SOME THEORETICAL TOPICS ON NUCLEAR MAGNETIC SURFACE RELAXATION

By

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in partial fulfillment of the requirements
for the degree of
MASTER OF SCIENCE
May, 1966

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PREFACE

During the last fifty years, the study of colloids has gradually developed into a branch of exact sciences. However, due to the difficulty in the experimental field, very few parameters have been checked seriously to the physicist's standard. The development of NMR technique brought new hopes in this field as well as many others. The present work is a preliminary theoretical consideration on the study of colloids and/or other surface phenomena.

Theories concerning about the relations among quantities such as viscosity, diffusion constants, electric field, shearing modulus etc. are still vaguely written in the literature. So the study of any direct effect on the relaxation rate has been limited to the knowledge of the author. Direct effect on relaxation times due to the pressure from electrostriction effect has been found negative.

The treatment of Brownian motions of a colloid by correlation analysis seems promising. The author feels certain that information theory will be a powerful tool in handling liquid-state problems. Preliminary formulas relating to the relaxation rates have been derived. Lastly, the fundamentals of BPP theory is included in Appendix B partly because it is a good exercise to relate the knowledge learned in classroom to research work.

The author wishes to express his deepest gratitude to Dr. V. L. Pollak

for his guidance and the innumerable number of hours of discussions with him during this study. Graditute is also due the Army Research Office at Durham for financial support (Project No. 4768). A note of thanks is to be given to Richard Slater for showing me the unpublished data of his recent work.

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CHAPTER I

INTRODUCTION

Nuclear magnetic moment, owing to its relatively smaller interaction energy between itself and the applied magnetic field, (as comparing to the average thermal energy,) has long been considered as a favorable probe to explorate the structure of matter ever since even before the discovery of the technique of observing the NMR (nuclear magnetic resonance) singals in bulk material. Shortly after the initial discovery by Purcell (1) and by Bloch (2) independently, Pake (3) has made the use of it in study of the crystal structure of gypsum. Up till now several hundreds of papers are published each year on the structure of matter by using NMR technique. However, there are certain fields still remaining almost unattacked. One of these problems is the study of surface phenomena of certian sort by NMR methods. The enviroment of molecules in the fluid phase near the solid-fluid interface cannot be adequately described by a model used for pure liquids. It has been perturbed by the presence of the solid surfaces. The information from NMR technique, as we hope, may lead us to a better understanding to the surface and/or colloid phenomena; it may also serve as a check to the existing theories in these fields.

NMR Relaxation in Liquids

It is well known that, in most liquids, the transverse relaxation time T_2 of NMR signal is considerably longer than that of the solid of the same material. In certain range of the correlation time, T_2 is almost equal to the longitudinal relaxation time T_1. This phenomenon is well understood by the BPP theory (4) on the basis of line width narrowing due to the Brownian motions of liquid molecules. The theoretical estimates of T_1 and T_2 are quite close to the experimental values, which, for liquid water at room temperature, are about 3.6 seconds[1].

According to BPP theory[2], the transverse relaxation rate $1/T_2$ is inversely proportional to the spread of local field $\Delta B_{loc.}$ due to the neighboring spins. Therefore, we write

$$\frac{1}{T_2{}^{rl}} \sim \Delta\omega_{loc.} = \gamma \Delta B_{loc.}, \qquad (1\text{-}1)$$

where $T_2{}^{rl}$ stands for the transverse relaxation time in a rigid lattice, which, for ice, is about 10 μ-seconds. In the case of a liquid, due to the rapid motions of the molecule itself and the enviroment, the "effective" $\Delta B_{loc.}$ is considerably smaller[3] than that in the solid. If the correlation time τ_c is defined as the time needed for the

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[1] Experimental values of T_1, self diffusion constant, and viscosity of water as a function of temperature are listed in Appendix A.

[2] A part of the BPP theory related to the relaxation mechanism in liquids is given in Appendix B.

local field to change by an amount of the order of itself, then, following Pines and Slichter (5), the relaxation time T_2 in liquid is expressed as

$$T_2 = (T_2^{rl})^2/\tau_c \qquad (1\text{-}2)$$

This equation holds only for $\tau_c \ll T_2^{rl}$. If, in addition, $\tau_c \ll 1/\omega_0$, the reciprocal of Larmor frequency, we also have $T_1 = T_2$. The Pines and Slichter relation (1-2) is obtained from a particularly simple physical picture, and can easily be derived. (See Appendix C.)

Experimentally, the upper limit of longitudinal relaxation time T_1 is sometimes determined by the concentration of paramagnetic impurities in the sample. The presence of dissolved oxygen therefore shortens the relaxation time T_1 in some cases.

Surface Relaxation

In 1951, Bloch (6) first gave an explanation on the surface "catalytical" action of a fine powder of Fe_2O_3 on the relaxation rate of xenon gas. A sample with an estimated volume to surface ratio about 10^{-6} cm. was observed giving the same effect as an oxygen catalyst of 30 atm.(7).

M. Sasaki, T. Kawai, A. Hirai, T. Hashi, and A. Odajima (8)

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[3] For dipole-dipole interaction, the average field over a long period of time is actually zero, but the fluctuation of the field deviates from zero with a complex spectrum. The effective field which we used here is the root mean square value of the dipole-dipole component of the fluctuation, which gives us the same power density spectrum as the fluctuating field itself. For detail discussions, see Chapter V.

studied water sorbed on cellulose by pulsed NMR technique. They concluded two water phases are present. Two T_1's, but not two T_2's, were observed. The two T_1 values were reported as 20 msec. and 165 msec. respectively.

NMR relaxation of protons absorbed on catalytic solids such as those used in petroleum cracking processes was studied by T. W. Hickmott and P. W. Selwood (9). Single phase T_1's were observed as a fairly linear function of liquid content for both associated liquids such as water, methanol, ethanol, and non-associated liquid such as n-hexane. The relaxation time T_1 for water adsorbed on γ-alumina was reported in a range from 90 msec. to 300 msec. (varied with water content of the sample). When commerial catalysts with high paramagnetic oxide content were used, T_1 for water reduced to about 20 to 50 msec..

A series of careful measurement and some theoretical work have been published by Zimmerman, Woessner, and coworkers (10, 11, 12, 13, 14, 15, 16) on water vapor adsorbed on silica gel. Two phase behavior for both longitudinal and transverse relaxation was observed to exist simultaneously. With the exception of the data at very high vapor coverage, the transverse relaxation time of both phases are independent of surface coverage. For the phase which is believed to be strongly adsorbed, T_2' is 0.162 msec., while the transverse relaxation time of the other phase, T_{21}, is 0.828 msec.. When the coverage is higher than two times the monolayer coverage, T_{21} increases markedly. The longitudinal relaxation times are functions of surface coverage. The data show only single phase behavior when the coverage is below 0.5 or above 0.7 of the monolayer coverage. It shows a minimum in between. At a coverage about 0.6 of the monolayer, i.e., 0.126 gram of water per gram silica of 700 m^2/gm specific area, $T_1^{'}$ is 3.21 msec. while T_{11} is 14.5 msec..

Recently, Woessner (13, 14) investigated the temperature dependence of relaxation times of protons in water molecules adsorbed on silica gel with a sample of 3/4 monolayer coverage. These data were interpreted in terms of life time of water molecules in each phase and by a mechanism in which anisotropic motion of the molecules is considered. The data fits their theory beautifully. For details of their work, the reader should consult the original work. Unfortunately, due to some unknown reason, the sample has changed its character over a year of storage. It would be more interesting if the temperature dependence of relaxation times of various coverage were available.

A similar study was reported by Winkler (17) on water adsorbed by aluminum oxide. All these work indicates a common point. That is, in the presence of certain surfaces, the relaxation times of the liquid in the VERY VICINITY of the solid are reduced by a factor of several hundred as compared to that of pure liquid. The details of interactions which cause the change of enviroment states are still not clearly understood.

Some preliminary measurements have been made by V. L. Pollak (18) on the relaxation times of protons in water containing colloidal silica particles. In this problem, not only the low-coverage water molecules should be considered, but multilayer adsorption should also be taken into account. In this experiment, several samples of "Ludox[1]" were used. Under various conditions, T_2 ranges from 150 msec. to 250 msec. (See Fig. 1). In other words, T_2 (and also T_1 at small magnetic field B) reduced to about one-tenth of that of proton in pure water. Similar results were reported on the suspension of colloidal alumina. Further experimental work is underway by R. R. Slater (19). It shows in general the relaxation rate is field dependent.

Suggested Relaxation Models for "Ludox" Colloids

The stability of Ludox colloids are very good except toward freezing. The freezing point of various "Ludox" samples is 0°C. After freezing, the colloid is unstable, and irreversible precipitation occurs. The clear liquid after precipitation shows a relaxation time not very much different from that of pure water. This means the elements responsible for the increase of relaxation rate are gone with the precipitate.

A sample has been acidified by adding nitric acid. The relaxation rate changes immediately after acidification, and it stands almost constant during coagulation, which took a time of several weeks. The coagulation rate, as reported by the DuPont Technical Bulletin, depends on the pH value.

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[1] Ludox is a kind of colloidal silica manufactured by the DuPont Co.. Five types are available on the market. See Appendix D for their classification, physical properties, and approximate chemical compositions.

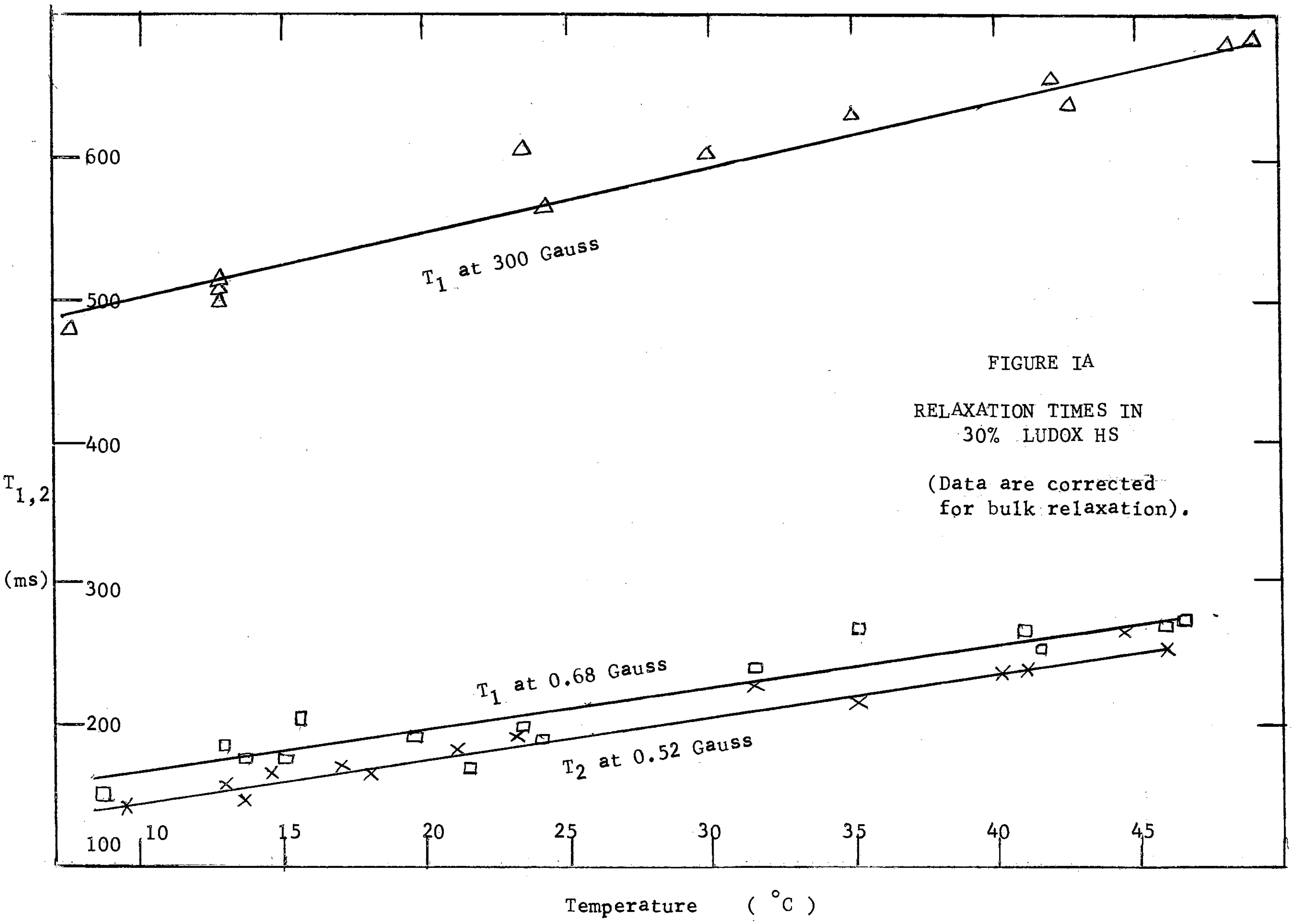


FIGURE IA

RELAXATION TIMES IN
30% LUDOX HS

(Data are corrected
for bulk relaxation).

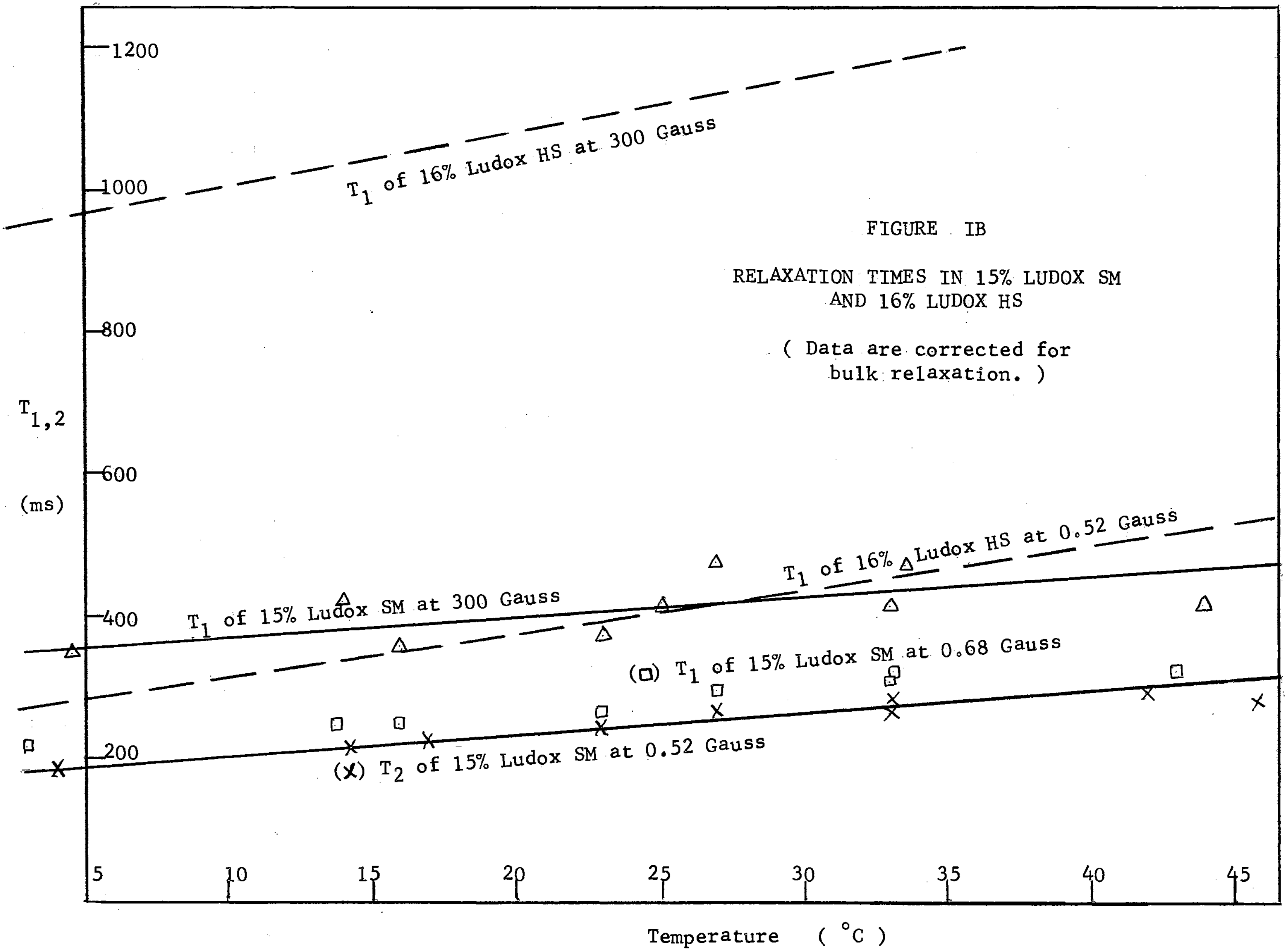


FIGURE IB

RELAXATION TIMES IN 15% LUDOX SM AND 16% LUDOX HS

(Data are corrected for bulk relaxation.)

In all the above cases, single relaxation time are observed, i.e., the signal follows the simple exponential decay law.

