He related mathematically the velocity of electroosmotic flow to charge separation in the double layer; the flow was shown to depend on an "electrokinetic potential" that corresponded to the potential drop across the layer of charge contained in the moving liquid.

At about that time it was also shown that certain colloid sols were rendered unstable and flocculated by the addition of electrolytes, and that multivalent ions had a disproportionate effect in this regard. In 1892 it was observed that colloidal particles migrate under the influence of an electric field. Determination of the sign of the particle charge from the direction of its movement

now made it clear that the flocculating effect of electrolytes was determined by the valency of the ions of opposite charge in the sol. This generalization is now called the Schulze-Hardy rule.

By the beginning of the twentieth century, results of the investigations described above, as well as other discoveries, had aroused great interest in electrokinetic phenomena, for these methods seemed to provide a way of investigating the structure and properties of the electric double layer. Stability of colloidal sols could now be qualitatively explained in terms of a coulombic repulsion, but the origin of the surface charge and its quantitative relation to the concentration and valency of dissolved ions were yet to be explained before the problem of stability could be completely resolved.

Since the initial theoretical work of Helmholtz, interpretation of electrokinetic effects in terms of the double layer structure has received more detailed consideration from many investigators; but a rigorously quantitative treatment has yet to be developed. Note, however, that useful approximations have been derived and used as the basic factors are known.

If a sample of solid is in contact with an electrolytic solution, the solid, according to the double layer

hypothesis, will acquire a certain charge density localized in the plane of its surface, thus creating a difference in electric potential between the surface and the bulk solution. Because the system as a whole is electrically neutral, the surface charge must be exactly balanced by an opposite excess charge in the liquid phase. Coulombic attraction causes the counterions to concentrate in the vicinity of the solid surface, while ions of similar charge are repelled. If no other forces were operating, the potential drop across the double layer from the solid surface through the layer of counterions would be sharp. However, the ions in solution are subject to diffusional forces arising from the thermal agitation of the molecules constituting the liquid; thus the abrupt concentration gradient that would otherwise exist is dissipated to some extent. The model of the double layer therefore involves an immobile surface-charge layer and a diffuse layer of counterions distributed in the adjacent solution according to some equilibrium density function. This results in a gradient decrease in potential with increasing distance from the surface (see Figure 3.1).

A theoretical treatment of the structure of the double layer relating the distribution of the dissolved ions and the potential gradient near the surface to the composition

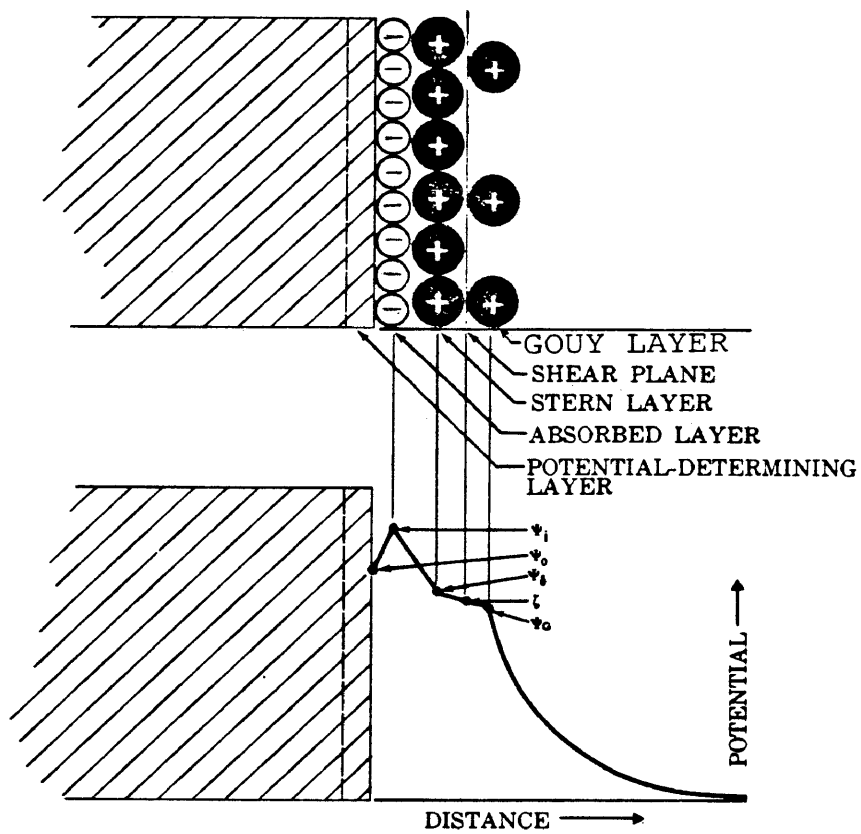


Figure 3.1 Double Layer Structure and the Electrochemical Potential Profile Near a Solid-Liquid Interface.

of the liquid phase was first performed by Gouy (1910), and independently by Chapman (1913). The Gouy-Chapman model was erroneous in that it considered the ions making up the diffuse layer as point charges. Stern (1924) recognized that the error caused by neglecting the finite size of the ions, was important only in the immediate vicinity of the surface; in fact, the first layer of ions at the surface is usually sufficient to decrease the potential to a value low enough so that the Gouy-Chapman model becomes reasonable. Stern proposed that the counterions could be considered as divided between a diffuse layer of point charges and an immobile surface layer of a definite thickness able to contain a certain maximum number of counterions per square centimeter. The Stern model, while still a crude picture of what we may imagine to be a complex situation, does display most of the properties of the double layer that have been inferred from experimental observations of the double layer capacity. A further modification to these models proposed by Grahame (1947) need not be introduced here. Some of the more recent papers will be brought up in the course of the following discussion.

In order to be able to predict the range of minerals to which our research is applicable, we must consider the various mechanisms responsible for the generation of net

electric charge at the solid surface. We can recognize three such mechanisms:

(a) the crystal lattice of the solid may contain a net positive or negative charge arising from interior defects or lattice substitutions. The net charge is therefore compensated by an equivalent ionic charge at the surface. In contact with water, the compensating ions dissociate to form the counterions of the double layer. This type of double layer formation is important in describing the behavior of certain ion exchanging minerals, such as zeolite and some clay minerals. Solids that contain ionizable groups at their surface may also be considered as belonging to this class, which is characterized by a surface charge density that is a fixed quantity independent of the concentration of ions in the surrounding liquid.

(b) In the case of soluble ionic solids dispersed in water, an equilibrium exists between the ions making up the surface of the crystal and these same constituent ions in the solution, where their concentrations are determined by the solubility product for the material. The potential of the solid will thus be fully

determined by a thermodynamic (adsorption) equilibrium. The potential determining ions for a given solid are usually apparent from its chemical composition. For most metallic oxides and hydroxides, H^+ and OH^- ions are potential determining. Solids of this class are characterized by having the potential at the solid surface fixed by the concentration of potential-determining ions and independent of the presence of other indifferent electrolytes; (the surface charge, however, is sensitive to the addition of indifferent electrolyte).

(c) The third mechanism by which the surface charge may originate or be affected is the adsorption of specific ions from the solution. Specific ions may be strongly adsorbed by formation of a surface complex or compound - for example, the formation of the polyphosphate anion complex with aluminum sites on the kaoline surface. Adsorption may also be aided by hydrogen bond formation or by London dispersion (Van der Waals) forces, particularly in the case of large molecules or ions. The adsorption mechanism is seldom responsible for the entire surface charge or potential of a solid surface (except for potential-determining

ions); it is frequently a complicating factor in the other mechanisms considered above.

B. Theory of Electrokinetic Effects.

1. Electroosmotic Flow.

To account for the different electrokinetic effects, it is only necessary to assume that the diffuse region of the double layer (the Gouy layer) is at least in part mobile -- i.e. free to move with the liquid phase. We can thus say that a shear plane may exist in the diffuse double layer at some unknown distance from the solid surface (Figure 3.1). Because of the electric charge on the solid surface there will be a difference in potential between this shear plane and the bulk of the fluid. This potential is called the electrokinetic potential or Zeta (ζ) potential. When an external electric field is applied tangentially to a fixed surface, the mobile portion of the diffuse double layer will flow because of the forces acting on the excess ionic charge contained within it. A constant flow rate will be reached when the force exerted by the external field on the counterions (and hence on the liquid as a whole) is exactly balanced by the frictional forces arising from the viscosity of the fluid. We shall now show, following Kruyt (1952, page 198), that a quantitative relation between the

electroosmotic velocity of flow, the double layer (zeta) potential at the shear plane, and the applied external field may be derived without further consideration of the double layer structure.

