A SPIN ECHO STUDY OF POLYION-COUNTERION INTERACTION

J. J. van der Klink

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door

JACQUES JOHANNES VAN DER KLINK
geboren te Schiedam in 1943

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Voor mijn vader

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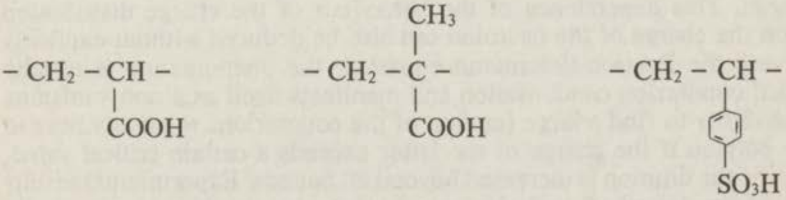
CONTENTS

CHAPTER I

Scope of Research

It is proposed in the present thesis to investigate the static and dynamic interactions of polyions and their counterions by non-thermodynamical means. Descriptions of these interactions will be in terms of linear-response theory (and mainly in terms of the oldest application of that theory, viz. the nuclear magnetic relaxation rates) rather than in terms of thermodynamic parameters. It is hoped that in this way a more clear-cut distinction can be made between static and dynamic aspects than is usually done. In this introductory Chapter an outline of this approach will be sketched without details; more extensive discussions and appropriate references will be found in the Introduction and Discussion sections of the individual Chapters. A review of experimental and theoretical techniques used will be found in Chapters II and III.

A polyelectrolyte then, is defined as any polymeric substance in which the monomeric units of its constituent macromolecules posses ionizable groups. In contrast to simple electrolytes, in which the sizes of the oppositely charged ions are similar in magnitude, a polyelectrolyte is always composed of a macroion in which the charged groups are interconnected by chemical bonds, together with an equivalent number of small oppositely charged counterions. The high charge of the macroion produces a strong electric field that attracts the counterions, and from this strong interaction virtually all of the unique properties of polyelectrolyte solutions result. Since, for suitably chosen counterions, the nuclear magnetic relaxation rates, which can be measured by spin echo methods, are determined by electric field gradients at the position of the counterions, these quantities provide a fairly direct insight in the electrical interaction and in the distribution of counterions around the polyion. In favorable cases also the selfdiffusion coefficient of the nuclei may be measured by the spin echo method: this possibility will be exploited to find the selfdiffusion coefficient of the polyion (for the counterion, results obtained by radiotracer methods are available in the litterature).



poly(acrylic acid) poly(methacrylic acid) poly(styrene-sulphonic acid)

Fig. 1. Repeating units of some polyacids.

Most of the results in the present thesis have been obtained on solutions of poly(acrylic acid), the structure of which, together with those of two other polyacids that have been used, is shown in Fig. 1. The degree of dissociation of the carboxyl groups of poly(acrylic acid) and poly-methacrylic acid) is small in pure water. On the addition of alkali, e.g. sodium hydroxide, the carboxyl groups are dissociated and the macroion gains an increasing number of negative charges, which to a good approximation is equal to the number of sodium counterions. So the charge on the macroion can be regulated by the amount of added alkali. The third example shown, poly(styrenesulphonic acid) is a strong acid, always completely dissociated into highly charged macroions and hydrogen ions when dissolved in water. In the following we consider specifically solutions of poly(acrylic acid), partially neutralized by sodium hydroxide.

Today's interpretations of experiments on polyelectrolyte solutions are mostly based either on the cylindrical solution of the Poisson-Boltzmann equation, or on the ion condensation concept (in fact the latter has been shown to be an asymptotic result of the former). Both take as starting point that the charged macroion can, at least sectionally, be described as a straight line charge, or as a uniformly charged cylinder (the so-called rigid-rod model).

The Poisson-Boltzmann equation states that the probability to find a counterion of charge e at a certain position $\boldsymbol{r}$ relative to the polyion is determined by a Boltzmann factor exp $(- e\,\psi\,(\boldsymbol{r})/kT)$ that contains the average electric potential ψ at $\boldsymbol{r}$, which in turn is connected to the probability distribution *via* Poisson's equation. The distribution function probably is a more useful quantity than the average potential found in this way, in the sense that the distribution function can be expected to predict correctly the average of certain properties of the counterion (e.g. the nuclear magnetic relaxation rates) that depend on the relative positions of the counterions with respect to the polyion, while the force derived from the average potential may not be very useful to determine the motion of the counterion with respect to the polyion.

The analytical solution of the Poisson-Boltzmann equation with cylindrical boundary conditions has a very remarkable property: it shows a quite different behaviour for low charge on the macroion than for high charge. This dependence of the behaviour of the charge distribution upon the charge of the nacroion can also be deduced without explicitly solving the Poisson-Boltzmann equation: the phenomenon is usually called counterion condensation and manifests itself as a non-vanishing probability to find a large fraction of the counterions relatively near to the polyion if the charge of the latter exceeds a certain critical value, even if the dilution is increased beyond all bounds. Experimental results are often described as being caused only by the 'free' part of the counterions, the 'condensed' part being regarded as effectively 'taken out of the solution'. As we will show, the nuclear magnetic relaxation rates of the counterions may be looked upon as caused by the condensed part only, the contribution of the free ions to the observed result being, under certain assumptions, negligible.

It is important to realize that the Poisson-Boltzmann and ion condensation theories are predictions about the average distribution of the counterions around a polyion; even if it is found that most of the counterions reside on the average very near to the polyion, this not necessarily implies that each individual ion stays there for a 'long' time (e.g. compared to the time that a sodium ion stays 'close to' a chloride ion in a NaCl solution). The assumption that will be made in the development of our theory of counterion nuclear magnetic relaxation in polyelectrolyte solutions is that the counterion stays in the ion cloud of a certain polyion for 10^{-10} seconds or longer. A sodium ion in a dilute solution of a simple salt travels (rootmeansquared) less than 10 Å in such a time.

We also investigate the nuclear magnetic relaxation rate of truly 'bound counterions', the counterion being deuterium in a heavy water solution of poly(acrylic acid) partially neutralized by NaOD. From comparison of the results of the sodium and deuterium nuclear magnetic relaxation we conclude that no association of sodium ions to specific carboxylic groups with a life time of the order 10^{-8} second (or longer) occurs.

To distinguish the concept of 'condensed' and 'bound' counterions, we might say that the former means 'being together', while the latter means 'moving together'. Usual interpretations of transport quantities (selfdiffusion, transference, conductance) do not make a clear distinction on this point. To find out what can be said about the polyion-counterion interaction as far as their motions are concerned, we develop a description based on the linear-response theory, rather than describing macroscopic flows of associated and non-associated species.