Three possible models may be suggested to explain this phenomenon:
Model I. The structure of the double layer is responsible for most of the changes of the enviroment state experienced by the water molecules.

If this is the case, either one or both of the following conditions have to be met in order that a single-phase relaxation curve may be observed: (1), the proton population in the double layer is large enough so that it contributes to the most part of the overall relaxation observed; (2), the exchange rate between protons in the double layer and those in the bulk water is so great that a sharp distinction between these phases is not possible. Zimmerman and Brittin (11) has calculated the condition for the later to be happened in their cases. The fact that precipitation of colloid by freezing brings the water-phase relaxation rate back to the order of pure water means in this model the destruction of the double layer enviroment state.

Model II. Sufficient amount of paramagnetic impurities are adsorbed on or near the colloid surface.

At the present time, experiments have not ruled out the possibility of paramagnetic contaminations. The disappearance of extra relaxation rate after precipitation can be count for if one is willing to use the assumption that these impurities co-precipitate with the colloid particles. If Model II is the true picture, the phenomenon can be used to study the behaviors of paramagnetic ions adsorbed on giant molecules. If the impurity were known, it should show the general character of field dependence of relaxation rates of that particular ion, suitably adjusted to take into account the motion of the giant molecule.

Model III. The Brownian motion OF THE COLLOID PARTICLES is assumed to be the reason of causing extra relaxation. This motion, superposed on top of the Brownian motion OF THE WATER MOLECULES, can be described by a very long correlation time; which therefore enters our relaxation time formula.

We will prove in Chapter V such a motion will lead to broadening of the line width. In this model, gelation will cause the long correlation time becoming infinity, thus dropping out of the formula. Only after coagulation will the true surface effect be observed, and Model I becomes the dominate factor.

We shall begin our discussion in Chapter II on some general properties of colloids. Based upon this discussion, an estimation of the surface charge density on the Ludox particles is given.

In Chapter III, we shall survey the theory of electro-chemical double layer, from which, the electric field intensity and potential as a function of distance in a flat double layer is estimated.

In Chapter IV, electrostriction effect is discussed. The magnitude of pressure and the pressure effect on the relaxation rates are also estimated. However, we found that these estimated values are several orders too smaller to be significant.

In Chapter V, a simple model of relaxation mechanism is introduced. The possibility of using multiple correlation times is also discussed. General correlation analysis from a more rigorous point of view was used through out the chapter.

Chapter VI contains several proposed experiments which might relate the models with observable data. It also contains several suggested methods to detect the paramagnetic impurities.

Since the purpose of a preliminary theory is to guide the experimental work, one should always keep in mind to revise his theory when it is necessary. We believe that, in a field such as colloid science, it is not advisable to let either the theory goes too far beyond the experimental, or vise versa, in order not to let the theory lose its physical background, or to let the experimental work go a unnecessary long way.

CHAPTER II

SOME PROPERTIES OF COLLOIDS

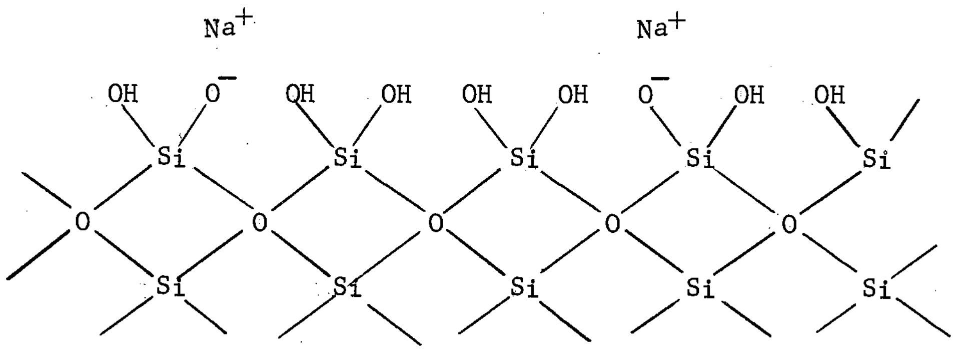
Classification of Colloids

Customarily, colloids are classified into two kinds, LYOPHOBIC and LYOPHILIC. In a lyophilic colloid, there is strong affinity between the particles and the molecules of the dispersion medium. The stability of an ideal lyophobic colloid depends upon the fact that the particles carry an electric charge. Solvation effect such as those in lyophilic colloid is neglected in IDEAL lyophobic colloids. Any real colloid lies between the two extreme cases. Purely phenomenologically, lyophobic colloids should be defined, at least when water is used as dispersion medium, as the colloidal sols whose stability is highly sensitive to added electrolytes (20). Lyophobic sols are thermodynamically unstable and the concept of their stability is a kinetic one. Ideal lyophilic sols are in thermodynamic equilibrium; therefore, no question of stability arises. In REAL lyophobic sols the colloidal particles are nearly always solvated; therefore, the non-ionic contribution to the stability from the special properties of the surface of the solid is not always zero (20).

Quartz suspension in water is classified as a lyophobic colloid(21).

An amorphous surface layer is formed when quartz crystals are pulverized (21). On the other hand, silicic acid is classified as lyophilic (22) because polar water molecules in the liquid phase have a certain affinity toward the polar ——OH groups in the silicic acid. (Starch is another example belong to this class, but no prominent effect on nuclear magnetic relaxation times has been observed.) The colloidal behavior of silica sols is very complicate, probably because these sols have properties intermediate between hydrophobic and hydrophilic(23).

According to Bechtold and Snyder (24), Rule (25), "Ludox" particles are made of amorphous silica seeds. They have surface hydroxyl groups resembling those in silicic acid. By the mean time they are alkali-stabilized to introduce negative charges on the surface. A simplified structure is believed to be as follows:



It is therefore reasonable to believe that Ludox has also a partly lyophobic and partly lyophilic character. It might probably be this character which is responsible for its extreme stability and relatively long gelation time over a wide pH range.

Surface Charge Density

The surface of Ludox particles is positively charged when the liquid phase is strongly acidic. In neutral and alkaline solutions, the surface is negatively charged. Various methods have been used to determine the surface density of hydroxyl groups of silicas. Zhuravlev and Kiselev (26) reported a surface density of 5.3 OH-groups per $m\mu^2$ on their "KSK-2" silica gel sample, by using a deuterium exchange method. The sample was first desorbed under high vacuum. They concluded that this method is more accurate than the complete calcination method, by which water may be liberated from the inside of the globule skeleton.

Electrophoresis data and titration data can also be used to estimate the surface density of the charged OH groups. The electrophoresis data are interpreted in terms of ζ-potential (the electrokinetic potential), which is defined as the potential at the slipping plane(the inner layer is considered stationary with respect to the particle). Since the relation between ζ-potential and the surface potential is still not clearly understood; therefore, one should be cautious at present to use the electrophoresis data to calculate potential and surface charge density of colloids (27).

As the properties of amorphous silica depend somewhat on the way it was prepared, direct determination of the properties of the Ludox samples is therefore preferred. A direct determination of the surface charge density of Ludox, using a titration method, was reported by

Heston, Iler and Sears (28). One of their sample (sol B) was prepared in the same way as Ludox is made (24, 25). The sol was prepared ion free by passing it through a bed of ion-exchange resin[1]. Known amount of NaOH was then added. The concentration of free OH^- ions (OH^- ions in the bulk liquid) was estimated from pH readings. The adsorbed OH^- was obtained by subtracting the free hydroxyl ions from the total NaOH added. The pH measurements were made with an alkali-resistant, type E-2 glass electrode at 25°C, using a Beckman Model-G pH-meter. The results of their experiments are plotted in Appendix D. They have reached the following conclusions:

(1). The adsorption of hydroxyl ions per unit of surface area is essentially independent of the specific area of the silica.

(2). The adsorption capacity of surface of silica for hydroxyl ions at pH $\geqq 12$ is about 3.5 ± 0.3 hydroxyl ions per $m\mu^2$.

(3). The number of hydroxyl ions adsorbed per $m\mu^2$ at any pH is a function of pH value. It increases as the pH value increases and reaches the saturation value of 3.5 as the pH value goes beyond 12.

Percent of Charged Silanol Groups

Now, let us compare the adsorption capacity with the total number

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[1] Examples of resins used in the preparation are Dowex 50 (H-form), (Dow Chemical Co.); Nalcite HCR (H-form), (National Aluminate Corp.); Amberlite IR-4B (OH-form), and Amberlite IRC-50 (H-form), (Rohm & Haas Co.). Dowex 50 and Nalcite HCR are sulfonated addition copolymer prepared from styrene and divinylbenzene (DVB). For further information and theories on ion exchange, see the famous treatise by Helfferich (Reference # 29).

of (charged + uncharged) silanol groups per unit area on the surface of Ludox particles. The latter is twice the number of the surface Si atoms.

Suppose, on the average, there are n Si atoms along the radius r of a spherical amorphous silica particle. The total number of Si atoms in this particle is $\frac{4\pi}{3} n^3$. The mass of each SiO_2 group is M/N_A, where M = 60 is the formula weight, and N_A is the Avogadro's number. The total mass is therefore

$$\frac{4\pi n^3}{3} \cdot \frac{M}{N_A} = \frac{4\pi r^3 \rho}{3} \tag{2-1}$$

where ρ is the density of amorphous silica. Solve for n, we have

$$n = r(N_A\rho/M)^{1/3} = (6.02\text{x}10^{23}\text{x}2.20/60)^{1/3} r = 2.80\text{x}10^7\ r$$
(r in cm.)

The number of Si atoms on the surface is $4\pi n^2$, while the area is $4\pi r^2$. Therefore, the number of Si atoms per unit area is n^2/r^2, which is 7.84×10^{14} atoms/cm^2., or 7.84 atoms per mμ^2.

This number indicates that the total silanol groups on the surface have a density of 15.6 groups per mμ^2. Only 22% of them carry charge under saturation conditions. Only about 4% of them carry charge at pH = 9.5 to 10.0. This is a remarkably low percentage that a saturation layer formed by closely packed counter-ions does not seem to be existing. We will come back to this point in next chapter when we discuss the Gouy-Chapman model.

CHAPTER III

THE THEORY OF ELECTRO-CHEMICAL DOUBLE LAYER

We shall now introduce the theory of electro-chemical double layer. Based upon this, estimation on magnitude of electrical field strength and potential will be made. Electrostriction effect and the effect of pressure on relaxation time will be discussed in next chapter.

Poisson-Boltzmann Equation

According to Gouy and Chapman (30, 31), the ionic charge in the solution surrounding the particle extends some distance into the liquid. In this theory, these dissolved ions are assumed to be point charges of negligible dimensions. The distribution of these ions along the normal coordinate of the surface is governed by the electric field and thermal motion. If we further assume the average concentration of these ions at a given point can be calculated from the average value of the electric potential at the same point, then, by Boltzmann's theorem,

$$n_-/n_-^o = \exp\,(V_- e\Psi/kT); \qquad n_+/n_+^o = \exp(-V_+ e\Psi/kT); \quad (3\text{-}1)$$

where e is the fundamental charge;

V_-, V_+ are the valences of ions respectively;

n_-, n_+ are the local concentrations in number of ions/cm^3;

n_-^o, n_+^o are the concentrations of ions far from the surface,

i. e., where $\Psi = 0$.

The space charge density

$$\rho = \rho^+ - \rho^- = e\,(n_+V_+ - n_-V_-). \qquad (3\text{-}2)$$

Since the solution far from the surface is electrically neutral,

$$V_-n_-^o = V_+n_+^o\ , \qquad \text{and} \qquad \rho = 0.$$

If, furthermore, $V_+ = V_-$,(which is only approximately true in the cases of Ludox,) then $n_-^o = n_+^o = n$,

$$\begin{aligned} n_- &= n\ \exp(Ve\Psi/kT) \\ n_+ &= n\ \exp(-Ve\Psi/kT) \end{aligned} \qquad (3\text{-}3)$$

In the theories treating the stability of colloids, expressions (3-2) and (3-3) are traditionally introduced into the Poisson's equation

$$\nabla^2\Psi = -\rho/\epsilon\ , \qquad (3\text{-}4)$$

which in term gives us the so-called Poisson-Boltzmann equation:

$$\nabla^2\Psi = \frac{2eVn}{\epsilon}\sinh\frac{eV\Psi}{kT} \qquad (3\text{-}5)$$

The Limiting Cases of Poisson's Equation

It should be point out that the above relation implies implicitly that the dielectric constant is independent of direction (isotropic) and of electric field strength. Otherwise, the general

Poisson's equation should take the form:

$$\nabla^2\Psi = -\frac{\rho - \nabla\cdot\vec{P}}{\epsilon_o} \tag{3-6}$$

At small field, $\nabla\cdot\vec{P} = \nabla\cdot(\chi\epsilon_o\vec{E}) = (\mathcal{K}-1)\epsilon_o\nabla\cdot\vec{E} = -(\mathcal{K}-1)\epsilon_o\nabla^2\Psi$, and equation (3-6) is reduced to equation (3-4).

On the other hand, at the high field limit, the dielectric near the charged particle is completely saturated. In the saturated region, $\vec{P} = P\hat{r} = Np\,\hat{r}$, where P is the polarization per unit volume; p, the elementary dipole; and $\hat{r}$, the unit vector along $\vec{r}$. Using the vector identities

$$\nabla\cdot\vec{P} = P\,\nabla\cdot\hat{r} + \hat{r}\cdot\nabla P,$$

$$\nabla\cdot\hat{r} = \frac{1}{r}(3) + \vec{r}\cdot\left(\frac{-1}{r^2}\,\frac{\vec{r}}{r}\right) = \frac{2}{r}$$

and the fact that $\nabla P = 0$ (P has been assumed to be constant), we have

$$\nabla\cdot\vec{P} = 2P/r. \tag{3-7}$$

Substitute (3-7) into (3-6):

$$\nabla^2\Psi = -\frac{\rho}{\epsilon_o} + \frac{2P}{\epsilon_o r}. \tag{3-8}$$

This is the high field limit of the Poisson's equation.

The Internal Field

In general, the electrical polarization is a function of field strength. At present, no existing theory gives satisfactory relation between them for liquids under sufficient high field. For liquids composed of permanent electric dipoles, the electric field produces induced dipoles as well as re-orients the permanent dipoles. Such a double action could therfore increase the internal electric field $\vec{F}$ far beyond the external field $\vec{E}$. Because of the thermal motions of the liquid molecules, the internal field has a complex a. c. component. The well-known Langevin relation relates polarization due to re-orientation to the internal local field strength F:

$$\vec{P}_{(\text{re-orien.})} = Np\left[L\left(\frac{pF}{kT}\right)\right]\hat{E}$$

where $L(A) = \coth A - \frac{1}{A}$ is the Langevin function. In isotropic media such as liquids, $\vec{F}$ is in the same direction as $\vec{E}$. However, theoretical difficulty arises because the relation between their magnitudes depends upon the choice of the model of cavity in the calculation. Different attempts were proposed by various authors. None of them is of complete success. The situation is even more serious for polar liquids. Among these existing theories, Onsager's (32) and Kirkwood's (33) give the best result. Booth (34), based upon Kirkwood's theory of polar liquids, reported an approximate relation between electrostatic dielectric constant of water and the applied electric field strength. In his theory, the dielectric constant approaches the value of the square of the refractive index in the high field limit. The experimental value of 79 for the dielectric constant at room temperature and low field strength is obtained only by adjusting the accepted dipole moment from 1.87 D. U. to 2.1 D. U. (One Debye Unit is equal to 10^{-18} esu.)