Consider the longitudinal cross section of a circular tube shown in Figure 3.2. The electric force per unit area exerted on a volume element of thickness dx under the influence of an external electric field E is

$$F_e = E\rho dx \quad (3.1)$$

where $\rho(x)$ is the charge density of the fluid at a point x .

The viscous force depends on the viscosity μ and on the velocity gradient at the specific field point. The net viscous force per unit area on our volume element is thus:

$$F_v = \lim_{\Delta x \rightarrow 0} \left\{ \mu \left[\left(\frac{dv}{dx} \right)_{x+dx} - \left(\frac{dv}{dx} \right)_x \right] \frac{\Delta x}{\Delta x} \right\} = \mu \frac{d^2v}{dx^2} dx \quad (3.2)$$

At steady state the friction force will just balance the electric force so that no acceleration occurs, thus setting $F_e = F_v$ we have

$$E\rho dx = \mu \frac{d^2v}{dx^2} dx \quad (3.3)$$

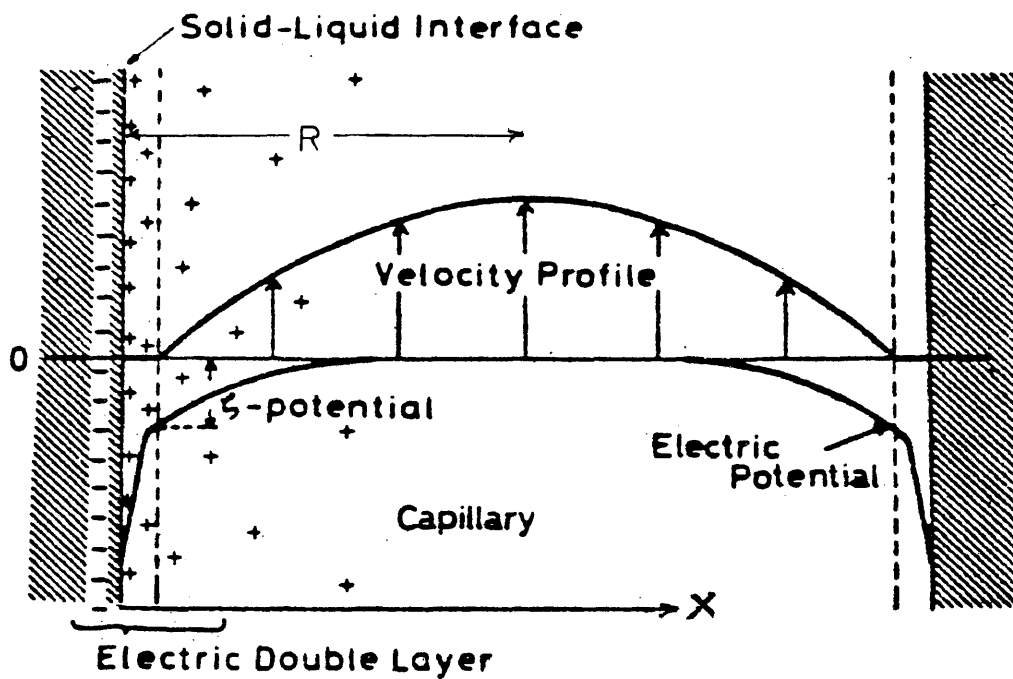


Figure 3.2. Schematic Diagram of Electric Double Layer and Velocity Profile in a Capillary.

Now, if $\phi(x)$ is the electric double layer potential a distance x from the wall, Poisson equation must be satisfied by the double layer. Thus

$$\nabla^2 \phi = - \frac{4\pi}{\epsilon} \rho \quad (3.4)$$

where ϵ is the dielectric constant of the liquid assumed to be constant throughout the liquid phase.

From (3.4) we can find $\rho = - \frac{\epsilon}{4\pi} \frac{d^2\phi}{dx^2}$. Substituting this in (3.3) and integrating yield:

$$- \frac{\epsilon E}{4\pi} \frac{d\phi}{dx} = \mu \frac{dv}{dx} + C \quad (3.5)$$

where C is a constant of integration.

Applying the boundary conditions

$$\frac{dv}{dx}_{x \rightarrow R} = 0 \quad (3.6a)$$

(i.e. the velocity reaches a maximum at the center of the capillary) and

$$\frac{d\phi}{dx}_{x \rightarrow R} = 0 \quad (3.6b)$$

(i.e. as we approach the center of the capillary the

electric field due to the charged wall is completely screened by the counterions of the diffuse layer.)

Substituting (3.6 a and b) in (3.5) implies that $C=0$. Integrating (3.6) once more gives

$$-\frac{\epsilon E}{4\pi} \psi = \mu v + C' . \quad (3.7)$$

Again, considering the boundary conditions we have at $x \rightarrow R$: (i) $\psi = 0$; (ii) $v \rightarrow v_e$ (where v_e is the electroosmosis velocity, the velocity of the liquid in the center of the capillary) and at $x = 0$ (i.e. at the shear plane): $v_{x=0} = 0$ and $\psi_{x=0} = \zeta$ (by definition of the zeta potential), and substituting these boundary conditions in (3.8) we conclude $C' = -\mu v_e = -\frac{\epsilon E}{4\pi} \zeta$ and we obtain the classical expression

$$v_e = \frac{\epsilon \zeta E}{4\pi \mu} \quad (3.8)$$

If we approximate the average flow velocity by v_e then v_e is also the flow rate of the liquid per unit area, or liquid current density. Denoting this quantity by \bar{J}_f and if the external electric field can be expressed as a gradient of an electromotive force ϕ (e.m.f.) then (3.8) becomes

$$\bar{J}_f = \frac{\epsilon \zeta}{\mu} \bar{\nabla} \phi . \quad (3.9)$$

We now have two mechanisms that can generate fluid flow, one is the mechanical pressure discussed earlier in this thesis and is expressed mathematically by Darcy's law $\bar{J}_f = \frac{k}{\mu} \bar{\nabla}P$, the other, as shown above is an external electric field expressed mathematically by Equation (3.9). The direction of the electroosmotic flow depends on the charge of the diffuse part of the double layer. In moderately pure water most solids acquire a negative charge so that flow of the water is generally towards the cathode.

2. Electroosmotic Pressure

When the electroosmotic effect is measured in terms of the counterpressure required to obtain zero rate of flow through the capillary or porous plug for a given applied field, the zeta potential may be calculated by realizing that the electroosmotic pressure P_e must cause a reverse flow of liquid in the capillary or porous plug exactly equal to the volume transported by electroosmosis. If we assume a capillary of uniform circular cross section, the backflow is given by Poiseuille's equation

$$V_e = \pi P_e r^4 / 8\mu l \quad (3.10)$$

where $V_e = Av_e$ is the volume flow rate ($A = \pi r^2$ is the capillary cross-sectional area) and r and l are the capillary radius and length respectively.

Multiplying Equation (3.8) by $A = \pi r^2$ and equating (3.8) and (3.10) we obtain after some rearranging

$$P_e = \frac{2\varepsilon\zeta(lE)}{\pi r^2} \quad . \quad (3.11)$$

The product El corresponds to the total applied potential. The expression derived above for the electroosmotic pressure states that it will be proportional to the applied voltage. When the generalization is made to the case of a porous plug, can be shown that this pressure is also independent of the plug dimensions and is proportional only to the applied voltage.