Within the framework of the linear-response theory clear connections of the Nernst-Einstein type exist between electrical and mass transport parameters. It is possible to derive from results available in the litterature the value of the selfdiffusion coefficient of the polyion, of which no direct experimental determination was available. The dependence of this latter quantity on degree of neutralization so predicted, is qualitatively confirmed by spin-echo measurements of the polyion's selfdiffusion coefficient. From these considerations it is concluded that the usual assumption of a 'bound' fraction in the treatment of conductivity and electrophoresis data is not generally justified.

CHAPTER II

Experimental Method

In the first part of this Chapter the interaction of the magnetic moment that is associated with non-zero spin, with external magnetic fields will be described. For more ample discussions of these interactions and actual descriptions of apparatus we refer to the literature. In the second part various aspects of experimental accuracy are discussed.

a) Basic Spin Echo Technique

The rate of change of the quantum-mechanical expectation value of an isolated nuclear magnetic moment in a magnetic field can be shown to be given by an equation that has the same structure as the classical equation of motion of a magnetic moment **μ** that has angular momentum $\mathbf{p} = \gamma^{-1}\mu$, in that magnetic field. We will therefore restrict ourselves to the classical description. In pulsed nuclear magnetic resonance techniques, the radio-frequent field during the pulse is so intense, that all other interactions of the nuclear magnetic moment may be neglected, so that the spin is effectively isolated. The classical equation of motion is

$$\frac{\mathrm{d}\boldsymbol{p}}{\mathrm{d}t} = \mu \times \boldsymbol{H} \qquad (1)$$

which gives

$$\frac{\mathrm{d}\mu}{\mathrm{d}t} = \mu \times (\gamma \boldsymbol{H}) \qquad (2)$$

This motion is a precession of μ around **H**, with angular velocity $\omega = -\gamma \mathbf{H}$. If the field **H** is the static (Zeeman) field $\mathbf{H_o}$, the precessional frequency $\omega_o = -\gamma H_o$ is called the Larmor frequency. So if we look at the motion of the magnetic moment from a coordinate system that rotates with angular velocity ω_o around $\mathbf{H_o}$, the magnetic moment effectively stands still.

If, in addition to the magnetic field $\mathbf{H_o}$, we have a second magnetic field $\mathbf{H}_1$ perpendicular to it, and rotating around $\mathbf{H_o}$ with exactly the Larmor frequency, this field $\mathbf{H}_1$ is static in the rotating coordinate system, and within this coordinate system again Eq. (2) applies with **H** replaced by $\mathbf{H}_1$. Thus, in the rotating coordinate system, the magnetic moment precesses around $\mathbf{H}_1$, and is turned away from $\mathbf{H_o}$, since $\mathbf{H}_1$ is perpendicular to $\mathbf{H_o}$. If we apply $\mathbf{H}_1$ only for a certain time τ such that

$$\omega_1 \tau = -\gamma H_1 \tau = \tfrac{1}{2}\pi \qquad (3)$$

(which is called a $\frac{1}{2}\pi$ pulse) we have, as seen in the rotating coordinate system, turned the magnetic moment to right angles with respect to $\mathbf{H_o}$, and it stands still after the removal of $\mathbf{H}_1$. This means that in the laboratory-fixed coordinate system we see the magnetic moment at right angles to $\mathbf{H_o}$, rotating around it with the Larmor frequency.

This is a non-equilibrium situation in *two* respects: firstly, each individual magnetic moment in a sample containing many nuclei is not aligned along $\mathbf{H}_0$, which does not minimize energy; secondly all individual magnetic moments rotate in phase with each other, which indicates an ordering that does not maximize entropy. Due to various possible interactions on the molecular level, some of which will be described in the next Chapter, the system of magnetic moments can be considered to be in a weak contact with a thermal reservoir (i.c. the molecular motions) that brings the system back to equilibrium: in principle at different rates for energy and for entropy. These processes are called longitudinal (or spin-lattice) and transversal (or spin-spin) relaxation respectively.

In a practical experiment there is still another reason why the observed rotation (a rotating magnetic moment can be observed by the voltage that it induces in a coil) does not persist: if the sample under study is so large that different parts of it sense slightly different Zeeman fields, due to imperfections of the magnet, the magnetic moments in the different parts rotate at slightly different rates, some faster than the average and others slower. Since what we observe is essentially the vector sum of the magnetic moments in these different regions, the voltage induced in the coil gradually decays to zero as the individual magnetic moments 'fan out' further and further. This is usually the reason for disappearance of the signal from liquid systems. It can be made to reappear however by a technique due to Hahn.

We consider the following sequence of events in the rotating coordinate system, with axes x, y, z and H_o along z:

a) Initially the system is in thermal equilibrium, and the magnetic moments are all parallel to $\mathbf{H}_0$.

b) We apply the field $\mathbf{H}_1$ along the axis x for the time τ determined by Eq. (3). τ is assumed short, so that relaxation and fanning-out during this time can be neglected: at the end of the pulse all magnetic moments are parallel to the y-axis.

c) Due to the inhomogeneity of H_o, the magnetic moments at a certain position in the sample rotate (in the x, y, z system) with an angular velocity

$$\Delta\omega = -\gamma \Delta H_o \tag{4}$$

If they do not change their position in the sample (i.e. if there is no thermal motion of the molecules which contain the nuclei under study) the angle $\alpha(t)$ between the direction of the magnetic moments at time t and the y-axis is given by

$$\alpha(t) = -\gamma \Delta H_o t \tag{5}$$

d) Now we apply the field $\mathbf{H}_1$ along the axis y for a time 2τ, so as to rotate all magnetic moments through an angle π; then the phase-angle with respect to the y-axis of the above-considered magnetic moments is

$$\alpha(t + 2\tau) = +\gamma \Delta H_o t$$

and they continue to rotate (in the x, y, z system) with the angular velocity of Eq. (4).

e. Thus we have for times $t' > t$, neglecting τ with respect to t:

$$\alpha(t') = \gamma \Delta H_o t - \gamma \Delta H_o (t' - \tau) \tag{6}$$

which for $t' = 2t$ gives $\alpha(2t) = 0$. Clearly at time $2t$ all magnetic moments are again aligned along the y-axis: their vector sum is no longer negligible and again a voltage is induced in the coil. This phenomenon is called a spin echo.

There are two reasons why the amplitude of the spin echo is less than that of the decay-signal after the first pulse: firstly, the relaxation effects, and secondly the diffusional motions of the spin-bearing molecules, due to which the 'refocusing effect' is not complete. Thus spin echo techniques can be used both to measure nuclear magnetic relaxation and selfdiffusion.