The Thickness of Dielectric Saturation Layer

If such a saturation layer can, at least in theory, be distinguished around a colloidal "Ludox" particle of 3 to 8 m μ in radius , the thickness of such a layer will not be very thick, as we will see it in the following discussion:

Suppose a charged solid particle of radius α and surface charge density σ is submerged in water, and suppose the region occupied by water can be divided into two distinctive regions: In the region between the spheres of radii α and r_o $(r_o > \alpha,)$ water is completely polarized, while outside of r_o, the medium can be described by a single dielectric "constant". A reasonable choice of r_o is that where the field strength $E(r_o)$ satisfies

$$pE(r_o) = kT \tag{3-11}$$

In the inner region, equation (3-10)

$$-\nabla\cdot\vec{E} = -\frac{\rho}{\epsilon_o} + \frac{2P}{\epsilon_o r} \tag{3-10}$$

is satisfied. Integrate (3-10) over the volume of the sphere of radius r_o, i. e., from $r = 0$ to $r = r_o$;

$$-\int_V \nabla\cdot\vec{E}\, dV = -\frac{1}{\epsilon_o}\int_V \rho\, dV + \frac{2}{\epsilon_o}\int_V \frac{P}{r}\, dV. \tag{3-12}$$

From the divergence theorem, we obtain

$$-\int_V \nabla\cdot\vec{E}\, dV = -\int_S \vec{E}\cdot d\vec{S} = -4\pi r_o^2 E(r_o) \tag{3-13}$$

The second term on the right hand side of (3-12) is

$$\frac{2P}{\epsilon_0}\int_V \frac{1}{r}\, dV = \frac{2P}{\epsilon_0}\int_{\alpha}^{r_0} \frac{4\pi r^2 dr}{r} = \frac{4\pi P}{\epsilon_0}(r_0^2 - \alpha^2). \quad (3\text{-}14)$$

If we further assume that the space charge density within this region is zero, i.e., no counter ions present, then the first term on the right hand side of (3-12) is

$$-\int_V \frac{\rho}{\epsilon_0}\, dV = -\int_A \frac{\sigma}{\epsilon_0}\, dS = -\frac{4\pi\alpha^2\sigma}{\epsilon_0}. \quad (3\text{-}15)$$

From (3-12), (3-13), (3-14), and (3-15), we have

$$r_0^2\, E(r_0) = \frac{\alpha^2\sigma}{\epsilon_0} - \frac{P}{\epsilon_0}(r_0^2 - \alpha^2), \quad (3\text{-}16)$$

from which r_0 can be obtained:

$$r_0 = \alpha\left[\frac{\sigma + P}{\epsilon_0 E(r_0) + P}\right]^{\frac{1}{2}} \quad (3\text{-}17)$$

Taking $\sigma = 0.112$ coul./m^2, i.e., 20% (from Appendix D) of the saturation surface charge density, which is 3.5 negative ions per mμ^2, or 0.56 coul./m^2; P as Np = (6.02x10^{23}x10^6÷18 molecules/m^3)x6.1x10^{-30} coul.-meter = 0.204 coul./m^2; E(r_0) as kT/p = 6.6x10^8 volts/meter; ϵ_0 = 8.85x10^{-12} coul./volt-meter, the ratio of r_0/α is estimated as

$$\frac{r_0}{\alpha} = 1.24$$

If such a relation is valid, then $r_0 - \alpha = 1.8$ mμ for a particle of 15 mμ in diameter. If we further estimate the distance between water molecules by the same method we estimated the distance between Si atoms on silica surface in Chapter II, then we have

$$n = r\,(N_A\rho/M)^{1/3},$$

and $r/n = (18/6.02\text{x}10^{23}\text{x}1.0)^{1/3} = 3.1\text{x}10^{-8}$ cm.

A water layer of 1.8 mμ in thickness corresponds to a layer of six water molecules. (Recall that the layer of chemisorption and the most intimate layers of physical adsorption, as observed by Zimmerman et al., has a thickness of about two to three molecules, which could be considered as a reasonable lower limit of the thickness of dielectric saturation layer.)

It is interesting to point out that the ratio between r_o and α is independent of α, the particle diameter. This is so because we have assumed that the space charge density is zero in the inner region, which is really not the case. The space charge shall give us another term in equation (3-15), which will offset the effect due to the surface charge σ; this in term gives us a smaller numerator in (3-17), and a smaller value of $r_o - \alpha$.

The criterion $pE(r_o) = kT$ should actually be $pF(r_o') = kT$. Since the local field F may be considerably larger than E at the same point, and since F may be assumed to be a monotonically increasing function of E, we may conclude that $r_o' > r_o$, or, in other words, equation (3-13) should be integrating at a lower value of E, which turns out to be a smaller denominator in (3-17), and a larger value of $r_o - \alpha$. However, the value of $\epsilon_o E(r_o)$, using $E = kT/p$, is less than 3% of the denominator; $(8.85\text{x}10^{-12}\text{x}6.6\text{x}10^8 = 0.0058)$, therefore, the substitution of $pF = kT$ by $pE = kT$ has little effect on the result. We can thus consider that equation (3-17) gives us a good estimation of the upper limit of the thickness of the saturated polarization layer.

One interesting conclusion can be reached from the above discussion.

If one wants to assume that complete polarization be a chief cause of change of enviroment state, he will find that the proton population in this enviroment state is directly proportional to the volume of solid in the sample

$$4\pi\alpha^2(r_o - \alpha) :: k4\pi\alpha^3 :: V_{solid},$$

and independent of particle size if σ, or equivalently, according to Hester, et al. (28), the pH value of the sample has been kept constant.

The Space Ion Density

In considering the problem of space charge, however, there is one more trouble one has to meet with if the Gouy-Chapman picture is used. Since the ions are assumed to be point charges of negligible dimensions, it is possible to reach an extremely high density of estimated space ions such that there is not enough space for them. According to Bier (p. 14, Ref. 27), in a usual case, the surface potential of a colloid is as high as 250 millivolts. Assuming that the ion concentration in the bulk of the solution is 0.01 molar, which is a reasonable value, the concentration of counter-ions near the surface is then, according to equation (3-3),

$$\frac{1}{100} \exp \frac{250 \text{ mv}}{25 \text{ mv}} = 220 \text{ molar} \qquad (kT/e = 25 \text{ mv})$$

for uni-valent ions, which is physically impossibly large[1].

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[1] For example, pure water is about 55 molar, pure sulfuric acid, 18 molar.

The counter ion concentration may therefore exhibit saturation behavior near the surface. This behavior also depends upon ion valence, ion size, hadration number, etc. As a consequence, the thickness of the diffuse layer will then be considered greater than that predicted by the Gouy-Chapman theory.

Fortunately, such situation will not be met in most of the Ludox samples. We will be back to this point during the calculation of potentials in a flat double layer.

The Flat Double Layer

The traditional Poisson-Boltzmann equation is a non-linear differential equation. It has been solved analytically for plane interface between "particle" and solution. However, no analytical solution was obtained in spherical coordinates. Debye and Hückel treated it approximately by taking only the first term of the expansion of the hyperbolic sine function. This approximation is too rough for most of the cases of colloids, where surface charge densities are so large that the exact solutions are required. Loeb, Overbeek, and Wiersema (35) solved the spherical problem with the aid of a computer. Unfortunately, their numerical tables are difficult to handle. At present, it is not clear how detailed a picture will be required to account for the NMR data. We therefore confine ourselves to a study of the flat double layer for the time being.

In a flat double layer, the Poisson-Boltzmann equation (3-5) has only one variable, —— the normal distance from the surface. The equation is

$$\frac{d^2\Psi}{dx^2} = \frac{2eVn}{\epsilon} \sinh \frac{eV\Psi}{kT} \quad . \tag{3-5a}$$

If we call $y = eV\Psi/kT$, and rewrite equation (3-5a), we have

$$\frac{d^2y}{dx^2} = \frac{2e^2V^2n}{\epsilon kT} \sinh y.$$

Multiply both sides by $2\frac{dy}{dx}$, and integrate between x and ∞, with boundary conditions $y = 0$ and $\frac{dy}{dx} = 0$ at $x = \infty$,

$$\int_x^\infty 2 \frac{dy}{dx}\frac{d^2y}{dx^2}\, dx = \frac{4e^2V^2n}{\epsilon kT} \int_x^\infty \sinh y \frac{dy}{dx}\, dx \ ,$$

$$0 - \left(\frac{dy}{dx}\right)^2 = \frac{4e^2V^2n}{\epsilon kT}\left[\cosh 0 - \cosh y\right] .$$

$$\therefore \quad \frac{dy}{dx} = -\sqrt{\frac{4e^2V^2n}{\epsilon kT}(\cosh y - 1)} = -\sqrt{\frac{8e^2V^2n}{\epsilon kT}} \sinh \frac{y}{2} \tag{3-18}$$

The minus sign is chosen in order that the solution may have a physical meaning. On separation of variables, we have

$$\frac{2dy}{e^{y/2} - e^{-y/2}} = -\sqrt{\frac{8e^2V^2n}{\epsilon kT}}\, dx \tag{3-19}$$

This equation is readily integrable if a factor of $e^{y/2}$ is multiplied to both the denominator and the numerator of the left side. The result is

$$\ln \frac{e^{y/2}-1}{e^{y/2}+1} = -\sqrt{\frac{2e^2V^2n}{\epsilon kT}}\ x + C$$

Recall that $y = y_o = \frac{eV\Psi_o}{kT}$ at $x = 0$; the integration constant is then obtained as: $C = \ln\frac{e^{y_o/2} - 1}{e^{y_o/2} + 1}$, and

$$e^{y/2} = \frac{(e^{y_o/2}+1) + (e^{y_o/2}-1)\exp\left(-\sqrt{\dfrac{2e^2V^2n}{\epsilon kT}}\ x\right)}{(e^{y_o/2}+1) - (e^{y_o/2}-1)\exp\left(-\sqrt{\dfrac{2e^2V^2n}{\epsilon kT}}\ x\right)} \ . \qquad (3\text{-}20)$$

In the following equations, we shall call

$$A = e^{y_o/2} + 1 = \exp(eV\Psi_o/2kT) + 1 \ ,$$

$$B = e^{y_o/2} - 1 = \exp(eV\Psi_o/2kT) - 1 \ , \qquad (3\text{-}21)$$

and

$$\beta = \sqrt{\frac{2e^2V^2n}{\epsilon kT}} \ .$$

Rewrite equation (3-20); solve for Ψ :

$$\Psi = \frac{2kT}{eV} \ln\left(\frac{A + Be^{-\beta x}}{A - Be^{-\beta x}} \right). \qquad (3\text{-}22)$$

Differentiate equation (3-22); we obtain

$$E = -\frac{d\Psi}{dx} = \frac{4kT\beta}{eV} \cdot \frac{AB\ e^{-\beta x}}{A^2 - B^2e^{-2\beta x}} \ . \qquad (3\text{-}23)$$

A relation between surface potential and surface charge density is

$$\sigma = -\int_0^\infty \rho\, dx = \epsilon \int_0^\infty \frac{d^2\Psi}{dx^2}\, dx = -\epsilon \left.\frac{d\Psi}{dx}\right|_{x=0} \ . \qquad (3\text{-}24)$$

Using (3-18), we have

$$\sigma = +\sqrt{8\epsilon kTn}\ \sinh \frac{eV\Psi_o}{2kT} \ , \qquad (3\text{-}25)$$

or

$$\Psi_o = \frac{2kT}{eV} \sinh^{-1}\left[\frac{\sigma}{\sqrt{8\epsilon kTn}} \right] . \qquad (3\text{-}26)$$

In order to obtain numerical data from equations (3-22), (3-23), and (3-26), it is essential to use the correct value of n. Physically, the stability of the colloid is highly dependent upon ion concentration (36). In Ludox, sodium chloride and sodium sulfate salts are added to improve its stability. It is rather unfortunate that several salts are present in the sample; therefore, no straightforward way of calculating n is available . Several assumptions have to be made in the calculation.

The sulfate ions are di-valent. This fact has not been taken into account in equation (3-5a), which otherwise will contain several terms each for a different kind of ion. However, the co-ions (ions which have the same sign as the surface charge,) are less effective to the stability of colloids (36); we thus treat the number n as the number of the mono-valent counter-ion (Na^+) per unit volume far from the surface. From Appendix D, we see that the sodium ions come from three sources: (1), from added NaCl; (2), from added Na_2SO_4; and (3), from ionized NaOH diffused into the bulk.

The amount of total titratable alkali is far much greater than that could be expected from pH calculation (Table I). Therefore, only a small portion of the titratable alkali is present in the bulk liquid. This portion of the titratable alkali is ionized into Na^+ and OH^-, and these OH^- ions are presumably responsible for the pH measurement. Sodium ions from this source can be neglected both in evaluation of σ and of n (Table I, II). Thus, we have

$$n = \sum_i \left(\frac{f_i \rho}{M_i}\right) V_i N_A \cdot \frac{V_c}{V_w} \quad ,$$

where the summation is carried over all sources of sodium ions;

f_i is the weight fraction of NaCl or Na_2SO_4,

M_i, the molecular weight, V_i, the valence respectively,

TABLE I

THE TOTAL TITRATABLE ALKALI AND THE OH^- ION CONCENTRATIONS CALCULATED FROM pH VALUES IN UNDILUTED LUDOX COLLOIDS

Type of Colloid	HS	LS	SM	AM	AS
pH at 25°C	9.9	8.3	8.5	9.1	9.6
$[OH^-]$ (in 10^{-5}N)	7.9	.20	.32	1.3	4.0
Wt. % of Na_2O from pH Data	.00020%	.000005%	.000009%	.00003%	.00006%*
Wt. % of Na_2O (total) from duPont Data Sheet	.31%	.10%	.10%	.13%	.25%*

*These numbers are % ammonia.

TABLE II

NUMBER OF SODIUM IONS PER c.c. WATER IN UNDILUTED LUDOX COLLOIDS

Types of Colloid	HS	LS	SM	AM	AS
V_w/V_c	0.846	0.845	0.932	0.846	0.845
From Added NaCl*	59.0	3.0	1.2	10.4	1.48
From Added Na_2SO_4*	60.6	12	3.3	7.3	6.05
From NaOH*, Using pH Data	0.48	0.012	0.019	0.076	0.24
Total Numer of Na^+ ions*	120	15	4.5	17.7	7.53

*In 10^{17} ions per c.c. water.

ρ is the density, and V_c/V_w, the volume ratio of the sample and water in it; N_A, the Avogadro's number.

If we assume that all the remaining portion of the titratable alkali are on the surface, then

$$\sigma = k \frac{(f/M)N_A}{AF}$$

where f is the weight fraction of titratable Na_2O,

$M = 31$, the formula weight of $\frac{1}{2}Na_2O$,

A, the specific area per gm. of silica, and

F, the weight fraction of silica in the sample.

k is a conversion factor of 10^{-18} if the unit of σ is expressed in ions/square m μ.

The numerical values of n are given in the last line of Table II. In Table III, the values of σ are given in two different units, namely, in ions/m μ^2 and in Coul./m^2. We also give the values of β and β^{-1}at 25°C. Notice that β has the dimension of the reciprocal of length. The value of β is obtained from the formula

$$\beta = 2.30 \times 10^{-3} \sqrt{\frac{n}{T}}$$

where n is expressed in number of ions per cubic meter. The values of y_o and Ψ_o at 25°C are listed in the last two lines of Table III. To these values of Ψ_o, only that of ammonia stabilized Ludox has a possibility of reaching ionic saturation.

With these numerical values, we have calculated the field strength at any point by equations (3-23) and (3-21), the potential Ψ at any

TABLE III

SURFACE CHARGE DENSITIES AND SURFACE POTENTIAL OF LUDOX

Type of Colloid	HS	LS	SM	AM	AS
σ (in # ions/m μ^2)	0.98	0.31	0.34	0.41	1.44
σ (in Coul./m^2)	-0.155	-0.050	-0.055	-0.066	-0.232
β (in meter^{-1})*	$4.62\text{x}10^8$	$1.63\text{x}10^8$	$0.39\text{x}10^8$	$1.77\text{x}10^8$	$1.16\text{x}10^8$
β^{-1} (in m μ)*	2.16	6.14	25.6	5.65	8.4
y_o (=$e\Psi_o/kT$)*	+5.86	+5.68	+7.07	+6.06	+9.44
Ψ_o (in mv)*	-150	-145	-181	-155	-241

* At 25°C.

point by equations (3-22) and (3-21), and the space charge density by the following formula,

$$\rho = -\, 2eVn \sinh \frac{e\Psi}{kT}$$

$$= -8eVn \frac{ABe^{-\beta x}(A^2 + B^2e^{-2\beta x})}{(A^2 - B^2e^{-2\beta x})^2} \, . \qquad (3\text{-}27)$$

These values are listed in Table IV.