3. Streaming Potential.

The streaming potential E_s is just the reverse of the electroosmosis; it is the voltage developed between the ends of a capillary tube or a porous diaphragm through which liquid is forced to flow by an applied pressure difference P . An expression relating E_s to P and the zeta potential may be derived rather easily for laminar flow through a circular capillary of uniform diameter if we realize that at

steady state (i.e. $dE_s/dt = 0$) the charge transported by the moving double layer per unit time will be balanced by the current conducted through the fluid (assuming a relatively nonconducting solid) due to the influence of the streaming potential. According to Ohm's law the conductance electric current in response to the streaming potential is

$$E_s = \frac{i\lambda}{g\pi r^2} \quad (3.12)$$

where r is the capillary radius; λ , its length; g , specific conductance of the fluid; and i , the electric current.

Velocity of flow in the fluid varies from zero at the shear plane to a maximum value at the capillary axis. The liquid velocity at a distance x from the shear plane (Figure 3.3) is

$$v(x) = P (2rx - x^2)/4\mu\lambda \quad (3.13)$$

the volume of liquid with a velocity $v(x)$ is

$$dV = 2\pi(r-x) v(x) dx = \frac{2\pi P}{4\mu\lambda} (2rx - x^2)(r-x) dx \quad (3.14)$$

thus the rate of mechanical charge transport i_t will be

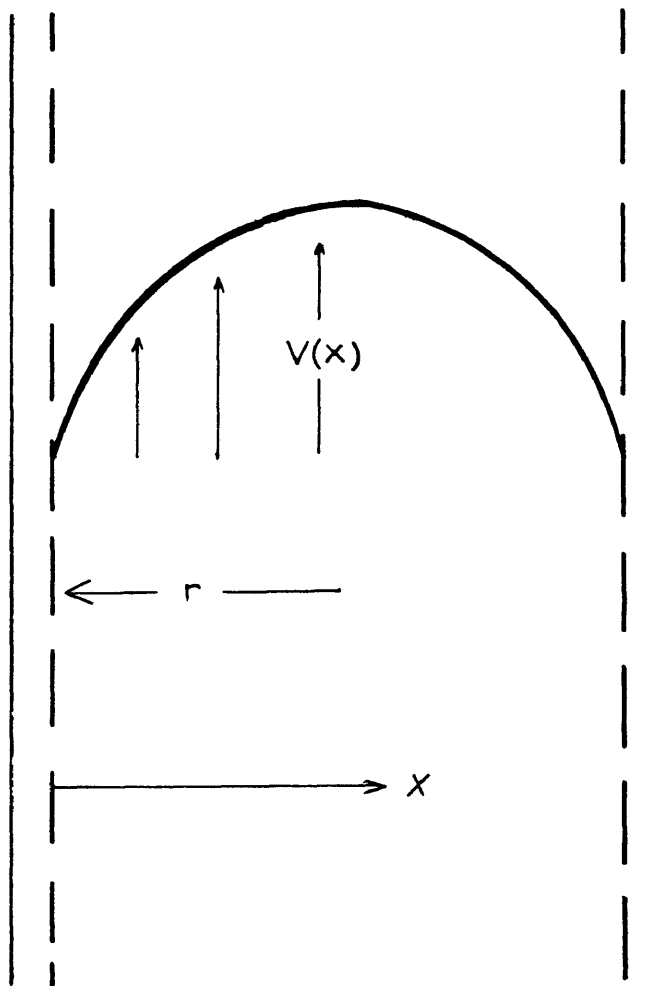


Figure 3.3. Velocity Profile and Capillarie Dimensions for Streaming Potentials Calculations.

$$i_t = \int_0^r \rho dV . \quad (3.15)$$

Substituting Poisson's Equation (3.4) and Equation (3.14) into (3.15) and assuming that x is negligible with respect to r , we obtain

$$i_t = \frac{P\epsilon r^2}{4\mu\lambda} \int_0^r x \frac{d^2\psi}{dx^2} dx . \quad (3.16)$$

If Equation (3.16) is solved by partial integration and if boundary conditions are applied such that at $x = 0$, $\psi = \zeta$; and at $x = r$, $\psi = 0$ and $\frac{d\psi}{dx} = 0$, then

$$i_t = \frac{P\epsilon r^2 \zeta}{4\mu\lambda} . \quad (3.16')$$

Under the assumption of steady state conditions $i = i_t$ and we can equate (3.16') and (3.12) and rearrange terms to obtain the final expression for the streaming potential

$$E_s = \frac{\epsilon \zeta P}{4\pi \mu g}$$

or (if we set $E_s = \phi$) (3.17)

$$\nabla \phi = \frac{\epsilon \zeta \nabla P}{4\pi \mu g} .$$

A more general derivation of Equation (3.17) shows that it is also applicable to the porous plug (Kruyt 1952, page 204).

4. Electrophoresis.

The phenomenon of electrophoresis occurs when the solid is not fixed in position as part of a diaphragm, but is free to move, while the suspending liquid as a whole is stationary. Just as in the case of electroosmotic flow, forces acting on the double layer as a result of an applied potential gradient produce a relative movement; thus the electrophoretic velocity is given by the same expression.

$$\bar{v}_e = \frac{\epsilon \zeta \bar{E}}{4\pi\mu} \quad . \quad (3.18)$$

As was the case with electroosmosis, shape and size of the particles have no effect on the resulting velocity.

C. Thermodynamical Considerations.

Since the electrokinetic phenomena are irreversible the thermodynamics of irreversible processes can be applied as was done by Overbeek and Mazur (1953). The most general linear relations between the "fluxes" (i.e. the electric current density \bar{J}_e and the fluid flow density \bar{J}_f) and the

generalized "forces" (i.e. $\bar{v}P$ and $\bar{v}\phi$) were found to be expressible in the form

$$- \bar{J}_e = L_{11} \bar{v}\phi + L_{12} \bar{v}P \quad (3.19a)$$

$$- \bar{J}_f = L_{21} \bar{v}\phi + L_{22} \bar{v}P \quad . \quad (3.19b)$$

The coefficients L_{ij} are called kinetic coefficients and are functions of the local intensive parameters only (e.g. pore diameter, fluid conductivity, viscosity, etc.). They result from an expansion of the "fluxes" J 's in power series of the affinities (i.e. the "forces" $\bar{v}P$ and $\bar{v}\phi$).

The first term on the right hand side of 3.19a is simply the familiar Ohm's law. The second term on the right hand side of 3.19b represents Darcy's law which was discussed before. The terms with the coefficients L_{12} and L_{21} correspond to the electrokinetic phenomena and the coupling of mechanical and electrical effects.

Onsager's theorem of irreversible thermodynamics states that $L_{ij} = L_{ji}$ and therefore, in our case, $L_{12} = L_{21}$. We can now obtain explicit expressions of the different L_{ij} coefficients from Ohm's law, Darcy's law and the expressions for the electrokinetic effects developed above. We thus write, for a capillary tube:

$$L_{11} = g$$

where g is the electrical conductivity,

$$L_{22} = k/\mu$$

where k is the specific permeability,

$$L_{12} = L_{21} = - \epsilon \zeta/\mu .$$

where ϵ is the dielectric constant of the fluid, ζ is the zeta potential and μ is the viscosity.

Overbeek (1946, 1953), using some rather simple mathematical manipulation, has shown that the results obtained for a single capillary tube can be extended to a porous plug consisting of capillaries in series or in parallel. For simplicity we shall consider a straight capillaric model where the porous medium is supposed to be composite of a bundle of straight capillaries entering the porous medium on one face and emerging on the opposite face (Scheidegger, 1974). Although real structure of the porous medium is not as simplistic as represented by the straight capillaric

model, it is often sufficient for first order approximation. According to the capillarity model the bulk permeability of the porous plug K is given by $K = \beta k$ where β is the porosity of the porous plug. The basic equations describing the net fluid flow flux through the entire plug \bar{J}_f and the electric current density through the plug \bar{J}_e are thus

$$- \bar{J}_e = \beta g \bar{\nabla} \phi - \beta \epsilon \zeta \frac{1}{\mu} \bar{\nabla} P \quad (3.20a)$$

$$- \bar{J}_f = - \frac{\beta \epsilon \zeta}{\mu} \bar{\nabla} \phi + \frac{k}{\mu} \bar{\nabla} P \quad (3.20b)$$

Again, it is assumed that the electrical conductivity of the matrix substance is much much smaller than the conductivity βg due to the liquid phase.