In the steps a) – e) described above, we have a method to measure the relaxation of the magnetization that is transversal to the Zeeman field during the time $2t$ after creation of a non-equilibrium situation (in equilibrium the transversal magnetization is zero). By repeating the experiment with different choises for $2t$, a complete 'transversal relaxation curve' can be obtained.

Of course the $\frac{1}{2}\pi$ pulse at the beginning of the experiment also creates a non-equilibrium situation for the component of the magnetization that is longitudinal to the Zeeman field. The longitudinal magnetization cannot induce voltages in a coil, since it does not precess. Its magnitude can only be measured by applying a second $\frac{1}{2}\pi$ pulse, a time t after the first; this second pulse creates a transversal magnetization, whose value is equal to that of the longitudinal magnetization immediately before the pulse. Again by repeating the experiment for different values of t, a complete 'longitudinal relaxation curve' is obtained.

Further details on spin echo techniques may be found in:

E. L. Hahn, Phys. Rev. **80** 580 (1950)
C. P. Slichter, Principles of Magnetic Resonance, (Harper and Row, New York 1964) Chapter 2
A. Abragam, The Principles of Nuclear Magnetism (Clarendon Press, Oxford 1961) Chapter III
W. G. Clark, Rev. Sci. Instr. **35** 316 (1964)

b) Signal averaging in pulsed low-resolution NMR

Introduction

Signal averaging as a means to improve sensitivity in CW and pulsed high-resolution NMR has received a thorough theoretical description, especially in the work of Ernst [1]. Although in low-resolution work the problems are comparatively simple, we are not aware of any more or less complete description of the theoretical optima for the various experimental parameters, and it was thought worthwile to pay some attention to this problem. The qualification 'low resolution' is taken to mean that the shape of a decay after a RF-pulse is primarily determined by the inhomogeneity of the magnetic field, and not by transversal relaxation or by the structure of a spectrum. An important consequence of this is that the time-dependence of the decay can be described as the product of an amplitude-factor, determined by pulse length and relaxation, and a shape-factor, determined solely by the distribution of the field-inhomogeneity over the sample and the gyromagnetic ratio of the nucleus under study.

The objective of our measurements is the determination of the magnitude of the spin-magnetization as a function of the time elapsed since the application of a disturbance. We will consider only sequences of two RF-pulses; the first serving as the disturbance, the second for monitoring the magnitude of the spin magnetization. There are essentially three (sets of) experimental parameters in these measurements:

1. The integral over the decay (or echo) is proportional to the amplitude-factor: it is therefore preferable to measure the integral over (a part of) the signal, instead of its maximum value only. Surely, extending the integration over too long times will only add noise; there should be an optimum value for the length of the integration-interval.
2. The signal-to-noise ratio can be further improved by determining the average value of the time-integral over several repetitive measurements, instead of performing a 'single shot' measurement. This will however considerably increase the total time needed for the experiment.
3. Since our objective is not the determination of the time-integrals themselves, but of their variation with RF-pulse spacing, we should make a proper choice for the range of pulse spacings used, in order to obtain the relaxation rates as accurate as is possible in a given total experimenting-time.

Principles of Operation

It is well known that an operational amplifier can be used to compute the time-integral over an input voltage [2]. The basic configuration is shown in fig. 1. At the start of the computation switch *S*2 is closed, and *S*1 is connnected to ground. Clearly then $V_{out} = 0$ and this stays so as long as the switches are left in that position. When both switches are toggled, the integration starts. This can be most easily explained by referring to the

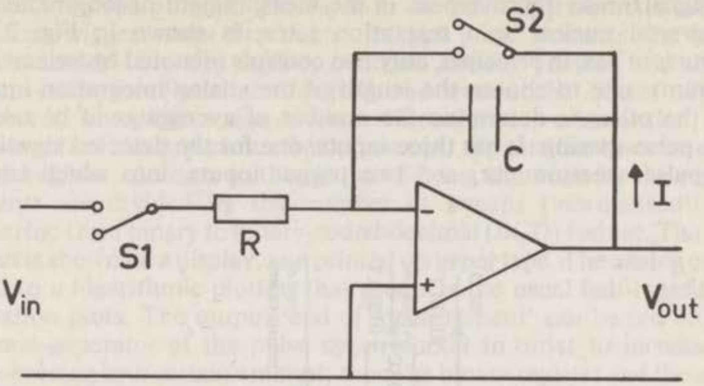


Fig. 1. Basic operational-amplifier integrator circuit.

well-known property of an operational amplifier with feedback that it tends to keep its inverting input at (virtual) ground potential. Therefore no net current flows into the inverting input, and such current as flows through *R* must also flow 'through' *C*, which implies

$$V_{out}(t) = \frac{Q(t)}{C} = \frac{\int_o^t I(t')\,\mathrm{d}t'}{C} = -\frac{1}{RC}\int_o^t V_{in}(t')\,\mathrm{d}t' \qquad (1)$$

Now, if after a certain time *T* we connect switch *S*1 to ground again, leaving *S*2 open, the output voltage will remain constant. If furthermore we choose *RC* such that *RC* = *T*, we have actually computed the average value of the input voltage. Of course, subsequently we might wait until the next signal of interest arrives, then connect *S*1 again for a time *T* to V_{in}, and have as output the average of two time-integrals (if we had taken from the beginning *RC* = 2*T*); and so on. This is the way a classical boxcar[3) integrator (more clearly called: a gated *RC*-integrator) works[4). For slow repetition rates, or averages over a large number of integrals, this scheme puts heavy demands on stability and leakage of the electronic components, especially of the (semiconductor) switches and integrating capacitor; in practice it is very hard to have *RC* exceed one second, and total measurement time is limited to a few hours. Therefore we prefer to bring V_{out} to digital form, and add the successively found values for the time-integral in a digital register. Between each pair of signal-integrals we perform an integration of 'baseline plus noise' over the same time interval and subtract this result in the register: therefore the average register contents are proportional to the amplitude of the signal with respect to the baseline. To do this with a classical boxcar, a dual system is needed[5). In our setup the maximum value of *RC* needed is of the order of 10^{-2} seconds, which is very easy to achieve, while the holding time of the binary register is essentially infinite.