TABLE IV

FIELD STRENGTH, POTENTIAL, AND SPACE CHARGE DENSITY IN A FLAT DOUBLE LAYER AS A FUNCTION OF DISTANCE

(A) 30% Ludox HS (25°C)

βx	0.0	0.1	0.2	0.3	0.4	0.6	0.8	1.0	1.5	2.0
x (in Å)	0	2.16	4.33	6.50	8.66	13.0	17.3	21.6	32.5	43.3
E (in 10^7v/m)	22.2	11.4	7.65	5.65	4.48	3.09	2.29	1.76	0.99	0.58
Ψ (in mv.)	-149	-116	-96	-82	-71	-55	-44	-35	-20	-7.7
ρ (in Coul./c.c.)	711	180	83	47.4	31	16.4	10.3	7.1	3.5	1.95

TABLE IV(CONTINUE)

(B) 30% Ludox LS (25°C)

βx	0.0	0.02	0.05	0.1	0.2	0.3	0.4	0.6	0.8
x (in Å)	0	1.23	3.07	6.14	12.3	18.4	24.6	36.8	49.1
E (in 10^7v/m)	7.1	6.06	4.96	3.82	2.60	1.95	1.55	1.07	0.80
Ψ (in mv.)	-145	-137	-126	-113	-94	-81	-71	-55	-43
ρ (Coul./c.c.)	79.6	50.7	34.0	20.4	9.6	5.7	3.72	2.0	1.26

(C) 15% Ludox SM (25°C)

βx	0.0	0.01	0.02	0.03	0.04	0.06	0.08	0.10	0.20
x (in Å)	0	2.56	5.13	7.70	10.25	15.4	20.5	25.6	51.3
E (in 10^7v/m)	3.43	2.95	2.58	2.28	2.04	1.70	1.44	1.26	0.77
Ψ (in mv.)	-181	-172	-165	-158	-154	-144	-136	-130	-105
ρ (in Coul./c.c.)	126.7	93.3	71.7	56.5	45.2	31.1	22.6	17.4	6.56

TABLE IV (CONTINUED)

(D) 30% Ludox AM (25°C)

βx	0.0	0.02	0.05	0.1	0.2	0.3	0.4	0.6	0.8	1.0
x (in Å)	0	1.13	2.82	5.65	11.3	16.9	22.6	33.9	45.2	56.5
E (in 10^7v/m)	9.04	7.25	5.97	4.48	2.96	2.22	1.74	1.20	0.89	0.68
Ψ (in mv.)	−152	−142	−131	−117	−97	−87	−72	−56	−44	−35
ρ (in Coul./C.c.)	151	72.5	49.4	28.1	12.6	7.2	4.6	2.4	1.5	1.0

(E) 30% Ludox AS (25°C)

βx	0.0	0.02	0.05	0.1	0.2	0.3	0.4	0.6
x (in Å)	0	1.68	4.2	8.4	16.8	25.2	33.6	50.4
E (in 10^7v/m)	33.4	30.0	17.0	9.6	4.9	3.18	2.29	1.39
Ψ (in mv.)	−240	−202	−173	−145	−113	−94	−81	−62
ρ (in Coul./c.c.)	1510	1223	392	127	33.2	14.6	7.8	3.2

TABLE V

TEMPERATURE DEPENDENCE OF E AND Ψ OF 30% LUDOX HS

βx		0.0	0.1	0.2	0.3	0.4	0.6	0.8	1.0	1.5	2.0
0°C	x (Å)	0	2.08	4.15	6.22	8.30	12.44	16.6	20.8	31.1	41.5
	E (10^7v/m)	21.8	11.2	7.45	5.50	4.32	2.98	2.20	1.70	0.95	0.56
	Ψ (mv.)	-151	-116	-96.5	-82.5	-71.3	-55.5	-43.8	-35.1	-21.9	-12.7
50°C	x (Å)	0	2.26	4.52	6.78	9.04	13.53	18.1	22.6	33.9	45.2
	E (10^7v/m)	22.4	11.52	7.80	5.82	4.61	3.20	2.36	1.83	1.03	0.60
	Ψ (mv.)	-147	-115	-94.8	-81.0	-71.0	-55	-43.3	-34.6	-21.9	-12.2
100°C	x (Å)	0	2.42	4.85	7.28	9.70	14.57	19.4	24.25	36.4	48.5
	E (10^7v/m)	23.1	11.88	8.11	6.15	4.86	3.36	2.52	1.93	1.09	0.64
	Ψ (mv.)	-144	-113	-93.8	-80.5	-70	-54.5	-42.8	-34.6	-20.4	-12.2

To illustrate the temperature dependence of equations (3-22) and (3-23), an example is given in Table V on 30% Ludox HS. The range of variation is smaller than expected. The numbers in Tables IV and V are plotted on the next few pages.

The values of surface charge densities listed in Table III agree fairly well with the experimental σ's of Hester et al (28). The places where $E \geqq kT/p$ are $x = 5$ Å for Ludox LS at room temperature, 7 Å for Ludox AM, 10 for HS, and 21 for AS. The value of E for Ludox SM has never reached the value kT/p even on the surface. Fortunately, all these values fall within or close to the upper limit of thickness of dielectric saturation layer as we have estimated on p.23. Space charge densities for most types of colloids are low to be accounted for an ion saturation layer; except in Ludox AS, the ammonia stabilized colloid, may possibly reach the saturation barrier.

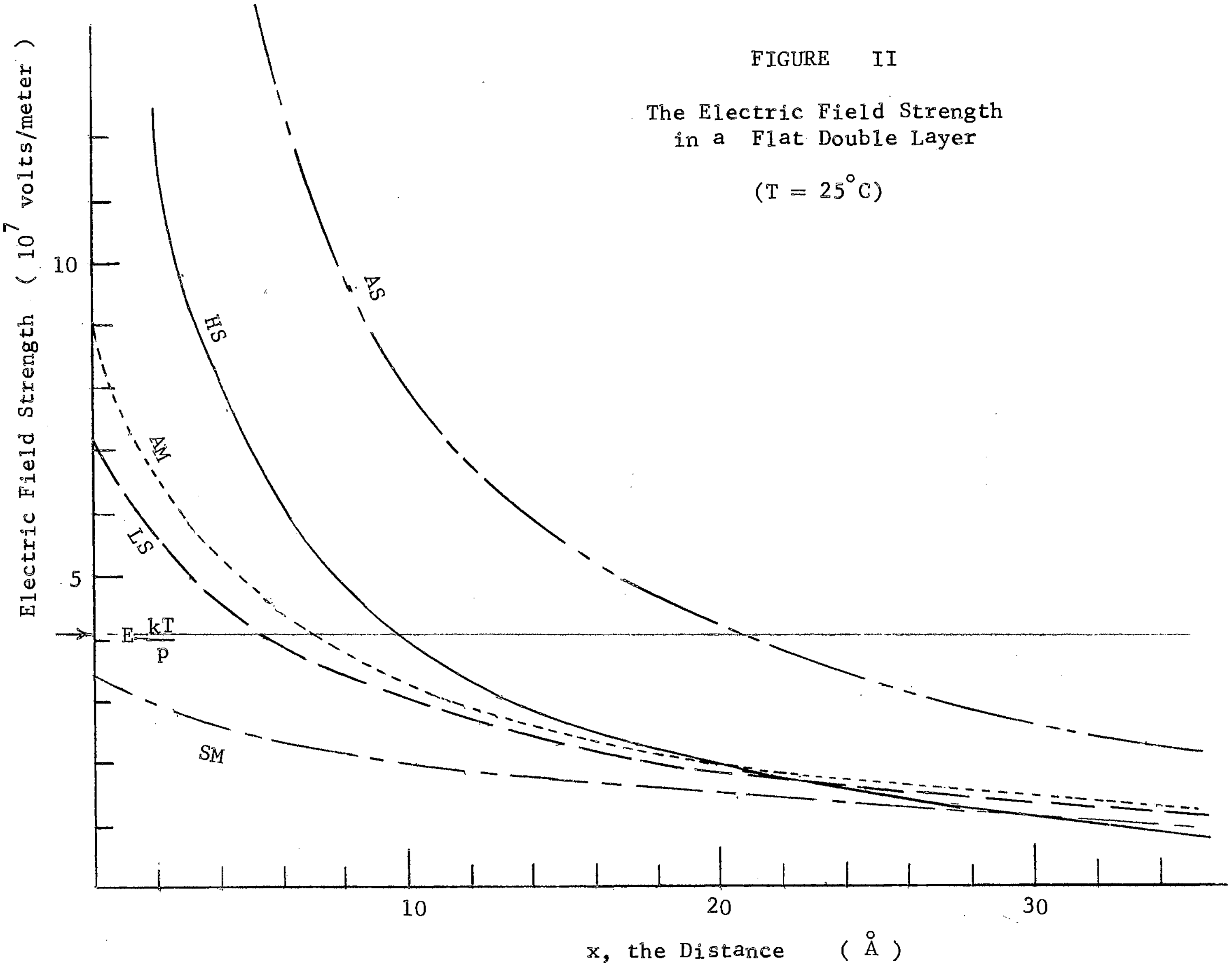

FIGURE II

The Electric Field Strength
in a Flat Double Layer

(T = 25°C)

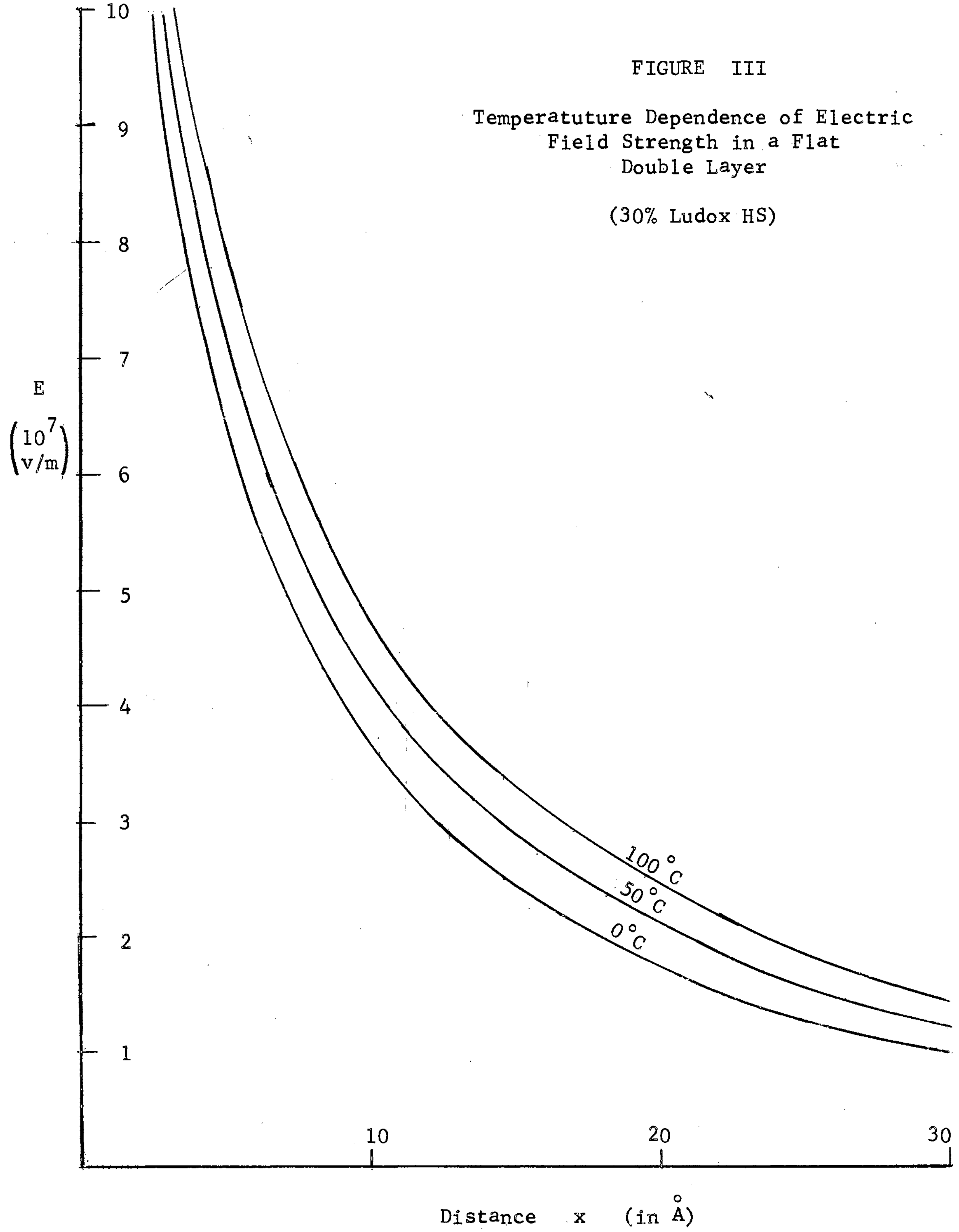

FIGURE III

Temperatuture Dependence of Electric Field Strength in a Flat Double Layer

(30% Ludox HS)

CHAPTER IV

ELECTROSTRICTION EFFECT AROUND THE DOUBLE LAYER

We shall now estimate the pressure change due to the strong electric field created by the electric double layer. The electric field strength and potential are obtained from previous chapter.

Forces Acting on a Volume Element

Consider a volume element ΔV of an (isotropic) liquid medium. The condition of equilibrium can be stated as

$$\vec{f} - \nabla p = 0 \tag{4-1}$$

where $\vec{f}$ is the body force per unit volume acting on ΔV, and p is the pressure in this element. The body force, as given by Stratton (37), is

$$\vec{f} = -\frac{1}{2} E^2 \nabla \varepsilon + \frac{1}{2} \nabla\left(E^2 \tau \frac{\partial \varepsilon}{\partial \tau}\right) , \tag{4-2}$$

where τ is the density. We save the letter ρ for the space charge density.

In the liquid space surrounding a colloid particle, there is a non-zero space charge density due to the difference in concentrations of positive and negative ions. A term $\rho\vec{E}$ has to be added to the above body force expression.

$$\vec{f} = -\frac{1}{2} E^2 \nabla \varepsilon + \frac{1}{2} \nabla\left(E^2 \tau \frac{\partial \varepsilon}{\partial \tau}\right) + \rho\vec{E} \tag{4-3}$$

According to Stratton, two important assumptions have been made in the derivation of equation (4-2); namely,

(1), ϵ depends only on $\vec{r}$ and τ;

(2), the boundary of solid is rigid so that no work is being done during the compression.

The first assumption gives us no problem in the case of colloids since the dielectric constant of water is a function of field intensity E, which is a function of space only. The second assumption could not be fully justified since the compressibility of water is only seven times greater than the compressibility of quartz[1].

A Relation between E, Ψ, and p

From equations (4-1) and (4-3), a differential relation between pressure and field intensity

$$-\frac{1}{2}E^2\,\nabla\epsilon + \frac{1}{2}\nabla\left(E^2\tau\,\frac{\partial\epsilon}{\partial\tau}\right) + \rho\vec{E} - \nabla p = 0 \qquad (4\text{-}4)$$

is obtained. Dot multiply equation (4-4) through by $d\vec{S}$ and integrate,

$$-\frac{1}{2}\int_{\infty}^{r} E^2\nabla\epsilon\cdot d\vec{S} + \frac{1}{2}\int_{\infty}^{r}\nabla\left(E^2\tau\frac{\partial\epsilon}{\partial\tau}\right)\cdot d\vec{S} + \int_{\infty}^{r}\rho\vec{E}\cdot d\vec{S} = \int_{\infty}^{r}\nabla p\cdot d\vec{S}\ . \qquad (4\text{-}5)$$

This equation can be reduced by using the following relations:

$$-\frac{1}{2}\int_{\infty}^{r} E^2\nabla\epsilon\cdot d\vec{S} = -\frac{1}{2}\int_{79}^{\epsilon} E^2\,d\epsilon\ , \qquad (I)$$

$$\frac{1}{2}\int_{\infty}^{r}\nabla\left(E^2\tau\frac{\partial\epsilon}{\partial\tau}\right)\cdot d\vec{S} = \frac{1}{2}E^2\tau\frac{\partial\epsilon}{\partial\tau}\Bigg|_{0}^{E} = \frac{1}{2}E^2\tau\frac{\partial\epsilon}{\partial\tau} \qquad (II)$$

$$\int_{\infty}^{r}\rho\vec{E}\cdot d\vec{S} = -\int_{0}^{\Psi}\rho\,d\Psi \qquad (III)$$

---

[1] According to International Critical Tables.

$$\int_{\infty}^{r} \nabla p \cdot d\vec{S} = \int_{p_o}^{p} dp = p - p_o \tag{IV}$$

Now, let us start our discussion by integral (II). A classical way of finding $\frac{\partial \epsilon}{\partial \tau}$ is by employing the Clausius-Mossotti's law, which is too simple and does not describe the situation correctly. Instead of using the Clausius-Mossotti's law, we are going to try a formula of dielectric constant for water given by Booth (34), which reads:

$$\frac{\epsilon}{\epsilon_o} = \eta^2 + \frac{28\, N\pi(\eta^2 + 2)\mu}{3\sqrt{73}\; E\epsilon_o}\, L\left(\frac{\sqrt{73}\; E\mu(\eta^2 + 2)}{6\; kT} \right) \tag{4-6}$$

where η is the refractive index,

N, the number of water molecules per c.c.,

μ, the permanent electric dipole moment of water molecule, and

L, the Langevin function. $L(x) = \coth x - \frac{1}{x}$.

Noticing that N is related to the density τ by the relation

$$N = \frac{N_A \tau}{M}$$

where N_A is the Avogadro's number, and M, the molecular weight, we may obtain from (4-6) a formula for $\tau\frac{\partial \epsilon}{\partial \tau}$:

$$\tau\frac{\partial \epsilon}{\partial \tau} = \frac{28N\pi\,(\eta^2+2)\;\mu}{3\sqrt{73}\;E}\,L\left(\frac{\sqrt{73}\;\;E\mu(\eta\;+2)}{6kT}\right) = \left(\frac{\epsilon}{\epsilon_o} - \eta^2\right)\epsilon_o \tag{4-7}$$

With the aid of equation (4-6), one should be able to solve, in principle, the general Poisson equation (3-6). The value of E thus obtained should be substituted into expression (I) and (II), and a relation between ρ and Ψ obtained from the general Poisson's equation should be used in expression (III). Such a procedure inevitably requires complicate iteration. Since our purpose is to obtain an order-of- magnitude estimation, we shall try to avoid unnecessary complication. For this reason, the Poisson-Boltzmann's picture is again adopted.

In Poisson-Boltzmann's picture, ϵ has been assumed a constant. This is a happy assumption because we can thus put expression (I) equal to zero. It is interesting to point out that it is possible to obtain the same result by assuming that the density τ is a constant in equation (4-4). By using a general relation

$$\nabla\epsilon = \frac{d\epsilon}{d\tau}\nabla\tau,$$

we can easily reduce (4-4) to its equivalent form:

$$\tfrac{1}{2}\nabla\left(E^2\frac{\partial\epsilon}{\partial\tau}\right) + \frac{\rho\vec{E}}{\tau} = \frac{1}{\tau}\nabla p \qquad (4\text{-}8)$$

Dot multiply term by term by $\vec{dS}$ and integrate. Since τ is regarded as a constant here, we can take it out of the integral sign. So,

$$\tfrac{1}{2}E^2\frac{\partial\epsilon}{\partial\tau} - \frac{1}{\tau}\int_0^{\Psi}\rho\, d\Psi = \frac{1}{\tau}(p - p_o)$$

This is the same equation as we obtained in the Booth-Poisson-Boltzmann treatment.