The equations above are the fundamental equations for the electrokinetic phenomena in the case of a steady state flow and include all the different aspects of these phenomena. Equations (3.20) a and b will thus constitute an important check as to the validity of our theory since our general equations of motion must yield these expressions in the steady state limit.

IV. EXTENSION OF BIOT'S THEORY

A. General Considerations.

In chapter (II) we showed that Biot arrived at a set of six equations of motion for the six generalized coordinates U_i and u_i . Biot's equations contain three inertial terms on one hand, four elastic and one frictional force on the other. In order to extend this theory to include electrokinetic effects associated with the mechanical system we need an additional force in Biot's equations of motion, namely the electrical force on the solid and liquid components due to an electric potential gradient. The electric force per unit volume on either the solid or liquid phase will thus be of the form,

$$F_e^f(x_i) = \sigma_f(x_i) \phi(x_i),_i \quad (4.1)$$

and

$$F_e^s(x_i) = \sigma_s(x_i) \phi(x_i),_i$$

where $\sigma_f(x_i)$ and $\sigma_s(x_i)$ are the local charge densities at the field points x_i and $\phi(x_i)$ is the electric potential at the same field point.

Including the electric force in the equations of motion introduces two new quantities: the local charge density σ_e and the electric potential ϕ . By means similar to those introduced in Chapter III we hope to be able to express the electric charge densities σ_e in terms of the electrokinetic parameters, i.e. the dielectric constant ϵ and the zeta potential ζ ; however, the electric potential ϕ introduces a new seventh unknown into our six equations of motion. It is clear from the mathematical situation that a seventh equation is needed. Physical considerations, provided we neglect electromagnetic effects, will naturally lead us to an electrical field equation of the form of Poisson's equation modified by electromechanical coupling terms due to the electrokinetic phenomena.

B. The Modified Field Equations.

Based on the general considerations expressed above, I propose the following seven equations as our new set of field equations:

$$\begin{aligned} \rho_{11} \ddot{u}_i + \rho_{12} \ddot{U}_i - N u_{i,jj} - (A+N) (u_{n,n})_{,i} - Q (u_{k,k})_{,i} \\ + b (\dot{u}_i - \dot{U}_i) + \beta \sigma_s \phi_{,i} = 0 \end{aligned} \quad (4.2a)$$

$$\begin{aligned} \rho_{22} \ddot{U}_i + \rho_{12} \ddot{u}_i - (R U_{n,n} + Q u_{k,k})_{,i} - b (\dot{u}_i - \dot{U}_i) \\ + \beta \sigma_f \phi_{,i} = 0 \end{aligned} \quad (4.2b)$$

$$\begin{aligned} \beta \sigma_n - \epsilon \phi_{,ii} - \int [\beta g \phi_{,ii} + \beta (\dot{U}_i \sigma_f + \dot{u}_i \sigma_s)_{,i}] dt \\ = 0 \end{aligned} \quad (4.2c)$$

where ρ_{11} , ρ_{22} and ρ_{12} are the mass coefficients discussed extensively in Chapter II; A , N , Q and R are the elastic coefficients, b is the drag coefficient in Darcy's law, and β the porosity. All have been also introduced in the course of the discussion of Chapter II. The new parameters are: σ_s , which is charge per unit volume of the pores in the solid phase; σ_f which is the charge per unit volume of the pores in the liquid phase; $\sigma_n = \sigma_s + \sigma_f$ is the net charge per unit volume of the pores; ϵ and g are the dielectric constant and electric conductivity, respectively.

Let us assume that the seven equations (4.2) are the fundamental field equations which describe the electro-mechanical behavior of the liquid-solid composite under the conditions specified earlier. Under conditions of zero acceleration, $\ddot{u}_i = \ddot{U}_i = 0$, they should yield the familiar steady-state flow equations of electrokinetic phenomena and the equations of state of elastostatic. I will prove that this is indeed the case in the next chapter. Meanwhile, let us reintroduce Lagrange's formalism and derive Equations (4.2) from this point of view. Following this approach will also help us realize the physical meaning of each term.

C. Lagrange's Formalism

Lagrange's formalism approach for a continuous media requires that we will form the Lagrangian density function L . This function is the difference between the kinetic energy density of the system T and its potential energy density w , i.e. $L = T - w$. When the Lagrangian density function is substituted into Lagrange's equations, they must yield the desired field equations. Non-conservative effects can be introduced into Lagrange's equations by using the concept of the dissipation function D (as was done by Biot for the case of mechanical dissipation).

To form these two functions let us find the energy densities discussed above. The kinetic energy density of the system was already introduced by Biot. It is given by

$$T = \frac{1}{2} \rho_{11} u_i^2 + \frac{1}{2} \rho_{22} \dot{U}_i^2 + \rho_{12} \dot{U}_i \dot{u}_i . \quad (4.4)$$

The potential energy density is due to both elastic and electric conservative forces. It is thus given by

$$w = \left(\frac{1}{2} A \delta_{ij} \delta_{kl} + N \delta_{ik} \delta_{jl} \right) e_{ij} e_{kl} + \frac{1}{2} R (U_{i,i})^2 \\ + Q(u_{i,i}) (U_{j,j}) + \beta \sigma_n \phi + \frac{1}{2} \epsilon (\phi_{,i})^2 \quad (4.5)$$

as before $e_{ij} = \frac{1}{2} (u_{i,j} + u_{j,i})$ is the elastic strain.

The first term on the right hand side is due to elastic forces in the solid, the second term is due to elastic forces in the liquid, the third is a result of the solid-liquid interaction, the fourth is the potential energy density of an electric charge density in an electric field, while the last term is simply the electric field self energy density.

Before substituting Equation (4.3) in Lagrange's equation, we must find the dissipation function and the appropriate operator which can be introduced into Lagrange's

equation in such a manner that dissipative forces will also result. The correct dissipation function which will yield the desired non-conservative forces was found to be

$$D = \frac{1}{2} b (\dot{u}_i - \dot{U}_i)^2 + \frac{1}{2} \beta g(\phi_{,i})^2 + \beta (\sigma_s \dot{u}_i - \sigma_f \dot{U}_i) \phi_{,i}. \quad (4.6)$$

The first term is just Biot's dissipation function for the case where only mechanical friction was considered; the second term is the power per unit volume lost due to Joule heating dissipation; the term $(\sigma_s \dot{u}_i - \sigma_f \dot{U}_i)$ represents the convective electric current density, thus the third term corresponds to power per unit volume due to electromechanical coupling.

Let us introduce Lagrange's equations with the dissipative function in the form

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{\eta}} + \frac{\partial}{\partial x_j} \frac{\partial L}{\partial \eta_{,j}} - \frac{\partial L}{\partial \eta} + \left[\frac{\partial}{\partial \dot{\eta}} + \int \frac{d}{dx_j} \frac{\partial}{\partial \eta_{,j}} dt \right] D = 0 \quad (4.7)$$

where η is a generalized coordinate (u_i , U_i or ϕ) and the operator in the bracket operates on the dissipation function D . When the functions L and D are substituted into Equation (4.7), we obtain Equation (4.2.a) for the choice $\eta = u_i$,

Equation (4.2.b) when our generalized coordinate is $\eta = U_i$, and Equation (4.2.c) for $\eta = \phi$.

It is now easier to see the physical meaning of each term in Equations (4.2): In Equations (4.2.a) and (4.2.b), in addition to the already familiar inertia, elastic and friction forces, we have a new electric force due to the action of the existing electric field on the solid and liquid charge densities, respectively. In Equation (4.2.c) which can also be written as

$$\beta \sigma_{\eta} - \epsilon \phi_{,ii} - \int \beta [g \phi_{,ii} - (\sigma_s \dot{u}_i - \sigma_f \dot{U}_i)_{,i}] dt = 0 . \quad (4.2.c)$$

The first two terms alone will simply yield Poisson field equation for the porous medium; the time integral provides a modification to the charge density term due to charges transported by conductive and convective currents, which are given by the first and second integrals, respectively. It can also be seen that if we take the time derivative of Equation (4.2.c) we will arrive at the equation for continuity of charge.

$$\frac{d\sigma_{\eta}}{dt} = -\bar{\nabla} \cdot \bar{J} \quad (4.8)$$

where

$$\bar{J} = \frac{\partial D}{\partial t} + \beta g E + \beta \sigma (\sigma_s \dot{u}_i - \sigma_f \dot{U}_i) \quad (4.9)$$

is the total current density, which is the sum of conduction, convection and displacement current densities.