The functional block diagram of an apparatus developed in our laboratory for signal/noise improvement in the measurement of longitudinal and transversal nuclear spin relaxation rates, is shown in Fig. 2. The instrument has, in principle, only two controls (denoted by 'select' in the diagram): one to choose the length of the analog integration interval, and the other to determine the number of averagings to be taken at each pulse-spacing. It has three inputs: one for the detected signal from the pulse spectrometer, and two trigger inputs, into which triggers,

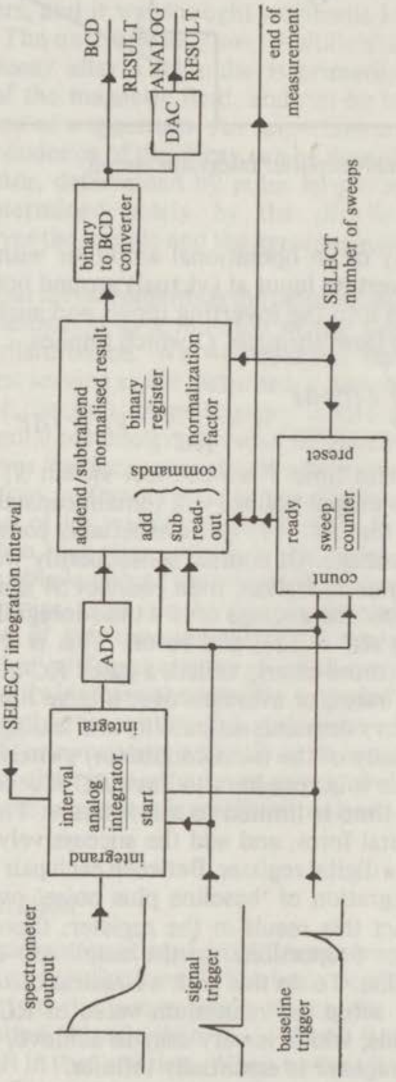


Fig. 2. Functional Block Diagram of Digital Boxcar Integrator.

derived from the program generator in the pulse spectrometer are fed. The first trigger starts the 'signal integral', and controls the binary register to add it to the register contents already present; the second trigger starts the 'baseline integral' and makes the binary register subtract it. The triggers also advance a binary sweep counter that, upon completion of the preset number of sweeps, triggers the transfer of the binary register contents to the output. During this transfer the register contents are divided by the number of sweeps ('normalised'), and converted from binary to binary-coded-decimal (BCD) format. The BCD output is shown on a display, and printed on paper tape. The analog output is fed to a logarithmic plotter, that products the usual half-logarithmic relaxation plots. The output 'end of measurement' can be fed into the program-generator of the pulse spectrometer in order to increase the pulse-spacing by a certain amount; then the binary register and the sweep counter are reset, and a new measurement is started. Thus the instrument can record a complete relaxation curve without any attendance.

Choice of the integration-interval

If we always take $RC = T$, the input-output relation of our integrator is

$$V_{\mathrm{out}}\,(t) = \frac{1}{T} \int_{t-T}^{t} V_{\mathrm{in}}\,(t')\,\mathrm{d}t' \tag{2}$$

this may also be written as a convolution:

$$V_{\mathrm{out}}\,(t) = \int_{-\infty}^{+\infty} V_{\mathrm{in}}\,(t')\,h\,(t-t')\,\mathrm{d}t' \tag{3}$$

Where $h\,(t)$ is a gating function such that

$$h\,(t) = \begin{cases} \frac{1}{T} & \text{for } 0 \leqslant t \leqslant T \\ 0 & \text{otherwise} \end{cases} \tag{4}$$

If the input voltage contains white noise up to a frequency ω_c that is high compared to $2\,T^{-1}$ and having a Gaussain distribution, it can be shown that the ratio of mean-squared input noise to mean-squared output noise is given by[6)]

$$\frac{n_{\mathrm{out}}^2}{n_{\mathrm{in}}^2} = \frac{\pi}{\omega_c} \int_{-\infty}^{+\infty} h^2\,(t)\,\mathrm{d}\,t = \frac{\pi}{\omega_c\,T} \tag{5}$$

If we add the noise-output of the integrator $2\,N$ times in a digital register of sufficient resolution (see next) the mean-squared noise in the digital output is

$$n_{\mathrm{dig}}^2 = 2\,N \;\; n_{\mathrm{out}}^2 = \frac{\pi}{\omega_c}\,\frac{2\,N}{}\;n_{\mathrm{in}}^2 \tag{6}$$

After N measurements of the 'signal' integral and N measurements of the 'baseline' integral (that is, for simplicity, assumed to be zero on the average) the average register contents are

$$S_{\mathrm{dig}} = N\, S_{\mathrm{out}} = \frac{N}{T} \int_0^T S_{\mathrm{in}}(t')\,\mathrm{d}t' \tag{7}$$

and the signal-to-noise ratio in our register is

$$\frac{S_{\mathrm{dig}}}{n_{\mathrm{dig}}} = \left(\frac{2\pi}{\omega_c}\, n_{\mathrm{in}}^2\right)^{-\frac{1}{2}} N^{\frac{1}{2}}\, T^{-\frac{1}{2}} \int_0^T S_{\mathrm{in}}(t')\,\mathrm{d}t' \tag{8}$$

(It can be shown that a classical boxcar performs nearly as well, provided its time constant RC is chosen equal to 0.77 NT.)

Thus, in order to get a maximal signal-to-noise ratio we must choose T such that

$$\frac{1}{T} \int_0^T S_{\mathrm{in}}(t')\,\mathrm{d}t' = 2\, S_{\mathrm{in}}(T) \tag{9}$$

(which can be shown to be the optimal choice for a classical boxcar as well).

Since the shaps $S_{\mathrm{in}}(t)$ of the signal is independent of the particular sample used, the time T may be determined with the aid of a sample that contains a large quantity of the nuclei of interest, so that the signal $S_{\mathrm{in}}(t)$ may be observed directly on an oscilloscope and compared with

the readout $\frac{1}{T} \int_0^T S_{\mathrm{in}}(t')\,\mathrm{d}t'$ of the averaging device.

Digital resolution.

If the digital averaging of subsequent time-integrals is to work properly, the data handling has to fulfill certain requirements with respect to its resolution. Specifically, the digitizing process itself should not contribute to the noise in the digitized result. This problem has been considered by Ernst[7)]. There is however another, and more severe, requirement on the resolution of the analog-to-digital converter (ADC) if it is desired to have the average value of the register output after 2^N *) averagings independent of N. Then we will have to divide the register contents by 2^N prior to readout, and care should be taken that no significant information is lost by 'rounding-off errors' in the division. This implies that a relation exists between N and the number of bits M of the ADC, which of course is equal to the (maximum) number of bits in the final result after division. In the following, input voltages to the ADC will be measured in unities of the analog voltage corresponding to one count of the ADC.