Expression (III) can readily be evaluated under Poisson-Boltzmann picture, which says that ρ can be expressed as:

$$\rho = -2eVn\sinh\frac{Ve\Psi}{kT}.$$

Therefore,

$$-\int_0^{\Psi} \rho\, d\Psi = 2eVn \int_0^{\Psi} \sinh \frac{eV\Psi}{kT}\, d\Psi = 2nkT(\ \cosh \frac{eV\Psi}{kT} - 1) \tag{4-9}$$

Combine (4-5), (4-7), (4-9), and expression (IV); we have

$$p - p_o = \tfrac{1}{2}E^2(\frac{\epsilon}{\epsilon_o} - \eta^2)\epsilon_o + 2nkT\ (\cosh \frac{eV\Psi}{kT} - 1) \tag{4-10}$$

Estimated Pressure and Its Effect on T_1

To obtain the upper limit of Δp due to eletrostriction effect, let us take the maximum values of E and Ψ of 30% Ludox HS. From Tables II, III, and IV,

$E = 22.2\text{x}10^7$ volts/meter,

$\Psi = -149$ mv. (or $y_o = eV\Psi_o/kT = 5.86$),

$n = 120\text{x}10^{17}$ ions/c.c.

Taking $(\epsilon/\epsilon_o) - \eta^2 = 76$, $\epsilon_o = 8.85\text{x}10^{-12}$ farad/meter, we have

$$\frac{1}{2} E^2(\frac{\epsilon}{\epsilon_o} - \eta^2)\epsilon_o = 1.65\text{x}10^7 \text{ Newtons/meter}^2, \text{ and}$$

$$2nkT\ (\cosh y_o - 1) = 1.72\text{x}10^7 \text{ Newtons/meter}^2.$$

The maximum total pressure is only about $3.4\text{x}10^7$ Newtons/meter^2, or 340 kg./cm^2..

Benedek and Purcell (38, 39) has measured the longitudinal relaxation time of proton in water up to 10,000 kg./cm^2. A more careful work was done later by Nolle and Mahendroo (40). They found only small negative pressure coefficient of T_1. At 340 kg/cm^2, the pressure effect is essentially negligible.

CHAPTER V

THE MULTIPLE CORRELATION-TIME THEORY

In this chapter, we shall try to give a theoretical basis to justify the use of the phenomenological equation of multi-correlation-times in colloids. As we have seen, estimations of change of properties in the double layer fail to give us proper considerations on the increase of relaxation rates of protons in water in the colloids; we shall therefore look from a different point of view. It is clear from the fundamental theory (Appendix B) that all the informations about the motions of the molecules are contained in the orientation functions. These informations, except a random phase factor, are subsequently passed into the correlation functions; therefore, a study of correlation functions are essential to the problem. A complete knowledge about the correlation functions of a particular system is of course a problem of statistical physics; we shall leave it for future investigation.

Harmonic Analysis

In the general theory of harmonic analysis (41), an expression of considerable interest and importance is

$$\varphi_{12}(\tau) = \lim_{T\to\infty} \frac{1}{T} \int_{-T/2}^{T/2} f_1(t) f_2(t+\tau)\,dt, \qquad (5\text{-}1)$$

where t is time and τ is a "time displacement" independent of t. In case either or both of the functions are complex, (5-1) should read:

$$\varphi_{12}(\tau) = \lim_{T\to\infty} \frac{1}{T} \int_{-T/2}^{T/2} f^*_1(t) f_2(t+\tau)dt \qquad (5\text{-}1')$$

If $f_1(t) = f_2(t)$, $\varphi_{11}(\tau)$ is called the autocorrelation function of f_1; if $f_1(t)$ and $f_2(t)$ are two statistically related but otherwise independent functions, $\varphi_{12}(\tau)$ is called the cross-correlation function of f_1 and f_2, in the specified order. Autocorrelation functions are frequently mentioned in physics literature; sometimes, they are simply referred as correlation functions.

If we write $f_1(t)$ and $f_2(t)$ in their Fourier integral form:

$$\begin{aligned} f_1(t) &= \int_{-\infty}^{\infty} F_1(\omega)\ e^{i\omega t}\ d\omega \\ f_2(t) &= \int_{-\infty}^{\infty} F_2(\omega)\ e^{i\omega t} d\omega \end{aligned} \qquad (5\text{-}2)$$

we can easily prove that

$$\frac{1}{T}\int_{-T/2}^{T/2} f_1^*(t)f_2(t+\tau)dt \quad \text{and} \quad F_1{}^*(\omega)F_2(\omega)$$

are Fourier transforms of each other. If $f_1 = f_2$, then $F_1{}^*F_1$ is called the "power spectrum" of f_1. The term power spectrum is misleading; only if f_1 is related to such quantities as voltage, current, velocity, displacement in a harmonic oscillator, etc., the expression $F_1{}^*F_1$ has the physical meaning of "power".

So far we have not stated the nature of $f_1(t)$ and $f_2(t)$. They may be periodic functions of time, aperiodic functions of only single occurance, random time series of any sort, or a mixture of any two of the above. The analysis of autocorrelation and cross-correlation functions of periodic or aperiodic functions is of conceptional importance; since they are "definite" function of time, we know their "future" quite well from the analysis of their past. These functions bring us no new informations, and no statistics is needed in their analysis.

The original idea of correlation was introduced by the statisticians. For certain problems associated with the strength of the relation between two random variables, the statisticians introduced the correlation coefficient defined as

$$\rho_{xy} = \frac{\sum_n x_n y_n}{\sqrt{\sum_i x_i^2 \sum_j y^2{}_j}}$$

From this historical background and the frequent application of correlation functions on problems dealt with random variables, it may mislead us to the idea that only random functions have to do with correlation. In fact, the energy density spectra of periodic or aperiodic functions are well known in the field of Fourier analysis. These spectra are also a periodic or aperiodic functions to which we definitely cannot assign a correlation time. Only a certain type of ensemble of random variables are qualified to be assigned a single correlation time. One of the examples is the ensemble whose probability distribution follows the Poisson distribution.

We shall first state some of the general theorems about correlation functions; the proof of these theorems is given in Appendix E.

THEOREM I: The autocorrelation function is real and even.

THEOREM II: The autocorrelation function approaches to zero as τ approaches to infinity, if $f_1(t)$ contains no d.c. or periodic components

THEOREM III: The autocorrelation function is continuous everywhere if it is continuous at the origin.

THEOREM IV: The maximum value of the autocorrelation function occurs at the origin; i.e., $\varphi_{11}(0) > |\varphi_{11}(\tau)|$ for every $\tau \neq 0$.

THEOREM V: The autocorrelation function at the origin is the mean square value of $f_1(t)$.

It is clear from the definition (5-1) of correlation functions, in order that $\varphi_{12}(\tau)$ be a definite function of τ, the integral has to be independent of time t. Such a requirement is obviously fulfilled in the cases of periodic or aperiodic functions, but it is not necessarily true for an ARBITRARY random function. The ensemble of random functions (which we shall call it the random process) which fulfills this condition is a stationary random process. This is an important catagory of random processes because each of them may be defined by a set of time independent probability functions (42) and therefore may be handled by using the ergodic theorem. The ergodic theorem states that: for an ergodic system, the time average of a member function of an ensemble is equal to the ensemble average of the system. In the case of autocorrelation function, this statement is equivalent to

$$\varphi_{11}(\tau) = \lim_{T\to\infty} \frac{1}{2T}\int_{-T}^{T} f_1^*(t)f_1(t+\tau)dt = \int_{-\infty}^{\infty} y_1y_2P(y_1,y_2;\tau)dy_1dy_2. \quad (5\text{-}3)$$

Here y_1 and y_2 are the heights of TWO member functions of the ensemble at the SAME instant of time, and τ is here considered as a parameter, $P(y_1,y_2;\tau)$ is the unconditional probability of occurance of y_1 and y_2. If we reconize τ as the time difference between t_1 and t_2, we can write

$$P(y_1,y_2;\tau) = P(y_1)P(y_2/y_1;\tau),$$

where $P(y_1)dy_1$ is the probability that y_1 lies in the range (y_1, y_1+dy_1), and $P(y_2/y_1;\tau)dy_2$ is the conditional probability that, knowing y_1, we find y_2 lies in the range (y_2, y_2+dy_2) at a time interval $\tau = t_2 - t_1$ later. Therefore,

$$\begin{aligned}\varphi_{11}(\tau) &= \lim_{T\to\infty} \frac{1}{2T}\int_{-T}^{T} f_1^*(t)f_1(t+\tau)dt \\ &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} y_1y_2P(y_1)P(y_2/y_1;\ \tau)dy_1dy_2. \qquad (5\text{-}4)\end{aligned}$$

Both (5-3) and (5-4) serve as useful formulas in evaluating the correlation functions.

The Brownian Motions in a Colloidal System

Having discussed some general properties of correlation functions, let us take a look on the general features of Brownian motions. The equation of motion of a particle executing Brownian motion in a simplest medium can be written as

$$m\frac{d\vec{u}}{dt} = -f\vec{u} + \vec{F}(t) \qquad (5\text{-}5)$$

where m is the mass of the particle; $\vec{u}$, its velocity; $-f\vec{u}$, a symmetrical frictional part; and $\vec{F}(t)$, a fluctuating part whose microscopic nature may or may not be well understood. Following Uhlenbeck and Ornstein (43), we will assume the mean value of F(t) at given t, over an ensemble of particles which have the same initial velocity at t_0 is zero, i. e.,

$$\overline{F(t)}^{u_o} = 0$$

In systems such as colloidal sols, there are two types of interrelated Brownian motions which we are interested, i.e., the Brownian motion of the water molecules and the Brownian motion of the colloid particles. The number of independent equations of motion is equal to the degree of freedom. However, they may be divided into the following two groups:

$$m_w \frac{du_w}{dt} = - f_w u_w + F_w(t) + K_w[x(t)] \ , \qquad (5\text{-}6a)$$

$$m_c \frac{du_c}{dt} = - f_c u_c + F_c(t) + K_c[x] \ , \qquad (5\text{-}6b)$$

where w and c stand for the water molecules and the colloidal particles respectively. Both of these equations are written in the laboratory system of coordinates. The treatment of such a set of equations is obvious statistical in nature. The term K[x] is added here to take account of the "external" forces which may be a function of space, such as the gravitational force, the applied electrical field as in an electrophoresis experiment, or a slow-varying spatial-dependent time function which may generally happen in colloids. In general, the K fluctuations are of much lower frequencies than the F fluctuations. We shall show this is the case in the next few paragraphs.

We shall exclude all those "external" forces such as gravitational force, non-equilibrium thermal diffusions, etc.; therefore, let us set $K_c[x] = 0$. For $K_w[x(t)]$'s, we may include such kind of fluctuations generally brought into our attention in the study of colloids, for example: the motion of electric double layer, of "gaint" macromolecule-size magnetic impurity particles, the migration of water molecules or ions on the surfaces, and the forced motion of water molecules by their giant neighbors, etc.. For the sake of clearness of discussion, we will not specify it at the present time.

To a first approximation, equation (5-6b)

$$m_c \frac{du_c}{dt} = - f_c u_c + F_c(t) \qquad (5\text{-}6b)$$

may be interpreted physically as the equation of motion of a colloid particle surrounded by a homogeneous, incompressible, continuous medium so that we may neglect the molecular character of the medium temporarily. Under this picture, a volume element dV containing mass m_V of the medium in the space around the macro-particle will execute a motion which can be described by the equation (5-7).

$$m_V \frac{dv_c}{dt} = - f_w v_c + G_c(t) \;, \qquad (5\text{-}7)$$

where v_c is a velocity of the same order of magnitude of u_c. We may image that v_c is related to u_c in the ordinary hydrodynamic sense. The term $G_c(t)$ in (5-7) is a fluctuating force of the same frequency range of $F_c(t)$ but of a smalleramplitude. Such a velocity field provide us a relative coordinate system for each volume element. If we choose the volume element such that it contains only one water molecule, we can rewrite (5-7) in the laboratory system as

$$m_w \frac{dv_c}{dt} = - f_w v_c + G_c(t) \qquad (5\text{-}7')$$

An observer in the moving system of coordinates should find the relative velocity $u_w' = u_w - v_c$ satisfies the equation

$$m_w \frac{du_w'}{dt} = - f_w u_w' + F_w(t) + \left\{ K_w\left[x(t)\right] - G_c(t)\right\} \qquad (5\text{-}8)$$

Equation (5-8) is simply the difference between equations(5-6a) and (5-7'). Since this observer should find himself in the same situation as an observer in the laboratory system looking at the molecular Brownian motion of pure water, we may assume equation (5-8) is identical to equation (5-5), and $u_w' = u$;

$$m_w \frac{du}{dt} = - f_w u + F_w(t). \qquad (5\text{-}5)$$

Substitute (5-5) into (5-8), we find

$$K_w\left[x(t)\right] = G_c(t) \qquad (5\text{-}9)$$

which states that the fluctuating force exerting on a molecule due to the push-around by the colloid particle is of the same frequency range as the fluctuating force exerting on the colloid particle.

So far we have only discussed the translational Brownian motion. In a similar way, we can easily extend our discussion to the rotational case. The fluctuating terms in equations (5-6a), (5-6b), (5-7), and (5-8) has a physical dimension of force. In the later discussion of correlation functions, we will not make distinctions in notations between the fluctuating force, the fluctuating velocity, or the random displacement. Since they are related to each other by an integration, their correlation property is the same.

The Correlation Function of Mixed Fluctuations

Having established that the frequency of $F_w(t)$ is much higher than that of $K_w(t)$, let us go back to the definition of autocorrelation function,

$$\varphi_{11}(\tau) = \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{T} f_1^*(t) f_1(t+\tau)\,dt. \qquad (5-1)$$

Under experimental conditions, T can never reach infinity. For practical purpose, only a time interval ΔT during which $f_1(t)$ has passed the zero value a sufficient number of times is required. Suppose now we choose the length ΔT in such a way that $F_w(t)$ has changed many cycles while $K_w(t)$ remains essentially a constant (say, C) during the interval, then,

$$\begin{aligned}
\varphi_{11}(\tau) &= \lim_{T\to\infty} \frac{1}{2T}\int_{-T}^{T} \left[F_w(t)+K_w(t)\right]^*\left[F_w(t+\tau)+K_w(t+\tau)\right] dt \\
&\cong \frac{1}{2\Delta T}\int_{-\Delta T}^{\Delta T}\left[F_w(t) + C\right]^*\left[F_w(t+\tau) + C\right]dt \\
&= \frac{1}{2\Delta T}\int_{-\Delta T}^{\Delta T} F_w^*(t)F_w(t+\tau)\,dt + \frac{C}{2\Delta T}\int_{-\Delta T}^{\Delta T} F_w^*(t)\,dt \\
&\quad + \frac{C^*}{2\Delta T}\int_{-\Delta T}^{\Delta T} F_w^*(t+\tau)\,dt + C^2 \qquad (5-10)
\end{aligned}$$

The first term is the correlation function related to the molecular random motion in a pure water sample; the second term is the mean value of $F_w(t)$, which we have assumed it be zero; the third term, as far as $\tau \ll \Delta T$, can also be proven as the mean value of $F_w(t)$.

As it is frequently cited in the literature, the correlation function is assumed of the form:

$$\frac{1}{2\Delta T}\int_{-\Delta T}^{\Delta T} F_w^*(t)F_w(t+\tau)\,dt = \langle F_w^*(t)F_w(t)\rangle_{av}\, e^{-|\tau|/\tau_c} . \qquad (5\text{-}11)$$

We shall postpone the discussion of the validity of this assumption in next section, and start to use this form of correlation function in our discussion.

If relation (5-11) is used in (5-10), the autocorrelation function in our "petite" ensemble has the form shown in Fig. IV. It has a constant tail at t equals to "infinity". Notice that the value of C^2 is arbitrary.

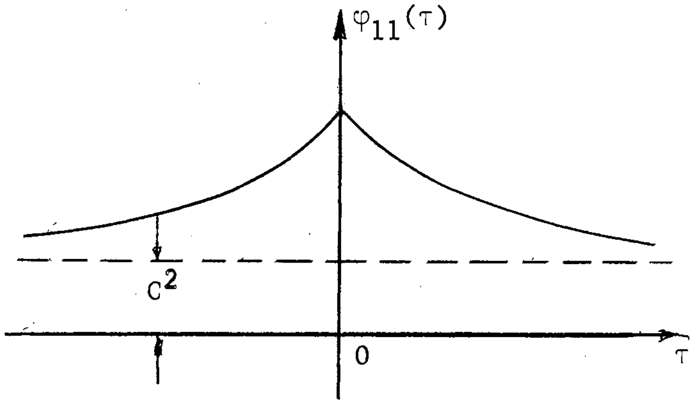

FIGURE IV. The autocorrelation function of a random process with a hidden d.c. component.