We must note here that the expression for total current density, Equation (4.9), should actually include the contribution of polarization currents in order to be complete. However, the effect of polarization current will be neglected at this point since it introduces non-linearity into our third differential equation, Equation (4.2c). We must bear in mind however, that neglecting polarization effects must introduce a limitation on the applicability of Equation (4.2c). We must consider materials with low polarization or with small divergence of the polarization and velocity fields. In a complete treatment of all electrical effects, the polarization current must also be accounted for. Only after careful consideration of the validity of the assumptions made with regard to material polarization properties may we continue to use Equation (4.2c) in its present form. (Please refer to Appendix A for a more detailed treatment of the polarization current problem.)

D. Earlier Theoretical Treatments.

It is interesting at this point to compare earlier treatment of the mechanics of elastic wave propagation in fluid-saturated porous media, and the electrokinetic phenomena associated with it, to Biot's equations of motion and the extension of Biot's theory proposed in this thesis.

As was mentioned in the introduction, such an early theoretical treatment was offered by J. Frenkel (1944) and consisted of a derivation of the equation of motion for the liquid-solid composite, detailed solution of these equations for the case of plane wave propagation and lastly, application of some of the results of electrokinetic theory (as in Chapter III of this thesis) to the expressions arrived at for solid and fluid dilatations.

Frenkel's two equations of motion for the solid and fluid phases are respectively, (using the present notation)

$$(\rho_{11} + \rho_{12}) \ddot{u} = (A+N)(u_{n,n})_{,i} + N u_{i,jj} + b (\dot{U}_i - \dot{u}_i) \quad (4.10a)$$

and

$$(\rho_{22} + \rho_{12}) \ddot{U} = \beta R (U_{n,n})_{,i} - b (\dot{U} - \dot{u}_i). \quad (4.10b)$$

A comparison of Frenkel's Equations (4.10a) and (4.10b) with Biot's Equations (4.2a) and (4.2b) reveals the limitations

of Frenkel treatment of the mechanical aspect of the theory:

In Equation (4.10a), for the solid phase, the dynamic coupling coefficient ρ_{12} is multiplied by the solid acceleration. This is incorrect since, as we have seen in the discussion of Chapter II, the force $\rho_{12} \ddot{U}$ is an inertial coupling force which arises from the coupling term in the expression for the kinetic energy—Equation 2.7. This force is exerted on the solid due to fluid acceleration and thus must represent fluid acceleration. Only in the special case of no relative motion ($u_i = U_i$) does Frenkel's equation hold true and coincide with our Equation (2.8'a). Note that the same criticism holds true for Frenkel's Equation (4.10b). In addition, Frenkel did not introduce the effect of the fluid elastic strain on the solid phase using the coupling elastic coefficient Q , i.e. the force term $Q(u_{k,k})_{,i}$ is completely ignored. The coupled elastic force $Q(u_{k,k})_{,i}$ is also neglected in Equation (4.10b). As we have seen from Equation (2.6), Q is a coupling coefficient between elastic strains of the solid and the fluid phases. Indeed, if we somehow set the hydrostatic pressure equal to zero, we get from relation (2.6) $U_{i,i} = -Q/R u_{i,i}$ from which the importance of this term in either equation of motion is evident.

In addition to the incompleteness of the fundamental equation of motion let us only note that Frenkel's treatment

of electrokinetic effects associated with the elastic waves is also deficient in two major areas:

1. It introduces these electrokinetic effects after the mechanical problem has been solved and thus does not allow for electrical feedback on the mechanical system. In addition Frenkel gives no equation analogous to (4.2.c) which is an electric field equation modified by the mechanical system.
2. The electrokinetic relations which are being used result from derivation under the assumption of steady state flows as was shown in Chapter III. These results are not correct for time varying conditions and can be used with confidence only in steady state cases (i.e. when $\dot{J} = \dot{\phi} = \dot{\sigma}_e = \ddot{u}_i = \ddot{U}_i = 0$).

The last two points apply also to two more recent treatments offered by Mizutani et al. (1976) and Chandler (1981). Mizutani applied the steady state relations (3.20) to problems of diffusive water flow into the dilatant zone preceding and following earthquake occurrences. He then used the assumption of zero electric field or, alternatively,

infinite water resistivity such that no backflow of conduction current can occur, to predict the order of magnitude of the induced magnetic field resulting from this mechanical charge transport. While this may give us an idea about the possibility that magnetic field fluctuations prior to earthquake occurrence will result from electroosmosis, it is also clear that such approximations can be in considerable error and that inclusion of Maxwell's equations are required for an exact solution.

Chandler (1981) applied Biot's acoustic wave propagation theory to the quasistatic limit and coupled to it electrokinetic streaming potentials using relation (3.17). Biot's equations of motion in this zero frequency limit, together with the expression for the steady state-laminar flow derivation of the streaming potential on pressure gradient, enabled Chandler to predict the electric potential space-time dependence for various samples of porous plugs in laboratory experiments. His predictions were shown to be in excellent agreement with actual laboratory measurements. I would like, nonetheless, to offer here the same criticism suggested in this section earlier, namely that one must account for the electrical feedback on the mechanical system through the introduction of electrical forces into Biot's equations of motion before a solution is

found. The fact that excellent predictions were obtained by Chandler in spite of his failure to consider electrical forces on the medium component, may be attributed to the smallness of the time constant ϵ/g for water ($g \approx 10^{-3} - 10^2 \frac{\text{mho}}{\text{m}}$), the liquid used in Chandler's experiments. As a result, the streaming potential and the electric forces on the liquid-solid composite were rather small and could not play a significant role in the equations of motion. However, if the liquid involved is highly resistive (e.g. petroleum with $g = 10^{-5}$ to 10^{-16} mho/m), one can clearly see from (3.17) that the electric forces due to streaming potential will increase by several orders of magnitude and its effect on mechanical motion must be considered.

V. STEADY STATE RESULTS

The field Equations (4.2a,b,c) should yield, under steady state conditions, the familiar electrokinetic Equations (3.20a) and (3.20b) as well as the elastostatic equilibrium equation. By steady state conditions we mean zero acceleration and time independence of the electric charge density, the electric potential and the electric current density, i.e. $\ddot{u}_i = \ddot{U}_i = 0$ and $\dot{\phi} = \dot{\sigma}_f = \dot{\sigma}_s = \dot{J}_f = \dot{J}_e = 0$.

A. The Elastostatic Equation.

Under the assumption of steady state conditions and if we take, for simplicity, the solid velocity to be zero (i.e. $\dot{u}_i = 0$), Equation (4.2a) becomes

$$\begin{aligned} Nu_{i,jj} + (A+N)(u_{n,n})_{,i} + Q(U_{k,k})_{,i} \\ = -b\dot{U}_i + \beta\sigma_s \phi_{,i} \end{aligned} \tag{5.1}$$

This equation says that the sum of the forces acting on the solid phase is zero; i.e. the elastic forces (due to either solid or liquid stresses), equals the friction forces (due to liquid flow) plus the electric forces. If we assume no

fluid flow and no electric potential gradient we arrive at the desired elastostatic equation modified by Biot fluid-solid coupling

$$\tau_{ij,j} = Nu_{i,jj} + (A+N)(u_{n,n})_{,i} + Q(U_{k,k})_{,i} = 0. \quad (5.1')$$

B. Generalized Darcy's Law

Equation (4.2.b) is the equation of motion for the liquid component under the steady-state conditions assumption. If we still take $\dot{u}_i = 0$ for simplicity, (4.2b) is reduced to

$$(RU_{n,n} + Qu_{k,k})_{,i} - b\dot{U}_i - \beta\sigma_f \phi_{,i} = 0 \quad (5.2)$$