Let the average value of the signal input voltage be 2^s. Let the rms noise voltage be 2^n. If we are willing to accept four chances in 10^5 that a single voltage is so large that it cannot be properly processed by the ADC, we must amplify (or attenuate) the total input voltage in such a way that

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*) In this section only all numbers are in binary notation.

$$2^s + 2^{n+2} = 2^M \tag{10}$$

(of course these considerations apply to the largest signal that occurs during the determination of a relaxation rate; in this section we neglect the measurement of the baseline, which is taken to be zero).
Let the desired signal-to-noise ratio after 2^N measurements be 2^p, then the input voltage has to fulfill the condition:

$$2^S / 2^n = 2^p / (2^N)^{\frac{1}{2}}$$

or

$$2^S = 2^{p+n-\frac{N}{2}} \tag{11}$$

and, from the fact that the total input is adjusted so as to use the full analog range of the ADC

$$2^n = 2^M \, (2^{p-\frac{N}{2}} + 2^2)^{-1} \tag{12}$$

After 2^N averagings, the rms count in the register due to noise is

$$2^{n+\frac{N}{2}} = 2^N \, (2^{p-M} + 2^{2-M+\frac{N}{2}})^{-1} \tag{13}$$

If the division by 2^N of the total register contents is not to introduce rounding-off errors, the noise-count in the register has to be greater than 2^N, or

$$2^{p-M} + 2^{2+\frac{N}{2}-M} < 1 \tag{14}$$

This condition will certainly be met if we have simultaneously

$$p - M < -1 \textit{ and } 2 + \frac{N}{2} - M < -1$$

which can be written as

$$\mathrm{M} > p + 1 \textit{ and } M > 3 + \frac{N}{2} \tag{15}$$

For ‘single-shot’ measurements the former condition will prevail, and for multiple averagings the latter. In our machine $N_{\max} = 13$ and $M = 10$.

Choice of RF-pulse spacings

The minimal number of measurements required for the determination of a relaxation rate (assumed exponential) are: Two measurements of the amplitude of the magnetization at different pulse-spacings, plus a determination of the ‘baseline’, i.e. the value of the magnetization for very long times. If we measure these amplitudes at times t_1 and t_2 after the disturbance, how should the interval $T = t_2 - t_1$ be chosen, in order that the relaxation rate R', determined from

$$R' = \frac{1}{T} \log \frac{A_1}{A_2} \tag{16}$$

where A_1 and A_2 are the measured voltages with respect to the baseline, is as accurate as possible?

If the amplitudes A_i consist of a signal part M_i, and a noise part that is independent of M, and has a Gaussian distribution with variance n^2, we have for the variance l_i^2 in ($\log A_i$) due to the variance n^2 in the A_i themselves

$$l_i^2 = M_i^{-2}\, n^2 \tag{17}$$

provided that n is small compared to M_i, since in that case

$$\log (M_i + n) = \log M_i + M_i^{-1}\, n \tag{18}$$

The variance n'^2 in ($\log A_1 - \log A_2$) is then

$$n'^2 = l_1^2 + l_2^2 = (M_1^{-2} + M_2^{-2})\, n^2 = M_1^{-2}\, n^2\, (1 + \exp 2RT) \tag{19}$$

where the last equation comes from the observation that $M_2 = M_1 \exp(-RT)$ due to the assumption of exponential relaxation rates. If we want to minimize the uncertainty in R', determined according to Eq. (16) we should minimize the ratio n'/RT at a given value of n (T is a very accurately known quantity).

It is required to determine the time T such that

$$\frac{n'}{RT} = \frac{n}{M_1\, RT}\,(1 + \exp 2RT)^{1/2} \tag{20}$$

is minimal. The figure of merit clearly is the quotient of the relative error in R and the noise-to-signal ratio of the first point

$$q = \left(\frac{n'}{RT}\right)\left(\frac{n}{M_1}\right)^{-1} = (RT)^{-1}\,(1 + \exp 2\,RT)^{1/2} \tag{21}$$

The dependence of q on RT is shown in fig. 3; it has a minimum value $q = 2.9$ for $RT = 1.1$.

If the noise-to signal ratio is too high, we will have to use time-averaging in order to improve this figure. Now if we are allotted a total measurement time of N shots, performing in each shot an ‘amplitude’ and a ‘baseline’ measurement, how are we to divide these shots over the various RF-pulse spacings? In order to keep the distribution of the noise in each averaged result identical, we must perform an equal number of shots for each RF-pulse setting. It is easy to see that the relative error in R, as determined from any pair of RF-pulse spacings other than as chosen above, is worse than in this ideal case. But clearly the advantage of the use of several RF-pulse spacings is the possibility to detect systematic errors and/or non-exponential behaviour: we will now see what price in accuracy we have to pay for this additional information.

Let us therefore perform measurements of the amplitude (with respect to the ‘baseline’) at $2K$ different, equally spaced time points. (We restrict ourselves to equal spacing, since the commercial instrument that is most widely used for spin-echo measurements has a possibility of automatically increasing the pulse distance by constant amounts.) We wish to determine what time $T \approx 2K\,d$ these points should span, in order that the relative accuracy in R, at constant K, be maximal. Now of course

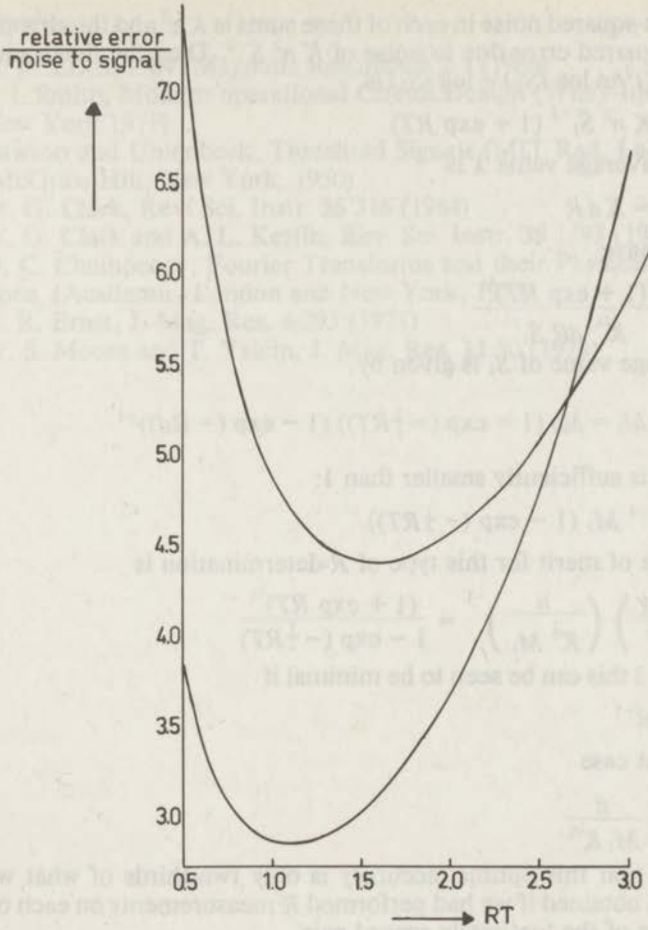

Fig. 3. Relative error in determination of *R*, divided by the noise-to-signal ratio of the first measured point, as a function of time-span of measured points. Upper curve: series of equidistant points. Lower curve: two points only.