The treatment in the last paragraphs has an obvious weakness because the random process it handled is not a STATIONARY process. It can only be considered approximate to a stationary process if we choose our ensemble in such a small volume that K(x) is constant in it, and such a small time interval ΔT that K(x) has not changed substantially. However, (5-10) is a good approximation for the overall process in that small region near the origin.

Fig. IV is an example of correlation functions with a hidden d.c. component. Another interesting example of correlation function is that of a function with a hidden infinitely-narrow band of sine-cosine components. In the central portion near the origin, one finds the correlation function of thermal noise, which satisfies assumption (5-11), and therefore its correlation function has an exponential form. In the region far from the origin, the noise correlation function decays away, and the signal correlation function shows up, which has a (periodic) cosine form. This is the way the communication engineers used to separate weak signals from strong random noise(44, 45).

In the case of colloids, the "signal" is actually some long wavelength noise, which will show up in the correlation diagram far from the origin as a slow variation of C^2 with τ. This is so because we have selected a non-stationary small ensemble.

Since a water molecule will eventually pass through all the possible phase space in a colloid sample, it is evident that the overall process is stationary, and there will be no further d.c. or periodic component; therefore, its correlation function has to approach zero as $\tau \to \infty$. Since the fast fluctuation has already decayed away, it must approach to zero in a slower fashion:

$$\varphi_{11}(\tau) = \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{T} \left[F_w(t)+K_w(t)\right]^{*}\left[F_w(t+\tau) + K_w(t+\tau)\right] dt$$

$$= \varphi_{FF}(\tau) + \varphi_{FK}(\tau) + \varphi_{KF}(\tau) + \varphi_{KK}(\tau)$$

The cross-correlation functions $\varphi_{FK}(\tau)$ and $\varphi_{KF}(\tau)$may be proved to be zero if we assume:

(1), the F_w process and the K_w process are statistically independent, and

(2), either of them has a zero mean value. (See Appendix E.)

Thus we can write the autocorrelation function for a colloid system as:

$$\varphi_{11}(\tau) = \varphi_{FF}(\tau) + \varphi_{KK}(\tau) \ .$$

If assumption (5-11) is used for both $\varphi_{FF}(\tau)$ and $\varphi_{KK}(\tau)$, we have

$$\varphi_{11}(\tau) = \langle F_w(t)F_w(t)\rangle_t \, e^{-|\tau|/\tau_f} + \langle K_w(t)K_w(t)\rangle_t \, e^{-|\tau|/\tau_k} \tag{5-12}$$

The Exponential Form of Correlation Functions

As we have point out, the fundamental task in evaluating the correlation function of a random process is to find first its probability density function. Direct integration of equation (5-1) can only be performed experimentally by a correlator. Sometimes, to find the probability density distribution is not an easy problem; one has to rely upon ingenious assumptions. One of the most often quoted assumption for NATURAL physical systems is (5-11). However, this is not a fundamental assumption, its sufficient condition concerning about probability distribution can be proved without difficulty; i. e., if the random process follows a Guassian distribution law, or equivalently, if the probability density function satisfies the diffusion equation, then a correlation time can be defined, and the correlation function has the form of (5-11).

Let us start with the two dimensional (rotational) diffusion equation,

$$\frac{\partial P}{\partial t} = \frac{D_s}{a^2} \nabla_s^{\,2} P \qquad (5\text{-}13)$$

The conditional probability $P(\omega/\omega_0;\tau)$ required in (5-4) is the solution of (5-13) with the initial condition

$$P(\omega, t_1) = \delta(\omega - \omega_0) \qquad (5\text{-}14)$$

In other words, we want $P(\omega , t_2) = P(\omega , \tau)$ satisfies the initial condition (5-14). By expanding $P(\omega , \tau)$ into spherical harmonics (we wish to use the orthogonality property of spherical harmonics in the integration (5-1), since $f_1(t)$ here is the orientation functions of the dipole-dipole interaction, i.e., they are spherical harmonics of $L = 2$;) we have

$$P(\omega , \tau) = \sum C_{L,M}(\tau)\, Y_{L,M}(\omega) \qquad (5\text{-}15)$$

Substitute (5-15) into (5-13), using $\nabla_s^{\,2} Y_{L,M}(\omega) = - L(L+1)Y_{L,M}(\omega)$

$$\sum \frac{dC_{L,M}(\tau)}{d\tau}\, Y_{L,M}(\omega) = - \frac{D_s}{a^2} L(L+1)\, C_{L,M} Y_{L,M}(\omega) \qquad (5\text{-}16)$$

Multiplying both sides by $Y_{L',M'}(\omega)$, integrating over all ω, and using the orthogonality property

$$\int_{\omega} Y_{L,M}(\omega)\, Y_{L',M'}(\omega)\, d\omega = \delta_{LL'}\delta_{MM'}$$

we can separate (5-16) into a set of equations

$$\frac{dC_{L,M}(\tau)}{d\tau} = -\frac{D_s}{a^2} L(L+1)\, C_{L,M} ,$$

which has the immediate solution

$$C_{L,M}(\tau) = C_{L,M}(0)\, e^{-\tau/\tau_L}$$

in which τ_L is defined as $\dfrac{a^2}{L(L+1)D_s}$

Since we are interested only in the component of $P(\omega, \tau)$ with $L = 2$, we have

$$\tau_c = a^2/6D_s \qquad (5\text{-}17)$$

This is the correlation time given in the BPP theory.

In case that $P(\omega)$ can be written as the product of $P(\theta)$ and $P(\varphi)$, equation (5-13) can be separated into a θ-equation and a φ-equation. In this way, the degeneracy in M has been removed, and

$$\tau_{L,M} = a^2/M^2 D_s .$$

Einstein has found that , for a free particle under Brownian motion, the probability density function satisfies the diffusion equation

$$\frac{\partial P}{\partial t} = D\, \nabla^2 P ,$$

or in the rotational case,

$$\frac{\partial P}{\partial t} = \frac{D_s}{a^2} \nabla_s^2 P$$

This may be considered as another justification of using (5-11).

The a priori Probability

If equation (5-12) is being used to determine the relaxation times, we have to know the relative strengths of the time averages $<F_w^*(t)F_w(t)>_t$ and $<K_w^*(t)K_w(t)>_t$. In BPP theory (4), there is only one term involved; the a priori probability has been assumed constant (= $1/4\pi$) and integral (5-4) is performed as Abragam did on p.299, equation (101) in his treatise (46). The result of integration gives us the coefficient of the exponential form $<F_i^*(t)F_i(t)>_{av}$ the numerical values 4/5 for F_0, 2/15 for F_1, and 8/15 for F_2 (Appendix B).

Remember that both $F_w(t)$ and $K_w(t)$ which will be interested in NMR are fluctuations of the orientation functions defined in (B-16). Intuitively, we can split the a priori probability into two terms, each associates with its own exponential decay function, with their sum still equal to $1/4\pi$. We shall call these two parts $\frac{1 - k}{4\pi}$ and $\frac{k}{4\pi}$, where $0 < k < 1$. We can think of k as a function of the properties of the sample. Thus:

$$\varphi_{ii}(\tau) = \frac{N_i}{b^6}\left[(1 - k)e^{-|\tau|/\tau_F} + ke^{-|\tau|/\tau_K}\right] , \quad (5\text{-}18)$$

and the power spectra:

$$J_i(\omega) = \frac{N_i}{b^6}\left[\frac{2(1 - k)\,\tau_F}{1 + \omega^2\tau_F^2} + \frac{2k\,\tau_K}{1 + \omega^2\tau_K^2}\right] ,\quad (5\text{-}19)$$

where $N_0 = 4/5$, $N_1 = 2/15$; and $N_2 = 8/15$. In case that more than one τ_K should be considered, we can write, with $k = \sum_i k_i$,

$$J_i(\omega) = \frac{N_i}{b^6}\left[\frac{2(1 - k)\tau_F}{1 + \omega^2\tau_F^2} + \sum_i \frac{2k\,\tau_{K_i}}{1 + \omega^2\tau_{K_i}^2}\right] . \quad (5\text{-}20)$$

CHAPTER VI

PROPOSED EXPERIMENTS

Recent work by R. R. Slater (19) does show the experimental, field dependence curve of relaxation times of "Ludox" can be fitted into a scheme using two correlation times. Unfortunately, the curve is similar to that due to paramagnetic ions. So, the most important task at the present time is to determine whether there is a sufficient amount of paramagnetic contaminations in the sample. Various methods of determination have been proposed. Among them the most conclusive ones are mass spectroscopic analysis and ESR experiments. Separation of the solid particles from the liquid by centrifuge method is under way; thus we are able to determine where the responsible element lies. Probably a easier way is to run a "synthesis". The ion exchange resins needed in the experimental are easy to acquire. The particle size can be determined by the available BET equipment and the electron microscope. Suspect impurities can be doped into the sample during synthesis.

Another simple way to check on the foreign materials is as follows: Dissolve a known amount of "Ludox" sample in NaOH solution. Compare its relaxation time against a blank made of high quality silica dissolved in NaOH solution. For safety reason, they should be checked at two different field strengths.

If unfortunately, paramagnetic ions are found to be responsible, the system can be used to study adsorption of paramagnetic ions by gaint particles. Perhaps a better system to study this phenomenon is the ion exchange resin itself, since its surface character can be controled at ease by adding various chemicals. Another sort of different material called "molecular sieves" are available; they are synthetic zeolites with narrow, rigid, uniform pores which functions as a highly specific sorbent (29).

If paramagnetic contamination has been excluded, it is the task of experimental work to determine the values of τ_K and k in equations (5-19) and (5-20). In order to explore the relation between k and other factors, we shall have at least one curve for each of the following pair, keeping all the other factors as constant as possible: (1), k vs. temperature; (2), k vs. radius of particle; (3), k vs. % silica content; (4), k vs. pH value.

If the surface phenomenon can be established, it should in general exist in all lyophobic colloids. For those colloids whose maximum stable concentrations are much lower than that of Ludox, paramagnetic salts may be added to study its coagulation mechanism.

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APPENDIX A

THE TEMPERATURE DEPENDENCE OF RELAXATION TIME T_1 AND DIFFUSION CONSTANT OF O_2-FREE PURE H_2O[1]

T (°C)	$D\times10^6$ (cm^2/sec)	T_1 (sec)	$\frac{(D\eta/T)}{(D\eta/T)_{25°C}}$	$\frac{\eta}{\eta_{25°}}$	$\frac{(T_1/D)}{(T_1/D)_{25°C}}$	$\frac{(T_1\eta/T)}{(T_1\eta/T)_{25°C}}$
0	0.97	1.59	1.00	2.02	1.04	1.03
5	1.16	1.88	0.99	1.69	1.02	1.02
10	1.36	2.20	0.98	1.46	1.02	1.01
15	1.58	2.55	0.98	1.28	1.02	1.00
20	1.85	2.95	0.99	1.12	1.01	1.00
25	2.13	3.37	1	1	1	1
30	2.46	3.82	1.02	0.896	0.98	1.00
35	2.79	4.30	1.02	0.805	0.97	1.00
40	3.14	4.76	1.03	0.733	0.96	0.99
45	3.52	5.27	1.04	0.671	0.95	0.98
50	3.94	5.77	1.05	0.615	0.93	0.97
55	4.37	6.78	1.06	0.569	0.91	0.96
60	4.82	6.81	1.06	0.523	0.89	0.95
65	5.30	7.36	1.07	0.488	0.88	0.94
70	5.78	7.91	1.07	0.454	0.86	0.93
75	6.27	8.49	1.07	0.424	0.86	0.92
80	6.81	9.10	1.08	0.400	0.85	0.91
85	7.26	9.70	1.07	0.377	0.84	0.90
90	7.75	10.30	1.06	0.355	0.84	0.89
95	8.20	10.95	1.05	0.336	0.84	0.88
100	8.65	11.55	1.03	0.318	0.84	0.87

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[1] Taken from J. H. Simpson and H. Y. Carr, Phys. Rev. 111, 1201 (1958).

APPENDIX B

THE FUNDAMENTALS OF BPP THEORY

The following is a step by step derivation of a part of the BPP theory in which the dipole-dipole interaction is treated as a perturbation. The quantum mechanical method of "variation of constants" is in general used. No attempt is made to use the more rigorous "diagonal sum method." Such a treatment can be found in Kubo and Tomita: J. Phys. Soc. Japan, 9, 886 (1954) as well as scattered in the Abragam's book. Furthermore, we will concentrate our discussion on the application of BPP theory to the relaxation of liquid systems.

Classical Hamiltonian of Interaction

Classically, the potential energy of interaction of a magnetic dipole μ_i in a field B_i is

$$V = -\vec{\mu}_i \circ \vec{B}_i$$

If B_i is the field created by the j-th dipole at the location of the i-th dipole,

$$\vec{B}_i = -\nabla_i \varphi_i$$

where $\varphi_i = -\vec{\mu}_j \circ \nabla_i (1/r_{ij})$.

Therefore,

$$\vec{B}_i = \nabla_i[\, \vec{\mu}_j \cdot \nabla_i(1/r_{ij})]$$

$$V_{ij} = -(\vec{\mu}_i \cdot \nabla_i)[\, \vec{\mu}_j \cdot \nabla_i(1/r_{ij})] \qquad \text{(B-1)}$$

After expansion[1],

$$V_{ij} = \frac{\vec{\mu}_i \cdot \vec{\mu}_j}{r_{ij}^3} - \frac{3(\vec{\mu}_i \cdot \vec{r}_{ij})(\vec{\mu}_j \cdot \vec{r}_{ij})}{r_{ij}^5} \qquad \text{(B-2)}$$

Expression (B-1) indicates that V_{ij} has a tensorial character; it is the product of two irreducible (or spherical)tensors (47). Expression (B-1) can "readily" be expanded into a sum of three terms each of which multiplied by an appropriate Clebsch-Gordan coefficient (or as it is often called, the Wigner coefficient.) Instead of using this short-handed notation, we prefer the direct expansion which follows in the next three pages, which we believe will show up the physical insight more clearly.

Quantum Mechanical Analog

In quantum mechanics, the magnetic moments are described by the operators

$$\vec{\mu}_i \text{ ------ } \hbar\, \vec{I}_i; \qquad \vec{\mu}_j \text{ ------ } \hbar\, \vec{I}_j, \qquad \text{(B-3)}$$

where $\vec{I}_i$ and $\vec{I}_j$ are the corresponding spin angular momentum operators

---

[1] Expression (B-2) is generally found in treatise of electromagnetism. See, for example, Panofsky and Phillips, Classical Electricity and Magnetism, Addison-Wisley, 1955.

of the i-th and j-th nuclei respectively. If we substitute (B-3) directly into the classical equation (B-2), we have the interaction operator

$$V_{ij} = (\gamma^2\hbar^2/r^3_{ij})\left[\vec{I}_i\cdot\vec{I}_j - 3(\vec{I}_i\cdot\vec{u})(\vec{I}_j\cdot\vec{u})\right] \qquad \text{(B-4)}$$

where $\vec{u}$ is the unit vector along r_{ij} with direction cosines α_1, α_2, and α_3. In the original papers by Bloembergen et al. (48, 4), expression (B-4) is first expanded into Cartesian components, then the spin part is transformed into the components I_z, I_+, and I_-; and the space part into spherical coordinates. The terms were regrouped into groups of equal Δm values. By reverse the procedure of calculation, i. e., by doing the transformation before the expansion, we find it is possible to cut down the labor of calculation to less than one third of the original.