However, from Chapter II

$$S = RU_{n,n} + Qu_{k,k} = -\beta P \quad (2.6)$$

where P is the hydrostatic pressure in the liquid. Thus (5.2) can be written as

$$-\beta P_{,i} - \beta\sigma_f \phi_{,i} = b\dot{U}_i \quad (5.3)$$

Let us look at the electric force term $\beta\sigma_f \phi_{,i}$ first: σ_f is

the liquid electric charge per unit volume of the composite. Under steady-state conditions the total charge density of the composite is zero and thus $\sigma_f = -\sigma_s$ where σ_s is the solid charge per unit volume of the composite. However the origin of σ_s is the surface charge density of the capillary wall, σ . If we assume the cylindrical tube model for our capillaries, then

$$\sigma_s = \beta \frac{\sigma 2\pi r \ell}{\pi r^2 \ell} = \frac{2\sigma}{r} \beta \quad (5.4)$$

where r is the radius of a single capillary, ℓ is its length and β , the porosity, is now also the ratio of capillaric volume to composite volume. For the steady state case the double layer formation approximates a parallel plate capacitor (a model often used in the literature). We can therefore approximate the electric field of the double layer by $E = \frac{2\pi}{\epsilon} \sigma$ (I have used Gaussian units, since these are the units in which Equations (3.20) are expressed in the literature). Also, using the zeta potential and the capillaric radius r , we can write $E = \zeta/r$, and arrive at an approximation for the solid surface charge density

$$\sigma = \frac{\epsilon \zeta}{2\pi r} \cdot \quad (5.5)$$

Substituting this in (5.4) we have

$$\sigma_f = -\sigma_s = -\frac{\beta \epsilon \zeta}{\pi r^2} = -\frac{\beta \epsilon \zeta}{k} . \quad (5.6)$$

Considering now the two other terms of Equation (5.3), we can write

$$\beta \dot{U}_i = J_i^f \quad (5.7)$$

where J_i^f is fluid volume per unit time per composite cross-sectional area.

If we substitute (5.6), (5.7) and $b = \mu \frac{\beta}{k}$ into Equation (5.3) we get

$$-\beta P_{,i} + \frac{\beta \epsilon \zeta \phi_{,i}}{k} = \frac{\mu \beta}{k} \frac{J_i^f}{\beta} \quad (5.8)$$

or, upon rearranging and since the permeability for our capillaric model is $K = \beta k = \beta \pi r^2$, we arrive at the equation

$$-J_i^f = -\beta \frac{\epsilon \zeta}{\mu} \phi_{,i} + \frac{K}{\mu} P_{,i} \quad (5.9)$$

which is identical to Equation (3.20b).

C. Generalized Ohm's Law

To arrive at Equation (3.20a) we begin by taking the time derivative of the third field Equation (4.2.c) which becomes

$$\begin{aligned} \beta \dot{\sigma}_n - \epsilon \dot{\phi}_{,ii} - [\beta g \phi_{,ii} + \beta (\dot{u}_i - \dot{U}_i) \sigma_{f,i} \\ + \beta \sigma_f (\dot{u}_i - \dot{U}_i)_{,i}] = 0 . \end{aligned} \quad (5.10)$$

Under steady-state condition, taking, once again, $\dot{u}_i = 0$, we have

$$\beta g \phi_{,ii} + \beta \dot{U}_i \sigma_{f,i} + \beta \sigma_f \dot{U}_{i,i} = 0 . \quad (5.11)$$

The second term in (5.11) can be written in terms of the convective derivative, thus

$$\beta \left(\frac{D\sigma_f}{Dt} - \frac{\partial \sigma_f}{\partial t} \right) + \sigma_f \beta \dot{U}_{i,i} + \beta g \phi_{,ii} = 0 \quad (5.12)$$

where $\frac{D\sigma_f}{Dt}$ is the total time derivative which is equal zero at steady state. We also have from the continuity Equation for the porous composite

$$- \frac{\partial (\beta \sigma_f)}{\partial t} = J_{i,i}^e \quad (5.13)$$

where J_i^e is the current density for the porous composite.

We have already found that

$$\sigma_f = - \frac{\beta \epsilon \zeta}{\pi r^2} . \quad (5.6)$$

Also, from Darcy's law we have

$$\dot{U}_i = \frac{k}{\mu} P_{,i} = \frac{\pi r^2}{\mu} P_{,i} . \quad (5.14)$$

Substituting Equations (5.13), (5.6) and (5.14) in (5.12) we get

$$(J_i^e - \beta \frac{\epsilon \zeta}{\mu} P_{,i} + \beta g \phi_{,i})_{,i} = 0 \quad (5.15)$$

which implies that the quantity inside the parentheses must vanish too. We thus arrive at the desired expression for the generalized Ohm's law:

$$-J_i^e = \beta g \phi_{,i} - \beta \frac{\epsilon}{\mu} \zeta P_{,i} \quad (5.16)$$

which is equivalent to (3.20a).

These short derivations of well-established results are important for two reasons: First, they allow us to verify

the validity of the three field Equations (4.2); second, they demonstrate how the electric charge densities can be expressed as functions of the electrokinetic parameters (which will be seen to be useful for future work).

VI. DISCUSSION

In Chapters IV and V I have proposed a system of field equations which provides for a synthesis of Biot's theory of fluid saturated porous media with the theory of electrokinetic phenomena. A solution for the set of differential Equation (4.2) will result in seven functions describing the space and time dependence of the solid displacement $\bar{u}(\bar{r}, t)$, the fluid displacement $\bar{U}(\bar{r}, t)$, and the electric potential $\phi(\bar{r}, t)$.

The assumption of steady state flow of the fluid phase was shown to produce the familiar elastostatic behavior in the solid phase and the standard results of electrokinetic theory. Some authors (e.g. Frenkel 1940, Mizutani et al. 1976, Damowska et al. 1977, Chandler 1981) have used the steady state electrokinetic results for streaming potential and electroosmotic flow together with solutions to the elastic wave propagation problem (and the resulting fluid's strain and pressure), to obtain approximations for the magnitudes of the streaming potentials. In some cases (e.g. Chandler 1981) close agreement with experimental observation was achieved. It is appropriate to point out here that in cases where the influence of the electrokinetic effects is strong (for example due to low fluid conductivity and high

polarizability), significant electric forces may arise. The affect of these electric forces on wave propagation could no longer be neglected and the treatments described above would result in a significant error. The set of field Equations (4.2) and the treatment of Chapter IV describe more completely the electromechanical interactions and should therefore result in more nearly correct expressions for both material displacements and electric potential.

It should be emphasized here again, that in the treatment of Chapter IV I have completely excluded the electromagnetic interaction. This deficiency can be completely removed, it should be noted, by introducing the electromagnetic vector potential into the Lagrange's formalism problem. The complete set of field equations will then include the modified fluid and solid wave equations along with Maxwell's electromagnetic field equations in moving media. A thorough treatment of this complete set of equations is considerably more complicated than that of Equations (4.2).

At low frequencies, it may be possible to approximate the magnetic field behavior using the equations of magnetostatics. In this case, since the magnetic induction \bar{B} is a constant of time or changing very slowly, no electromotive force can be generated this way, and we may write

$$\bar{\nabla} \times \bar{E} = - \frac{\partial \bar{B}}{\partial t} \approx 0 . \quad (6.1)$$

Under these conditions, the magnetic field itself can be approximated by the generalized Ampere's law for the system:

$$\bar{\nabla} \times \bar{B} = \mu' \bar{J}_T . \quad (6.2)$$

Where μ' is the magnetic permeability, and \bar{J}_T is the total current density of Equation (4.2c).

If polarization currents are included, we may use Equation (A.3) for the total current density and write:

$$\bar{\nabla} \times \bar{B} = \beta \mu' [g\bar{E} + (\dot{\bar{u}} - \dot{\bar{U}}) \sigma_f + \epsilon \frac{\partial \bar{E}}{\partial t} + \bar{\nabla} \times (\bar{P} \times \dot{\bar{U}})] . \quad (6.3)$$

Where \bar{P} is the fluid polarization vector (i.e. the fluid dipole moment per unit volume).