the relative accuracy is a property of the data that is independent of how the results are extracted from them. We will use the following procedure [8]: We form the sum S_1 of the first K amplitudes, and the sum S_2 of the second K amplitudes:

$$S_1 = \sum_{i=1}^{K} A_i \qquad S_2 = \sum_{i=K+1}^{2K} A_i$$

Because of the equal spacing we have for the averages, denoted by a bar:

$$\bar{S}_2 = \bar{S}_1 \exp(-Kd)$$

The mean-squared noise in each of these sums is $K n^2$ and thus log *(S)* has a mean squared error due to noise of $K n^2 S^{-2}$. Then the mean squared error $(\Delta X)^2$ in log (S_1) − log (S_2) is

$$(\Delta X)^2 = K n^2 \bar{S}_1^{-2} (1 + \exp RT) \tag{22}$$

while its average value X is

$$X = \tfrac{1}{2} RT = K d R \tag{23}$$

Thus we have

$$\frac{\Delta X}{X} = \frac{n (1 + \exp RT)^{1/2}}{K^{1/2}\, dR\, \bar{S}_1} \tag{24}$$

The average value of S_1 is given by

$$\bar{S}_1 = \sum_{i=1}^{K} M_i = M_1 (1 - \exp(-\tfrac{1}{2} RT))(1 - \exp(-Rd))^{-1} \tag{25}$$

and if Rd is sufficiently smaller than 1:

$$\bar{S}_1 = (Rd)^{-1} M_1 (1 - \exp(-\tfrac{1}{2} RT)) \tag{26}$$

The figure of merit for this type of R-determination is

$$q' = \left(\frac{\Delta X}{X}\right) \left(\frac{n}{K^{\frac{1}{2}} M_1}\right)^{-1} = \frac{(1 + \exp RT)^{1/2}}{1 - \exp(-\tfrac{1}{2} RT)} \tag{27}$$

From fig. 3 this can be seen to be minimal if

$$T \approx 1.62\, R^{-1} \tag{28}$$

and in that case

$$\frac{\Delta X}{X} = 4.4 \frac{n}{M_1 K^{1/2}} \tag{29}$$

It is seen that this optimal accuracy is only two-thirds of what would have been obtained if we had performed K measurements on each of the amplitudes of the 'optimally spaced pair'.

Now if we are to perform N sweeps, and thus $N/2K$ sweeps per point:

$$\frac{\Delta X}{X} = 6.25 \frac{n_o}{M_1 N^{1/2}} \tag{30}$$

where n_o/M_1 is the single-shot noise-to-signal ratio in the first point. So, if n_o/M_1 equals 1, the final error in R is 1 percent after 3.9×10^5 sweeps in total, or e.g. 97 points, each averaged 2^{12} times, and spanning a time of approximately $1.6\, R^{-1}$.

Our result for the optimum interval disagrees with that of Moore and Yalcin[8)], apparently because they treat the noise as decreasing with the square-root of the time-interval, instead of with the square root of the number of points taken in that interval. This would only be the case if the spacing d could not be freely chosen; consequently their attainable accuracy is not given in terms of the same 'first point noise-to-signal ratio' as ours.

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CHAPTER III

Nuclear Magnetic Relaxation and Selfdiffusion in Liquids

Introduction[1-5]

In spin echo[6] work the quantity of interest is the expectation value **M** of the net nuclear magnetization $\mathbf{m}_N$ of a sample containing nuclei of non-zero spin in a magnetic field

$$M = \mathrm{Tr} < \rho_N \, m_N > \tag{1}$$

where ρ_N is the density matrix for the *N*-particle system under study. In liquids the coupling between different nuclei and the coupling of the nuclei with their molecular surroundings are usually weak compared to their Zeeman energy and we may write

$$M = \mathrm{Tr} <\rho \, m> \tag{2}$$

where ρ is a single-spin density matrix and **m** a single-spin magnetic moment operator (in some cases it is necessary to consider two- or three-spin systems), and the brackets indicate a classical ensemble average over molecular surroundings.

By applying an external disturbance (i.c. a pulse of radiofrequent radiation) we can drive **M** away from its equilibrium value. Still, in that case the deviation from equilibrium of the total system (nuclear spins plus their molecular surroundings) is very small, and the return to equilibrium of **M** obeys simple linear laws. In typical experiments the changes in energy of the spin system are smaller than 10^{-5} NkT. In most cases the return to equilibrium can be described by two transport parameters, the longitudinal and transversal relaxation rates. That we have two rather than a single transport parameter can be appreciated from the fact that the time evolution of the component of **M** that is parallel to the Zeeman field is not necessarily the same as that for the component transversal to the field, due to the commutation rules for the spin.

The interest of transport parameters usually does not lie simply in their values, but in the possibility of relating them to models for behaviour on the molecular scale. From the very fact that the spin system may be driven far away from equilibrium without affecting the equilibrium of the *total* system to any extent, the nuclear magnetic relaxation rates and selfdiffusion coefficient are ideally suited for this purpose.

After the disturbance has been switched off, **M** will return to its equilibrium value *via* the (weak) coupling of **m** (the single-nucleus magnetic moment operator) to its molecular surroundings. In most cases the time evolution of the transversal component has also a part due to the strong coupling to the Zeeman field, which is seldom perfectly spatially homogeneous over the collection of *N* spins. This part can, by suitable techniques, be separately measured and in fact yields the nuclear selfdiffusion coefficient.

In first instance we will consider only the weak interaction with the molecular surroundings. Due to the rapid molecular motion this interaction will vary in time, and at any moment be different for each member of the ensemble, while the ensemble-average is zero (for the more usual types of interaction, that depend on orientation of the molecules, this follows from the isotropy of a liquid system). It turns out that in all cases of interest the interaction Hamiltonian H_1 may be written as a sum of products of a spin operator with a (classical) 'lattice'-function, that contains time-dependent coordinates.