Using the relationships

$$\begin{cases} I_1 = \frac{1}{2}\,(\,I^+ + I^-\,) \\ I_2 = \frac{1}{2}\,(\,I^+ - I^-\,) \\ I_3 = \;I_z \end{cases} \qquad \text{(B-5)}$$

$$\begin{cases} \alpha_1 = x_{ij}/r_{ij} = \sin\theta_{ij}\,\cos\varphi_{ij} \\ \alpha_2 = y_{ij}/r_{ij} = \sin\theta_{ij}\,\sin\varphi_{ij} \\ \alpha_3 = z_{ij}/r_{ij} = \cos\theta_{ij} \end{cases} \qquad \text{(B-6)}$$

we have

$$\vec{\mu}_i \cdot \vec{\mu}_j \longrightarrow \gamma^2 \hbar^2 \left[I_{i1} I_{j1} + I_{i2} I_{j2} + I_{i3} I_{j3} \right]$$

$$= \gamma^2 \hbar^2 \left[I_{zi} I_{zj} + \tfrac{1}{2} \left(I^+_i I^-_j - I^-_i I^+_j \right) \right]$$

$$\vec{I} \cdot \vec{u} = \gamma \hbar \left[I_z \cos \theta_{ij} + \sin \theta_{ij} (I_x \cos \varphi_{ij} + I_y \sin \varphi_{ij}) \right]$$

$$= \gamma \hbar \left[I_z \cos \theta_{ij} + \tfrac{1}{2} \sin \theta_{ij} (I^+ \epsilon^{-i\varphi} + I^- \epsilon^{i\varphi}) \right]$$

Substitute these expressions into (B-4), and multiply them out term by term; thus we have a total of twelve terms. Regroup them according to their Δm values (the reason for doing so will be clear in the following discussion,) we obtain the expansion of V_{ij} operator in the six terms A, B, C, D, E, and F:

$$V_{ij} = (\gamma^2 \hbar^2 / r^3) \left\{ I_{zi} I_{zj} + \tfrac{1}{2} (I^+_i I^-_j + I^-_i I^+_j) \right.$$

$$- 3 \left[I_{zi} \cos \theta_{ij} + \tfrac{1}{2} \sin \theta_{ij} (I^+_i \epsilon^{-i\varphi_{ij}} + I^-_i \epsilon^{i\varphi_{ij}}) \right] \times$$

$$\left. \left[I_{zj} \cos \theta_{ij} + \tfrac{1}{2} \sin \theta_{ij} (I^+_j \epsilon^{-i\varphi_{ij}} + I^-_j \epsilon^{i\varphi_{ij}}) \right] \right\}$$

$$= (\gamma^2 \hbar^2 / r^3) \ (A + B + C + D + E + F)$$

where

$$A = I_{zi} I_{zj} \ (1 - 3 \cos^2 \theta_{ij}); \qquad \Delta m = 0;$$

$$B = \tfrac{1}{4} (I^+_i I^-_j + I^-_i I^+_j) \ (2 - 3 \sin^2 \theta_{ij})$$

$$= \tfrac{1}{4} (I^+_i I^-_j + I^-_i I^+_j) \ (1 - 3 \cos^2 \theta_{ij}); \qquad \Delta m = 0;$$

$$C = (3/2) (I^+_i I_{zj} + I^+_j I_{zi}) \epsilon^{-i\varphi_{ij}} \sin \theta_{ij} \cos \theta_{ij}; \qquad \Delta m = 1;$$

$$D = (3/2) (I^-_i I_{zj} + I^-_j I_{zi}) \epsilon^{i\varphi_{ij}} \sin \theta_{ij} \cos \theta_{ij}; \qquad \Delta m = -1;$$

$$E = \tfrac{1}{4}\,(I^+_i I^+_j)\,\epsilon^{-i2\varphi_{ij}} \sin^2\theta_{ij}; \qquad \Delta m = 2;$$

$$F = \tfrac{1}{4}\,(I^-_i I^-_j)\,\epsilon^{i2\varphi_{ij}} \sin^2\theta_{ij}; \qquad \Delta m = -2.$$

We have thus the total Hamiltonian

$$H = H_o + H_1 \tag{B-7}$$

$$= -\gamma\hbar B_o \sum_i I_{zi} + (\gamma^2\hbar^2/r^3_{ij})\,(A + B + C + D + E + F)$$

Unperturbed Eigenstates

Under the action of the unperturbed Hamiltonian, $-\gamma\hbar B_o \sum_i I_{zi}$, the system behaves as if it were a set of free spins, since the interaction terms have been neglected. The equation of motion of the unperturbed state of a single nucleus of spin ½ is

$$H_o\Psi(t) = -\gamma\hbar\,\vec{I}\cdot\vec{B}_o\Psi(t) = (\hbar/i)(\partial/\partial t)\Psi(t) \tag{B-8}$$

where $$\Psi(t) = C_{\frac{1}{2}}(t)\chi_{\frac{1}{2}} + C_{-\frac{1}{2}}(t)\chi_{-\frac{1}{2}} \tag{B-9}$$

Substitute (B-9) into (B-8) and express it in matrix form:

$$\frac{\hbar}{i}\begin{bmatrix} \dot{C}_{\frac{1}{2}} \\ \dot{C}_{-\frac{1}{2}} \end{bmatrix} = -\gamma\hbar \begin{bmatrix} B_o & 0 \\ 0 & B_o \end{bmatrix} \begin{bmatrix} C_{\frac{1}{2}} \\ C_{-\frac{1}{2}} \end{bmatrix}$$

The solution of this equation are

$$C_{\pm\frac{1}{2}}(t) = C_{\pm\frac{1}{2}}(0)\,\exp(-i\gamma B_o t)$$

which shows that the state vector precesses under the homogeneous field B_o, and that no transition can take place, i. e.,

$$\Psi(t) = C_{\frac{1}{2}}(0)\ \exp(-i\gamma B_o t)\chi_{\frac{1}{2}} + C_{-\frac{1}{2}}(0)\ \exp(-i\gamma B_o t)\chi_{-\frac{1}{2}} \tag{B-10}$$

For N identical spins, the unperturbed Hamiltonian is

$$H_o = -\gamma\hbar B_o \sum_{i=1}^{N} I_{zi} \tag{B-11}$$

A wave function of the form of equation (B-10), with energy eigenvalue $-\gamma\hbar B_o m$, is expected to be the solution of (B-11). Such a wave function, if operated by I^+, I_z, or I^-, will yield the eigenvalues $(m+1)$, m, $(m-1)$ respectively.

Expansion of the Total Wave Function

For this reason, it is desirable to expand the perturbation Hamiltonian into polynormials of I^+, I_z, and I^-, such as we have done in (B-7), since such an expansion will make the evaluation of the perturbation energy $< \chi_m | H_1 | \chi_{m'} >$ extremely simple.

The solution of the Schrodinger equation

$$i\hbar(\partial/\partial t)\Psi = (H_o + H_1)\ \Psi \tag{B-12}$$

of the total Hamiltonian can be expanded in terms of the unperturbed eigenfunctions $\Psi_m(0)$ and the unperturbed eigenvalues $E_m{}^o$:

$$\begin{aligned}\Psi(t) &= \sum_m C_m(t)\ \exp(-\tfrac{i}{\hbar} E_m{}^o t)\ \Psi_m(0)\\ &= \sum_m C_m(t)\ \exp(i\gamma B_o m t)\ \Psi_m(0)\end{aligned} \tag{B-13}$$

Substitute (B-13) into (B-12), and using the linear independence of

$\Psi_m(0)$'s, we have

$$i\hbar\frac{dC_{m'}}{dt} = \sum_m H_1{}^{m'm}C_m\exp(i\omega_{m'm}t) \qquad \text{(B-14)}$$

where $H_1{}^{m'm} = <\Psi_{m'}(0),\ H_1\Psi_m(0)>$ (B-15)

and $\omega_{m'm} = \dfrac{E_{m'}^{o} - E_m^{o}}{\hbar} = \gamma B_o(m - m') = -\gamma B_o\Delta m$, where $\Delta m = m' - m$.

Since $\Psi_m(0)$ and $\Psi_{m'}(0)$ are time independent, we can combine the phase factor in (B-14) into the perturbation Hamiltonian (B-15):

$$H_1{}^{m'm}\exp(i\omega_{m'm}t) = <\Psi_{m'}(0)|H_1\exp(-i\gamma B_o\Delta m)|\Psi_m(0)>$$

With this in mind, we can rewrite the expressions A through F as follows:

(A'), $A = I_{zi}I_{zj}\ (1 - 3\cos^2\theta_{ij});$

(B'), $B = \frac{1}{4}\ (I^+{}_iI^-{}_j + I^-{}_iI^+{}_j)(1 - 3\cos^2\theta_{ij});$

(C'), $C = \frac{3}{2}\ (I^+{}_iI_{zj} + I^+{}_jI_{zi})e^{-i\varphi ij}\sin\theta_{ij}\cos\theta_{ij}e^{-i\gamma B_ot};$

(D'), $D = \frac{3}{2}\ (I^-{}_iI_{zj} + I^-{}_jI_{zi})e^{i\varphi ij}\sin\theta_{ij}\cos\theta_{ij}e^{i\gamma B_ot};$

(E'), $E = \frac{1}{4}\ I^+{}_iI^+{}_je^{-i2\varphi ij}\sin^2\theta_{ij}e^{-i2\gamma B_ot};$

(F'), $F = \frac{1}{4}\ I^-{}_iI^-{}_je^{i2\varphi ij}\sin\theta_{ij}e^{i2\gamma B_ot}.$

Each of the above perturbation terms consists of three parts: the phase factor, the spin operator, and the "orientation functions". The last term is defined as the followings:

$$F_o = (1 - 3\cos^2\theta_{ij})r_{ij}^{-3},$$

$$F_1 = \sin\theta_{ij}\cos\theta_{ij}\ e^{i\varphi ij}\ r_{ij}^{-3}, \qquad \text{(B-16)}$$

$$F_2 = \sin^2 \theta_{ij}\, e^{i2\varphi_{ij}}\, r_{ij}^{-3} \qquad \text{(B-16)}$$

The Spectrum of the Orientation Functions

If the lattice is rigid, θ_{ij}, φ_{ij}, and r_{ij} are constants with respect to time; then the only time-dependent parts in the perturbation expressions are then the phase factors. Since expressions A and B do not contain phase factors, they become "secular" perturbations and will give non-zero transition probabilities[1]. Expressions C, D, E, and F give rise periodic perturbations. However, in the cases of liquids and gases, θ_{ij}, φ_{ij}, and r_{ij}, and consequently the orientation functions, are random functions of time, which may be expanded into Fourier frequency spectra, the Fourier components and phase factors cancel each other at certain part of the spectrum, thus making the perturbation integral non-zero, i. e., C. D. E, and F become secular at these frequencies. Through these channels of interaction, the spin system may transfer energy to the lattice.

The expressions of the orientation functions in Fourier integrals are

$$F_j(t) = \int_{-\infty}^{\infty} G_j(\upsilon)\, \exp(2\pi i\upsilon t)\, d\upsilon, \qquad (j = 0,\ 1,\ 2.) \qquad \text{(B-17)}$$

The Parzeval theorem[2] says that, if $F_j(t)$ and $G_j(\upsilon)$ are a pair of Fourier transforms, then

---

[1] For a detailed discussion of time-dependent perturbation theory, see, for example, Merzbacher, Quantum Mechanics (1961), pp. 439-443, pp. 466-470.

[2] See, for example, E. C. Titchmarch, Introduction to the Theory of Fourier Integrals (1937), Oxford.

$$\int_{-\infty}^{\infty} \left| F(t) \right|^2 dt = \int_{-\infty}^{\infty} \left| G(\upsilon) \right|^2 d\upsilon .$$

Divide both sides by a very long time interval T,

$$\frac{1}{T}\int_{-\infty}^{\infty} \left| F(t) \right|^2 dt = \int_{-\infty}^{\infty} \left| G(\upsilon) \right|^2 /T \ d\upsilon .$$

As $T \to \infty$, the left side is the time average of $\left| F(t) \right|^2$.

The function $J(\upsilon) = \left| G(\upsilon) \right|^2/T$ is called the spectral density or power spectrum. Notice that $J(\upsilon)$ is real and $\geqq 0$. As we will see later, the power density can also be obtained directly from correlation analysis (Chapter V).

In liquids, the functions $F_0(t)$, $F_1(t)$, and $F_2(t)$ are random functions of time. After a time interval τ, the random functions $F_j(t + \tau)$ can assume some arbitrary values governed by a certain probability distribution. Since $F(t+\tau)$ must assume the value $F(t)$ as τ approaches zero, $<F^*(t)\ F(t+\tau)>_{av}$ is a good combination[1] of functions to illustrate the statistical nature of the variation of F with respect to τ. The function $K(\tau) = < F^*(t)F(t+\tau) >_{av}$ is called the correlation function of F(t), and is independent of t for a stationary random process.

$$K(\tau) = \lim_{T\to\infty}\frac{1}{T}\int_{-\infty}^{\infty} F^*(t)F(t+\tau)dt \qquad \text{(B-18)}$$

By using the Fourier integral theorem, we have

---

[1] A better combination is the normalized correlation function $< F^*(t)F(t+\tau) >_{av}/< F^*(t)F(t) >_{av}$. For detailed discussion on correlation functions, see Chapter V.

$$K(\tau) = \int_{-\infty}^{\infty} J(\upsilon)\ \exp(-2\pi i\upsilon\tau)\ d\upsilon;$$

$$J(\upsilon) = \int_{-\infty}^{\infty} K(\tau)\ \exp(2\pi i\upsilon\tau)\ d\tau. \tag{B-19}$$

The Abragam-Pound Method

The relation between power spectrum and transition probability per unit time can be found as follows:

According to the time-dependent first-order perturbation theory, the transition probability per unit time between two eigenstates m and m' of the unperturbed Hamiltonian induced by the perturbation H' (H' has been expanded into a sum of six terms in order to apply it to the same set of eigenvectors;) can be written as

$$W_{mm'} = (1/\hbar^2 t)\left|\int_0^t H'_{mm'}(t')\ \exp(-i\omega_{mm'}t')\ dt'\right|^2 . \tag{B-20}$$

Since t' is a dummy variable, the product in (B-20) can be considered as a double integral

$$W_{mm'} = (1/\hbar^2 t)\int_0^t dt'\ H'_{mm'}(t')\int_0^t dt''\ H'^{*}_{mm'}(t'')\ e^{-i\omega_{mm'}(t'-t'')}$$

In order to reconize the correlation function in this expression, a new variable $\tau = t'-t''$ is introduced. During the performance of the first (right-side) integration, t' is considered constant; therefore, after changing the variable, the new independent variable is τ; and

$$t'' = t' - \tau, \qquad dt'' = d(t' - \tau) = - d\tau;$$

and the range of integration is from $\tau=t'$ to $\tau=t'-t$. Therefore,

$$W_{mm'} = -\frac{1}{\hbar^2 t}\int_0^t dt'\int_{t'}^{t'-t} d\tau H'_{mm'}(t')H'^{*}_{mm'}(t'-\tau)e^{-i\omega_{mm'}\tau} \tag{B-21}$$

By changing the order of integration, we realize that the first integral $\int_0^t H'_{mm'}(t)\, H'^*_{mm'}(t'-\tau)dt'$ is the correlation function $K_{mm'}$ times the time interval[1]. Thus, we have connected a relation between transition probability and the result from any correlation hypothesis.

To carry out the integration (B-21) explicitly, the domain of integration has been cut into two sections, as it is shown in Fig. B-1.

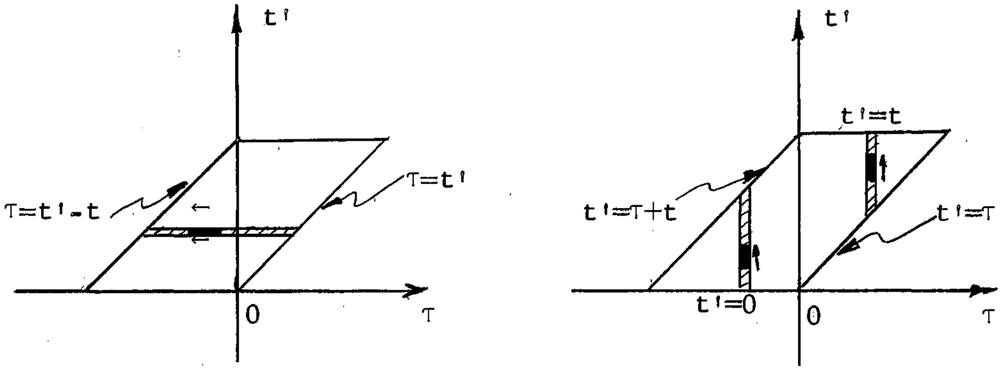

Fig. B-1. The domain of integration of $W_{mm'}$.

Thus,

$$\begin{aligned}
W_{mm'} &= \frac{1}{\hbar^2 t}\left[\int_{-t}^{0} d\tau\, \exp(-i\omega_{mm'}\tau)\int_{0}^{\tau+t} dt'\, H'_{mm'}(t')\, H'^*_{mm'}(t'-\tau)\right. \\
&\qquad \left. + \int_{0}^{t} d\tau \exp(-i\omega_{mm'}\tau)\int_{\tau}^{t} dt'\, H'_{mm'}(t')\, H'^*_{mm'}(t'-\tau)\right] \\
&= \frac{1}{\hbar^2 t}\left[\int_{-t}^{0} d\tau(\tau-t-0)\, \exp(-i\omega_{mm'}\tau)\, K_{mm'}\right. \\
&\qquad \left. + \int_{0}^{t} d\tau(t-\tau)\, \exp(i\omega_{mm'}\tau)\, K_{mm'}\right] \\
&= (1/\hbar^2)\int_{-t}^{t} K_{mm'}\, \exp(-i\omega_{mm'}\tau)d\tau + \frac{2}{\hbar^2 t}\int_{0}^{t} \tau K_{mm'}\cos(\omega_{mm'}\tau)d\tau .
\end{aligned}$$

---

[1] This interval should be long enough in order not to render the definition of correlation function meaningless.

$$\therefore \quad W_{mm'} = \frac{J(\omega_{mm'})}{\hbar^2} - \frac{2}{\hbar^2 t}\int_0^t \tau K_{mm'} \cos(\omega_{mm'}\tau)\,d\tau \ . \qquad \text{(B-22)}$$

Equation (B-22) is sometimes refered as the Abragam-Pound formula (49). So far we have not made any assumption on the nature of the perturbation and the shape of the correlation functions. Equation (B-22) is quite general, and its application is not limited to any particular form of interaction. Neither is it necessary that H' be a randomly fluctuating process.