Using (6.3) we can estimate the strength of the magnetic field associated with any particular electrokinetic phenomenon.

Mizutani et al. (1976) used this approximation to estimate the order of magnitude of the magnetic field associated with the streaming currents due to water filtration into the dilatant zone prior to earthquake occurrence. His results were of the same order as the

magnetic anomalies observed in the field, although his neglect of terms other than the convection current $(\dot{\bar{u}} - \dot{\bar{U}})\sigma_f$ must have introduced some error in his calculations.

Possible practical applications of this theory in the field of civil engineering, geophysics and within the petroleum industry were already suggested in papers by Martner and Sparks (1959) and Chandler (1981). Martner and Sparks suggested that the seismoelectric effect of the second kind be used to correlate seismic wave crossing of the weathered layer with the actual time of this crossing occurrence. This is possible because the potential fluctuations propagate with the speed of electromagnetic waves and are thus recorded virtually simultaneously with the time of their generation by the seismic wave. Thus a method to monitor wave passage of a stratigraphic layer at the instant of its occurrence may become feasible.

A second use was offered by Chandler and his experiment: By monitoring potential gradient changes within water or oil reservoirs (say by introducing electrodes into existing boreholes) it may be possible to measure underground reservoir pressure. In addition Chandler showed that the streaming potential can be very useful for the purpose of extracting rock permeability values. Chandler applied this

method in laboratory measurements, however the method could conceivably be used in the field too.

Possible use of electrokinetic streaming potentials in earthquake predictions have been discussed here before and were investigated by Dmowska et al. (1977), Sobolev et al. (1975), Mizutani et al. (1976) and others. Mizutani et al. even suggested the electroosmosis phenomenon of Chapter III as a means to control earthquakes occurrence: By providing a sufficiently large artificial electric field, it may become possible to prevent water flow into the dilatant zone, and thus prevent earthquakes which are triggered by the water filtration mechanism.

An additional use which immediately comes to mind is in geophysical exploration for underground water or oil and gas reservoirs: If the electric potential gradients are of a measurable order for the seismic frequencies range, we should be able to detect measurable electric signal fluctuations associated with seismic wave passage through fluid saturated reservoirs. For very deep reservoirs the method may possibly be implemented by using borehole technologies.

VII. CONCLUSIONS AND COMMENTS

The theoretical treatment offered in this thesis is an attempt to construct a general theory that accounts for the coupling of the electrokinetic effects to dynamic elastic strains in fluid saturated porous media while effects of fluid viscosity and resistivity are also included. As a result of this work, the following objectives have been realized:

1. A short review of the main results of Biot's theory of the propagation of elastic wave in a fluid saturated porous media has been presented.
2. The theory of electrokinetic phenomena has been presented (following Overbeek, 1953) in its most general form. Using Onsager's principle of reciprocity it has been shown that only three constants are needed for a complete description of all electrokinetic phenomena. Two of these constants are simply related to the electric and hydrodynamic resistance of the porous medium and only the third one is closely connected with the double layer electrochemical properties.

3. Using the method of Lagrange's formalism and the main results of the electrokinetic theory, a complete set of field equations describing the behavior of the electromechanical system has been constructed. It is a set of seven partial differential equations where the particles' displacements and the electric potential are the seven variables. It is given by

$$\begin{aligned} \rho_{11} \ddot{u}_i + \rho_{12} \ddot{U}_i - Nu_{i,jj} - (A+N)(u_{n,n})_{,i} - Q(U_{k,k})_{,i} \\ + b(\dot{u}_i - \dot{U}_i) + \beta\sigma_s \phi_{,i} = 0 \end{aligned} \quad (4.2a)$$

$$\begin{aligned} \rho_{22} \ddot{u}_i + \rho_{12} \ddot{U}_i + (Ru_{n,n} + Qu_{k,k})_{,i} - b(\dot{u}_i - \dot{U}_i) \\ + \beta\sigma_f \phi_{,i} = 0 \end{aligned} \quad (4.2b)$$

$$\beta\sigma_n - \epsilon\phi_{,ii} - \int \{ \beta g \phi_{,ii} + [\beta(\dot{u}_i - \dot{U}_i)\sigma_f]_{,i} \} dt = 0 \quad (4.2c)$$

4. The equilibrium elastostatic equation and the steady state results of the electrokinetic theory:

$$\tau_{ij,j} = 0 \quad (5.1')$$

$$-J_i^f = -\beta \frac{\epsilon \zeta}{\mu} \phi_{,i} + \frac{K_P}{\mu} P_{,i} \quad (5.9)$$

$$-J_i^e = \beta g \phi_{,i} - \beta \frac{\epsilon}{\mu} \zeta P_{,i} \quad (5.16)$$

have been reproduced by applying this limit to the composite field Equations (4.2). Equations (5.9) and (5.16), in turn, yield the electrokinetic expressions for the phenomena of electroosmosis, streaming potential, electroosmotic pressure, and electrophoresis.

5. Polarization currents and their relative importance are discussed in Appendix A. The possible influence of these currents on the composite field equations and the manner in which these effects can be accounted for by the theory are also described.
6. An expression which allows for the calculation of the magnetic field due to the various electric currents in the medium is suggested by the use of Ampere's law. If all current densities are

included and if the time rate of change of the magnetic field is small, correct predictions of the magnitude of the magnetic field will result.

While much has been learned in the course of this study, further refinements and extension of the theory to more complex specific physical models are needed.

An immediate extension of this initial work is the construction of plane wave solutions to the proposed field equations. Examination of these solutions will enable us to characterize different media according to their electromechanical response to different excitations.

Modifying this work to include a complete description of all electromagnetic interactions will help clarify the applicability of this theory to different types of field exploration techniques.

More work is needed in defining the exact relations between solid surface strains, fluid strains, and fluid flow types, and the resulting charge density fluctuations. The assumption made in this work as to the relative constancy of charge densities may be grossly inadequate if the restriction to infinitesimal strains does not hold, or if pore geometry allows significant charge separations to occur even under infinitesimal strains.

Before this theory could be extended to applied problems in the field, much experimental work in rock mechanics laboratories needs to be done in order to verify, under controlled conditions, the predicted frequency dependence of plane wave velocities, electric potential and particle displacements.

More theoretical research needs to be done on plane wave reflection and refraction under different boundary conditions when the assumption of material homogeneity is discarded. Such a work, which requires mathematical modeling of complex boundaries cases, is very important for possible geophysical prospecting in changing stratigraphic conditions.

Finally, much numerical analysis is needed for the exact classification of the dependence of fluid saturated porous media's seismoelectric responses on their characteristic parameters.

When the described additional work is completed we may have a very useful tool to aid us in the exploration for underground fluid reservoirs, in reservoir pressure control, in analysis of media porosity and permeability and, perhaps, it may even produce some measures in earthquakes prediction and control. In all, this is an exciting area of research which holds much promise for practical applications in the future.

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APPENDIX A

Polarization Currents

The current density term involves contributions of three terms: Displacement current $\epsilon \partial E / \partial t$, conduction current $g\bar{E}$ and convection current $\dot{\bar{u}}^1 \sigma_f$ [where $\dot{\bar{u}}^1 = (\dot{\bar{u}} - \dot{\bar{U}})$, is the relative velocity of fluid with respect to the solid, and σ_f is the fluid true charge density. The term, "true charge density," refers to a solution of ions with a net electric charge, thus avoiding a possible confusion with polarization charge density described hereafter.]