By approximation of the time evolution of **M** due to H_1 up to the second order (the first-order contribution being zero, since H_1 vanishes on the average) we will find the time evolution enclosed in the timecorrelation of the 'lattice function'; more precisely: in the components of the power spectrum of the lattice function at zero, one and two times the Larmor frequency, the restriction on the number of frequencies arising from the fact that we consider an approximation up to second order. Although it often occurs that the power spectrum is essentially flat over the frequency range of interest, this is by no means the general case, and generally the observed relaxation rates depend on the magnitude of the Zeeman field.

From the wide variety of possible couplings of the nuclear spin with its molecular surroundings we will encounter only two types: the electric quadrupolar and the magnetic dipolar coupling.

The Quadrupole Hamiltonian $^{7)}$

The electric multipole expansion of the charge distribution in nuclei with spin $I > \frac{1}{2}$ contains more terms then the point charge (monopole) term only. From parity considerations it can be shown that only the even multipoles can have non-zero values; so the first (and, in practice, only) correction to the point charge is the electric quadrupole term. Let us suppose that such a nucleus is placed in an electric potential V due to charges outside the nucleus. By expansion of V in a Taylor series at the position of the nucleus, whose center is assumed to be in the origin:

$$V(\mathbf{r}) = V(0) + \sum_j r_j \left(\frac{\partial V}{\partial r_j}\right)_{r=0} + \tfrac{1}{2}\sum_{j,k} r_j r_k \left(\frac{\partial^2 V}{\partial r_j\, \partial r_k}\right)_{r=0} \qquad (3)$$

and we can neglect the higher order terms since their contribution to the electrostatic energy of the nucleus in this potential can be neglected. We may write the last term as

$$\tfrac{1}{2}\sum_{j,k} r_j r_k V_{jk} = \tfrac{1}{2} \sum_{jk} V_{jk} \left(r_j r_k - \tfrac{1}{3} r^2\, \delta_{j\cdot k}\right) \qquad (4)$$

because the potential has to obey Laplace's equation. Here V_{jk} has been used to denote the second partial derivatives in the origin. If we were to consider the nucleus as a classical charge distribution, the electrostatic energy would be given by

$$E = V(0) \int \rho \, \mathrm{d}r + \tfrac{1}{2} \sum_{jk} V_{jk} \int \rho \, (r_j r_k - \tfrac{1}{3} r^2 \delta_{jk}) \, \mathrm{d}r \tag{5}$$

the second term being the quadrupole energy E_Q. Actually the nucleus is to be described by quantum mechanics; defining a set of operators Q_{jk} by

$$eQ_{jk} = e \sum_i \left[(r_j)_i \, (r_k)_i - \tfrac{1}{3} \, (r^2)_i \, \delta_{jk} \right] \tag{6}$$

where the index i runs over all protons in the nucleus, the r_j are position operators (x, y, z), and e is the protonic charge, we have

$$E_Q = \tfrac{1}{2} e \sum_{jk} V_{jk} < Q_{jk} > \tag{7}$$

where the angular brackets denote an expectation value.

Now the Q_{jk} are elements of a symmetric traceless tensor as can readily be verified from Eq. (6): hence only five of them are independent. To bring this out more clearly, we will determine the quadrupolar energy in a spherical coordinate system instead of in Cartesians, as was done in Eq. (7). Let us define an operator Q with elements Q_m, where $m = 0, \pm 1, \pm 2$, as follows:

$$\begin{aligned}
Q_0 &= \tfrac{1}{2} \sum_i (3 z_i^2 - r_i^2) = \left(\frac{4\pi}{5}\right)^{\frac{1}{2}} \sum_i r_i^2 \, (Y_{20})_i \\
Q_{\pm 1} &= \mp \tfrac{1}{2} (6)^{\frac{1}{2}} \sum_i z_i \, (x_i \pm i y_i) = \left(\frac{4\pi}{5}\right)^{\frac{1}{2}} \sum_i r_i^2 \, (Y_{2\pm 1})_i \\
Q_{\pm 2} &= \tfrac{1}{4} (6)^{\frac{1}{2}} \sum_i (x_i \pm i y_i)^2 = \left(\frac{4\pi}{5}\right)^{\frac{1}{2}} \sum_i r_i^2 \, (Y_{2\pm 2})_i
\end{aligned} \tag{8}$$

where we have used the normalised spherical harmonics[8)]

$$\begin{aligned}
Y_{20} &= \left(\frac{5}{4\pi}\right)^{\frac{1}{2}} \tfrac{1}{2} (3 \cos^2 \vartheta - 1) \\
-Y^*_{2-1} = Y_{21} &= -\left(\frac{5}{4\pi}\right)^{\frac{1}{2}} \tfrac{1}{2} (6)^{\frac{1}{2}} \sin \vartheta \cos \vartheta \exp (i\varphi) \\
Y^*_{2-2} = Y_{22} &= \left(\frac{5}{4\pi}\right)^{\frac{1}{2}} \tfrac{1}{4} (6)^{\frac{1}{2}} \sin^2 \vartheta \exp (2 i \varphi)
\end{aligned} \tag{9}$$

It can be seen that the components Q_{jk} can be expressed in the Q_m as

$$\begin{aligned}
Q_{xy} &= Q_{yx} = i \, (6)^{-\frac{1}{2}} \, (Q_{-2} - Q_{+2}) \\
Q_{xz} &= Q_{zx} = (6)^{-\frac{1}{2}} \, (Q_{-1} - Q_{+1}) \\
Q_{yz} &= Q_{zy} = i \, (6)^{-\frac{1}{2}} \, (Q_{-1} + Q_{+1}) \\
Q_{zz} &= \tfrac{2}{3} Q_0 \\
Q_{yy} &= -(6)^{-\frac{1}{2}} \, (Q_{-2} + Q_{+2}) - \tfrac{1}{3} Q_0 \\
Q_{xx} &= (6)^{-\frac{1}{2}} \, (Q_{-2} + Q_{+2}) - \tfrac{1}{3} Q_0
\end{aligned} \tag{10}$$

For the field gradient tensor we proceed in a similar way and define the components F_m as follows:

$$
\begin{aligned}
F_0 &= \tfrac{1}{2} V_{zz} \\
F_{\pm 1} &= \mp (6)^{-\frac{1}{2}} (V_{zx} \pm i\, V_{zy}) \\
F_{\pm 2} &= \tfrac{1}{2} (6)^{-\frac{1}{2}} (V_{xx} - V_{yy} \pm 2\, i\, V_{xy})
\end{aligned}
\tag{11}
$$

which can be shown to be the irreducible representation of the field gradient tensor.

Then the quadrupole Hamiltonian is given by

$$H_Q = \sum_{m=-2}^{+2} (-1)^m F_{-m} Q_m \tag{12}$$

and its expectation value yields the quadrupolar energy according to Eq. (7).