In most of the physical systems which have been investigated in the literature at the present time, the correlation functions can be assumed of having an exponential form:

$$K(\tau) = K(0)\ \exp(-|\tau|/\tau_c), \qquad \text{(B-23)}$$

where τ_c is the correlation time. The condition of justification on this assumption has rarely been mentioned in the literature. A sufficient condition was proved in Chapter V. If assumption (B-23) is adopted, the power spectrum $J(\upsilon)$ can easily be shown as being of a Lorentzian shape.

$$\begin{aligned}
J(\upsilon) &= \int_{-\infty}^{\infty} < F(t)F^*(t) >_{av} \exp(-|\tau|/\tau_c)\exp(2\pi i\upsilon\tau)\,d\tau \\
&= < F(t)F^*(t) >_{av} \Big[\int_{-\infty}^{0} \epsilon^{\tau/\tau_c + 2\pi i\upsilon\tau}\,d\tau + \int_0^{\infty} \epsilon^{(2\pi i\upsilon - \frac{1}{\tau_c})}\,d\tau \Big] \\
&= < F^*(t)F(t) >_{av} \Big[\frac{1}{2\pi i\upsilon + (1/\tau_c)} + \frac{1}{2\pi i\upsilon - (1/\tau_c)} \Big] \\
&= < F^*(t)F(t) >_{av} \frac{2\tau_c}{1+4\pi^2\upsilon^2\tau_c^2} \ . \qquad \text{(B-24)}
\end{aligned}$$

The second term in (B-22) is in general believed of second order. Using assumption (B-23), we can easily show by integration by parts that this term is of the order of magnitude $2\tau_c/\hbar^2 t$. If the condition $\tau_c \ll t$ is fulfilled, we can then write

$$W_{mm'} = (1/\hbar^2)\, J(\omega_{mm'}) \ . \qquad \text{(B-25)}$$

Examples of Relaxation Time Formulas

The relation between relaxation times and transition probabilities varies from system to system. The ensemble average in (B-24) can be calculated under various conditions such as isotropicity, etc.. For the relaxation of proton magnetic moments in water, the relaxation effect due to the nearest proton (in the same molecule) can be calculated readily by taking r_{ij}, the interproton distance, as a constant "b". Under no external orientating forces such as electric field, etc., we may assume the inter-proton axes are distributed in a random, isotropic way such that we can substitute the time average by a spatial average, i.e.,

$$(1),\quad < F^*_0(t)F_0(t) >_{av} = \frac{1}{4\pi b^6}\int_0^{\pi}\int_0^{2\pi}(1-3\cos^2\theta)^2\sin\theta\, d\theta\, d\varphi$$

$$= -\frac{1}{2b^6}\int_{+1}^{-1}(1-3x^2)^2 dx = 4/5b^6 \ ; \qquad \text{(B-26a)}$$

$$(2),\quad < F^*_1(t)F_1(t) >_{av} = \frac{1}{4\pi b^6}\int_0^{\pi}\int_0^{2\pi}\cos^2\theta\sin^2\theta\sin\theta\, d\theta\, d\varphi$$

$$= -\frac{1}{2b^6}\int_{+1}^{-1}x^2(1-x^2)\, dx = 2/15b^6 \ ; \qquad \text{(B-26b)}$$

$$(3),\quad < F^*_2(t)F_2(t) >_{av} = \frac{1}{4\pi b^6}\int_0^{\pi}\int_0^{2\pi}(\sin^2\theta)^2\sin\theta\, d\theta\, d\varphi$$

$$= -\frac{1}{2b^6}\int_{+1}^{-1}(1-x^2)^2 dx = 8/15b^6 \ . \qquad \text{(B-26c)}$$

A typical and correct example between relaxation times and transition probabilities between various eigenstates of the unperturbed Hamiltonian can be found in Solomon's paper (50) for a system of spin = ½. He found T_1 and T_2 for identical spins as

$$\begin{aligned} \frac{1}{T_1} &= \frac{6}{20}\,\frac{h^2\gamma^4}{b^6}\left[\frac{\tau_c}{1+\omega^2\tau_c^2}+\frac{4\tau_c}{1+4\omega^2\tau_c^2}\right] \\ \frac{1}{T_2} &= \frac{3}{20}\,\frac{h^2\gamma^4}{b^6}\left[3\tau_c+\frac{5\tau_c}{1+\omega^2\tau_c^2}+\frac{2\tau_c}{1+4\omega^2\tau_c^2}\right] \end{aligned} \qquad \text{(B-27)}$$

The derivation of (B-27) from (B-25), (B-26a, b, c) is straight forward. Readers who are interested in the details of derivation should consult the original paper.

There remains the problem of determining the correlation time(s) through some established theorems in certain other fields, such as the Debye's theory of dielectric relaxation, etc. Also, some of the assumptions used in the derivation are not quite justifiable in certain special systems. All these deviations are still open for further research.

APPENDIX C

PINES AND SLICHTER PICTURE OF MAGNETIC RELAXATION

Two magnetic moment vectors located at different magnetic enviroments will change their relative phase angle as time goes by. If the enviroment is essentially constant, the phase shift $\Delta\varphi$ is proportional to time t, i. e.,

$$\Delta\varphi = \Delta\omega_{rl} t \qquad \text{(C-1)}$$

where $\Delta\omega_{rl} = \gamma\Delta B$. If $\Delta\varphi \sim 1$ rad. when $t = T_2^{rl}$, i. e., two vectors originally in phase will lose its coherence afterward, we have $\Delta\omega_{rl} T_2^{rl} \sim 1$,

$$T_2^{rl} \sim \frac{1}{\Delta\omega_{rl}} \qquad \text{(C-2)}$$

This is equation (1-1).

However, if the enviroment fluctuates rapidly, $\Delta\varphi$will not proportional to time t if t is comparatively longer than the average period of fluctuation, i. e., if $t \gg \tau_c$. In this case we can devide this time interval into n smaller intervals τ_c. During this interval τ_c, the enviroment has changed an amount of the order of itself. We can then write, if $\tau_c < < T_2^{rl}$, i.e., if $\Delta\varphi < < 1$,

$$\overline{\Delta\varphi^2} = n(\Delta\omega_{rl}\tau_c)^2 = (\Delta\omega_{rl})^2\tau_c t \qquad \text{(C-3)}$$

When $\overline{\Delta\varphi^2}$ reaches the order of 1 rad^2., t is then defined as the transverse relaxation time. Therefore, $1 \sim (\Delta\omega_{r1})^2\tau_c T_2$, or

$$1/T_2 \sim (\Delta\omega_{r1})^2\tau_c \tag{C-4}$$

This is equation (1-2).

From equation (B-27), Appendix B, we can easily obtain that

$$\frac{1}{T_1} \sim (\Delta\omega_{r1})^2\frac{2\tau_c}{1+\omega_o^2\tau_c^2} . \tag{C-5}$$

If $\omega_o^2\tau_c^2 \ll 1$, we have

$$1/T_1 \sim (\Delta\omega_{r1})^2(2\tau_c).$$

Since this is a rough derivation, we can conclude that $T_1 \cong T_2$ if $\tau_c \ll 1/\omega_o$, by comparing the last equation with equation (C-4).

APPENDIX D

SOME PROPERTIES OF "LUDOX" COLLOIDS[1]

The designations used in the classification of "Ludox" colloids are:

HS - high sodium stabilization level,
LS - low sodium stabilization level,
SM - seven millimicron (particle diameter),
AM - alumina modified, and
AS - ammonia stabilized.

Types of Colloid	HS	LS	SM	AM	AS
% Silica (as SiO_2)	30.1	30.3	15	30	30.0
Density (gm./c.c.)	1.212	1.211	1.097	1.209	1.206
% Na_2O (titratable)	0.31	0.10	0.10	0.13	0.25[2]
Chloride (as % NaCl)	0.04	0.002	0.001	0.007	0.001
Sulfate (as % Na_2SO_4)	0.05	0.010	0.003	0.006	0.005
pH (at 25°C)	9.9	8.3	8.5	9.1	9.6

(Continued on next page.)

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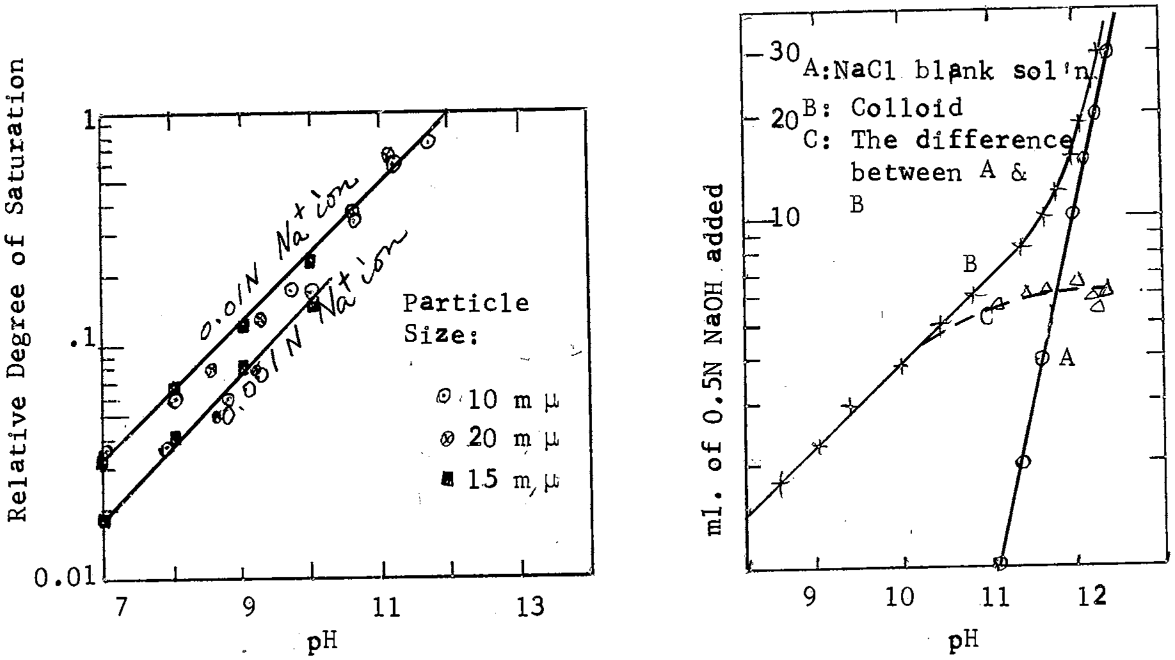
[1] Taken from duPont Product Information Bulletin.

[2] % ammonia.

[3] By B. E. T. method (nitrogen adsorption on dry solids). See Reference No. (51).

SOME PROPERTIES OF "LUDOX" COLLOIDS(Continued)

Type of Colloid	HS	LS	SM	AM	AS
Viscosity (c.p. at 25°C)	4	9	14	10	12
Approximate Particle Diameter (m μ)	14-15	14-15	7-9	14-15	14-15
Surface Area[3] (m^2/gm-silica)	195-215	195-215	350-400	195-215	195-215
Stability	Stable, except toward freezing, which causes irreversible precipitation. Freezing point 0°C.				



THE ADSORBED OH^- IONS ON THE COLLOIDAL SILICA SURFACES AS A FUNCTION OF pH

APPENDIX E

THE PROOF OF SOME THEOREMS ABOUT CORRELATION FUNCTIONS

The following is a proof about some of the important theorems on correlation functions stated in Chapter V.

Theorem I: The autocorrelation function is real and even.

The definition of cross-correlation function is

$$\varphi_{12}(\tau) = \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{T} f_1^*(t)\, f_2(t+\tau)dt. \qquad (E\text{-}1)$$

Change the variable τ to $-\tau$,

$$\varphi_{12}(-\tau) = \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{T} f_1^*(t)\, f_2(t-\tau)dt.$$

If we call $x = t - \tau$, then

$$\varphi_{12}(-\tau) = \lim_{T\to\infty} \frac{1}{2T} \int_{-T-\tau}^{T-\tau} f_1^*(x+\tau) f_2(x)dx\ . \qquad (E\text{-}2)$$

Since we are integrating from $-\infty$ to $+\infty$, the right hand side is just $\varphi_{21}^*(\tau)$. If $f_1 = f_2$, the right side of (E-2) is also $\varphi_{11}(\tau)$. By these two relations, we can show that $\varphi_{11}(\tau)$ is real and even.

Theorem II: The autocorrelation function approaches to zero as τ approaches to infinity, if $f_1(t)$ contains no d.c. or periodic components.

According to the ergodic theorem, the correlation function can be expressed as

$$\varphi_{11}(\tau) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} y_1 y_2 P(y_1)\ P(y_2/y_1;\ \tau)dy_1 dy_2.$$

As the time difference becomes very large, the system tends to "forget" its history ; therefore $P(y_2/y_1,\ \tau) \rightarrow P(y_2)$ as $\tau \rightarrow \infty$, if there is no hidden periodic or d.c. component, i.e., if there is no bias on the values of y. Therefore

$$\varphi_{11}(\tau) = \int_{-\infty}^{\infty} y_1 P(y_1)dy_1 \int_{-\infty}^{\infty} y_2 P(y_2)dy_2$$

$$= \bar{y}_1\ \bar{y}_2$$

If the random process is stationary, we can write $\bar{y}_1 = \bar{y}_2$, and the autocorrelation function is equal to the square of the mean value. If, furthermore, the mean value is equal to zero, then we have

$$\varphi_{11}(\infty) = 0.$$

Theorem III: The autocorrelation function is continuous everywhere if it is continuous at the origin.

Let us consider the autocorrelation function at any value τ, and the autocorrelation function at $\tau \pm \epsilon$:

$$\left|\varphi_{11}(\tau) - \varphi_{11}(\tau\pm\epsilon)\right| = \lim_{T\to\infty} \frac{1}{2T}\int_{-T}^{T} f_1(t)\left[f_1(t+\tau) - f_1(t+\tau\pm\epsilon)\right]dt$$

If we call

$$F(t) = f_1(t), \qquad \text{and} \qquad G(t) = f_1(t+\tau) - f_1(t+\tau\pm\epsilon),$$

then by the general Schwarz inequality, which states that if

$$\lim_{T\to\infty}\frac{1}{2T}\int_{-T}^{T}F^2(t)\,dt, \qquad \text{and} \qquad \lim_{T\to\infty}\frac{1}{2T}\int_{-T}^{T}G^2(t)dt$$

exist, then

$$\left|\lim_{T\to\infty}\frac{1}{2T}\int_{-T}^{T}F(t)G(t)dt\right|^2 \leqq \lim_{T\to\infty}\frac{1}{(2T)^2}\left\{\left[\int_{-T}^{T}F^2(t)dt\right]\left[\int_{-T}^{T}G^2(t)dt\right]\right\},$$

one obtains:

$$\left|\varphi_{11}(\tau) - \varphi_{11}(\tau\pm\epsilon)\right| \leqq \lim_{T\to\infty}\left[\frac{1}{2T}\int_{-T}^{T}f_1{}^2(t)dt\right]\left[\frac{1}{2T}\int_{-T}^{T}(f_1(t+\tau)-f_1(t+\tau\pm\epsilon))dt\right]$$

The integral in the first bracket is $\varphi_{11}(0)$, and the integral in the second bracket can easily be shown to be $\varphi_{11}(0) - 2\varphi_{11}(\pm\epsilon) + \varphi_{11}(0)$.

So

$$\left|\varphi_{11}(\tau) - \varphi_{11}(\tau\pm\epsilon)\right|^2 \leqq 2\,\varphi_{11}(0)\left[\varphi_{11}(0) - \varphi_{11}(\pm\epsilon)\right].$$

If the autocorrelation function is continuous at the origin, i.e., if we can make the quantity $\varphi_{11}(0) - \varphi_{11}(\pm\epsilon)$ as small as we please, we can also make $\varphi_{11}(\tau) - \varphi_{11}(\tau\pm\epsilon)$ as small as we please.

Theorem IV: The maximum value of the autocorrelation function occurs at the origin.

The value of the integral

$$\int_{-\infty}^{\infty}\left[f_1(t) \pm f_1(t+\tau)\right]^2 dt \tag{E-3}$$

is always greater than zero at $\tau \neq 0$ for any non-periodic function f_1. The equal sign is reserved for periodic functions. In order to make (E-3) zero, the integrand has to be zero everywhere, i.e., either $f_1(t) \equiv - f_1(t + \tau)$, or $f_1(t) \equiv f_1(t + \tau)$, which means either f_1 has a period of 2τ, or f_1 has a period τ.

Expand (E-3):

$$\int_{-\infty}^{\infty} f_1^2(t)dt + \int_{-\infty}^{\infty} f_1^2(t+\tau)dt \pm 2\int_{-\infty}^{\infty} f_1(t)f_1(t+\tau)dt > 0$$

Change the variable in the second integral above to $x = t + \tau$, and take average over the independent variable, we have

$$\varphi_{11}(0) + \varphi_{11}(0) > \pm 2\varphi_{11}(\tau)$$

i.e.,

$$\varphi_{11}(0) > |\varphi_{11}(\tau)| .$$

Theorem V: The autocorrelation function at the origin is the mean square value of $f_1(t)$.

This is evident by inspecting the definition of the autocorrelation function. We put this here because sometimes we want to know the physical meaning of $\varphi_{11}(0)$.

For more theorems, its proof, and applications, the reader is referred to the texts on Information Theory or The Statistical Theory of Communication.

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