If polarization effects are taken into account one must consider additional contributions to the expression for current density due to polarization charge density motion, time rate of change of the polarization vector, and the motion of the polarized media:

The contribution due to polarization charge density arises from a non-uniform polarized medium. It can be easily shown that a non-uniform polarized medium, with a nonzero polarization divergence, behaves like a material with a net volume charge density of $\sigma_p = -\bar{\nabla} \cdot \bar{P}$ (see for example Reitz, Milford and Christy 1979; pp. 77-80). This contribution must then be added to the true charge density σ_f in the convective current term such that

$$\bar{J}_{\text{convective}} = \dot{\bar{u}}^1 \beta \sigma_f - (\bar{\nabla} \cdot \bar{P}) \beta \dot{\bar{U}} . \quad (\text{A.1})$$

The expression for current densities associated with the time rate of change of the polarization and the motion of polarized media are given by the total derivative for a moving media

$$\frac{D\bar{P}}{Dt} = \frac{\partial \bar{P}}{\partial t} + \bar{\nabla} \times (\bar{P} \times \dot{\bar{U}}) + (\bar{\nabla} \cdot \bar{P}) \dot{\bar{U}} . \quad (\text{A.2})$$

The first term of this equation is the change of flux through the surface of a volume element that is caused by the time variation of the polarization vector field. The second term represents polarization flux loss across the boundary due to the motion of the fluid volume element. The third term arises from the passage of the volume element through an inhomogeneous vector field in which flux lines are generated. (For a complete derivation of Equation (A.2) the reader is referred to texts on electromagnetic theory in moving media, e.g. Panofsky and Phillips 1955, pp. 144-147).

When expression (A.2) is multiplied by β and substituted along with (A.1) into Equation (4.9) we find that the complete expression for the total charge density is:

$$\bar{J}_T = \beta g \bar{E} + \dot{u}^{-1} \beta \sigma_f + \beta \frac{\partial \bar{P}}{\partial t} + \beta \bar{v}_x (\bar{P} \times \dot{\bar{U}}) + \epsilon \frac{\partial \bar{E}}{\partial t} . \quad (A.3)$$

The cross product term can be rewritten using vector identity as

$$\bar{v}_x (\bar{P} \times \dot{\bar{U}}) = \bar{P} (\bar{v} \cdot \dot{\bar{U}}) - \dot{\bar{U}} (\bar{v} \cdot \bar{P}) + (\dot{\bar{U}} \cdot \bar{v}) \bar{P} - (\bar{P} \cdot \bar{v}) \dot{\bar{U}} . \quad (A.4)$$

If the polarization \bar{P} , is a constant of time and space, polarization currents would still exist due to the divergence of the fluid velocity field. Thus, eliminating derivatives of constant terms in the vector differential operation identity above, Equation (A.3) becomes

$$\bar{J}_T = \beta g \bar{E} + \dot{u}^{-1} \beta \sigma_f + \epsilon \frac{\partial \bar{E}}{\partial t} + \bar{P} (\bar{v} \cdot \dot{\bar{U}}) - (\bar{P} \cdot \bar{v}) \dot{\bar{U}} \quad (A.5)$$

or, with $\bar{P} = \epsilon_0 (\kappa - 1) \bar{E}$ (where $\kappa = \epsilon / \epsilon_0$ is the dielectric constant), we have

$$\bar{J}_T = g \bar{E} + \dot{u}^{-1} \sigma_f + \epsilon_0 \kappa \frac{\partial \bar{E}}{\partial t} + \epsilon_0 (\kappa - 1) [\bar{E} \bar{v} \cdot \dot{\bar{U}} - (\bar{E} \cdot \bar{v}) \dot{\bar{U}}] \quad (A.6)$$

Equation (A.6) tells us that even under the assumption of time and space independence of the polarization \bar{P} , the effect of polarization on the current balance, and thus on our original field Equation (4.2c), cannot be neglected for material with large dielectric constant κ , unless the fluid velocity gradient is small enough to warrant the last term in (A.6) negligible.

For practical problems, the influence of polarization on the net electric field must be put in perspective with respect to the conductivity of the medium (i.e. the conduction current term must be compared with contributions due to polarization currents). In general, we say that a medium has a dielectric-like behavior if the time scale of interest to us is much smaller than the medium relaxation time $\tau_c = \epsilon/g$, and that it has a conductor-like behavior if the time scale of interest is much larger than τ_c . For the purpose of examining the applicability of our theory, the time scale of interest is the period of seismic vibration, $T = 1/f$, where f is the frequency of the seismic waves. Thus, if $f_p = g/\epsilon = 1/\tau_c$ is the transition frequency from one type of behavior to the other, the condition $f \ll f_p$ results in a conductor-like behavior, while $f \gg f_p$ suggests a dielectric-like behavior.

Table (A.1) shows the dielectric constant and conductivity along with the resulting f_p for water (with different degrees of salinity at 20°C), petroleum, and oil and water mixtures. From these examples we can conclude that for the frequency range of up to $\sim 10^2$ Hz, petroleum with higher conductivity ($g > 10^{-9}$ mho/m) behaves like a conductor, while petroleum of the lower range of conductivity ($10^{-9} > g > 10^{-16}$ mho/m), behaves like a dielectric, and polarization effects of the type described before become very important. Note also that all waters can be regarded as conductors for frequencies smaller than 10 kilohertz, and also that the conductor-like behavior of water dominates water-oil mixtures for all frequencies smaller than 10^7 Hz.

If a material is found to possess dielectric-like properties (e.g. pure petroleum with conductivity of the order of 10^{-16} mho/m) we must introduce polarization current effects into Equation (4.2c). To do so we have to consider polarization effects in our original Lagrangian formalism. This will guarantee that any possible modification in Equations (4.2a) and (4.2b) will be considered too.

It seems natural to introduce polarization in a similar manner to that of the convection current, i.e. through the dissipation function D. Let us define the new term in the dissipation function as:

TABLE A.1

Dielectric Constants, Conductivity Values and Their Corresponding Behavior Types for Various Fluids.

MATERIAL	g(mho/m)	κ	ϵ (F/m)	$f_p = g/\epsilon$ (cps)	Behavior Type For $f < 10^2$
Water:					
Very Fresh Water	10^{-5}	80.4	$\sim 10^{-9}$	10^4	Conductor-like
Mine Water	10^{-2}	80.4	"	10^7	"
Surface Water (Rivers)	$10^{-1} - 10^{-2}$	80.4	"	$10^7 - 10^8$	"
Wells	$(10^{-1} - 10^{-3})$	"	"	$10^8 - 10^6$	"
Salt Water @ 20°C					
5%	1	"	"	10^9	"
40%	10	"	"	10^{10}	"
Petroleum	10^{-9} 10^{-16}	2.07-2.14 "	$\sim 10^{-11}$ "	10^2 10^{-5}	Border Dielectric-like
Oil%/Water%					
100/0	10^{-3}	~ 10	$\sim 10^{-10}$	10^7	Conductor-like
55/45	10^{-1}	"	"	10^9	"
15/85	1	"	"	10^{10}	"

$$D_p = (\beta \bar{\nabla} \phi) \cdot [\bar{\nabla} x (\bar{P} x \dot{\bar{U}})] . \quad (A.7)$$

Substitution of the new dissipation function in Lagrange's Equation (4.7) for the generalized coordinate $\eta = \phi$ will result in the desired polarization current's divergent term

$$\bar{\nabla} \cdot \bar{J}_p = \beta \bar{\nabla} \cdot [\bar{\nabla} x (\bar{P} x \dot{\bar{U}})] \quad (A.8)$$

inside the time integral of Equation (4.2c).

The presence of the fluid velocity in the new term D_p will introduce an additional force acting on the fluid component: Substituting D_p into Equation (4.7), with $\eta = U_i$ results in the additional force terms in the Equation of motion of the fluid phase (4.2.b):

$$\begin{aligned} \bar{F}_p &= \beta \phi_{,i} \frac{\partial}{\partial \dot{U}_i} [\bar{\nabla} x (\bar{P} x \dot{\bar{U}})]_j \\ &= \beta \phi_{,i} P_{j,j} + \beta \phi_{,i} P_{j,i} . \end{aligned} \quad (A.9)$$

If the polarization vector \bar{P} is independent of position in space, the force term (A.9) will vanish. However, if the polarization does depend on position, the interaction of the electric field with the polarization charge densities will

result in additional electric forces.

Note that when the additional terms \bar{F}_p and $\bar{\nabla} \cdot \bar{J}_p$ are introduced into Equations (4.2b) and (4.2c) respectively, a nonlinearity will result if both \bar{U} and \bar{P} depend on space and time. This, of course, will complicate the problem of finding solutions to these equations. However, the discussion in this appendix may help us determine if for given field conditions simplifying assumptions can be made such that linearity is restored.