Now, from the definition of the Q_m it can be seen that they transform under rotation as the second rank spherical harmonics. Then the set Q_m forms by definition an irreducible tensor operator of rank two, and, according to the Wigner-Eckhardt theorem[7, 8], the matrix elements of the Q_m are proportional to those of the second-rank irreducible tensor operator A_m formed from the components of the total nuclear angular momentum operator **I** (usually called the spin operator of the nucleus; it is, however, composed of spin *and* orbital momentum of the nucleons). From the similarity of the commutation relations of components of **I** and $\mathbf{r}_i$ with I_x, I_y and I_z:

$$
\begin{aligned}
[I_x, y_i] &= i\, z_i \\
[I_x, I_y] &= i\, I_z
\end{aligned}
\tag{13}
$$

(which is another way of stating that **I** and **r** have similar rotation properties) it follows that the A_m can be formed from the Q_m by replacing x by I_x, y by I_y, and z by I_z, and multiplying by a constant. Denoting the proportionality constant by $Q/I(2I-1)$ we have

$$
\begin{aligned}
A_0 &= [eQ/2I(2I-1)]\,[3 I_z^2 - I^2] \\
A_{\pm 1} &= \mp \tfrac{1}{2} (6)^{\frac{1}{2}} [eQ/2I(2I-1)]\,[I_2 I_\pm + I_\pm I_z] \\
A_{\pm 2} &= \tfrac{1}{2} (6)^{\frac{1}{2}} [eQ/2I(2I-1)]\, I_\pm^2
\end{aligned}
\tag{14}
$$

where $I_\pm = I_x \pm i I_y$. The quantity eQ is called 'the' quadrupole moment of the nucleus. Eq. (12) becomes

$$H_Q = \sum_{m=-2}^{2} (-1)^m F_{-m} A_m \tag{15}$$

The Dipolar Hamiltonian[1]

Nuclei of non-zero angular momentum **I** possess a magnetic moment μ that is collinear with **I**. The basic reason for this collinearity is again explained by the Wigner-Eckhardt theorem: since both form an irreducible tensor operator of rank one, their matrix elements are simply related by a proportionality constant, which, measured in units $\hbar$, is denoted by γ, and called the gyromagnetic ratio.

We consider the energy E'_d of a magnetic moment μ in the field of a second, similar magnetic moment μ':

$$E'_d = -\mu \cdot \left[\frac{3\,(\mu' \cdot r)\, r - \mu'\, r^2}{r^5} \right] \tag{16}$$

where $\mathbf{r}$ is the vector from the position of μ to the position of μ'. This equation may be rewritten as

$$E'_d = -r^{-5}\,(3 \sum_{jk} \mu_j\, \mu'_k\, r_j\, r_k - \sum_{jk} \mu_j\, \mu'_j\, r^2{}_k) \tag{17}$$

where the indices j, k denote Cartesian components. Defining two tensors B and M by

$$B_{jk} = r_j\, r_k - \tfrac{1}{3} r^2\, \delta_{jk} \qquad M_{jk} = \mu_j\, \mu'_k \tag{18}$$

we have

$$E'_d = -3\, r^{-5} \sum_{jk} B_{jk}\, M_{jk} \tag{19}$$

The total dipolar energy of this system of two magnetic moments is $E_d = 2\, E'_d$.

Clearly the B_{jk} are elements of a symmetric traceless tensor; in fact they are the same as those for the tensor Q_{jk} defined in Eq. (6), if there the summation index i is left out. Thus, by comparison with Eq. (8) the irreducible representation of B is found to be

$$\begin{aligned} B_0 &= \left(\frac{4\pi}{5}\right)^{\frac{1}{2}} r^{-3}\, Y_{20} \\ B_{\pm 1} &= \left(\frac{4\pi}{5}\right)^{\frac{1}{2}} r^{-3}\, Y_{2\pm 1} \\ B_{\pm 2} &= \left(\frac{4\pi}{5}\right)^{\frac{1}{2}} r^{-3}\, Y_{2\pm 2} \end{aligned} \tag{20}$$

With the irreducible representation of the tensor M, using the Wigner-Eckhardt theorem to replace μ with $\gamma\, \hbar\, \mathbf{I}$:

$$\begin{aligned} M_0 &= -\gamma^2\, \hbar^2\, [3\, I_z\, I'_z - I \cdot I'] \\ M_{\pm 1} &= \pm\, \gamma^2\, \hbar^2\, \tfrac{1}{2}\, (6)^{\frac{1}{2}}\, [I_z\, I'_\pm + I_\pm\, I'_z] \\ M_{\pm 2} &= -\gamma^2\, \hbar^2\, \tfrac{1}{2}\, (6)^{\frac{1}{2}}\, [I_\pm\, I'_\pm] \end{aligned} \tag{21}$$

The total dipolar energy is given by the expectation value of the dipolar Hamiltonian

$$H_d = \sum_{m=-2}^{2} (-1)^m\, B_{-m}\, M_m \tag{22}$$

The main reason for writing the Hamiltoninas H_Q and H_d as a contraction of a classical irreducible tensor (V resp. B) and an irreducible tensor operator (Q resp. M) lies in the fact that the rotation properties of their components are well known[8)] and relatively simple. For the tensor operators this implies that their commutation rules with the components of **I** are simple: this is an advantage because we are interested in the time evolution of the expectation value of the components of **I**. The irreducible representation of the classical tensors is particularly suitable in those cases where their values with respect to a laboratory fixed coordinate system are changed by rotational motion of the molecular surroundings. From a proper model for these molecular motions the changes in the values of the tensor components may be computed with the aid of their known rotation properties.

The Lattice Functions

The coupling Hamiltonians H_Q and H_d for each spin (or spin pair) vary in time due to the fact that the spin-part is space quantized (by the strong coupling to the Zeeman field) while the molecular part contains coordinates that, as seen from a coordinate system that is fixed with respect to the Zeeman field, are changed by thermal motion.

According to the general theory of nuclear magnetic relaxation in liquids, that we will not describe here, the return to equilibrium of the nuclear magnetization after a disturbance is governed by the power spectra of the random lattice functions F_m (Eq. (11)) for quadrupole relaxation or B_m (Eq. (20)) for dipolar relaxation. Furthermore it can be shown[9)] that in the case where the main Hamiltonian, that governs the *molecular* motion, is invariant under rotations, the power spectra of lattice functions with different m are equal to each other. Thus the nuclear magnetic relaxation is determined by

$$J(\omega) = \tfrac{1}{2} \int_{-\infty}^{+\infty} < F_o(t') F_o(t' + t) > \exp(i\omega t)\, \mathrm{d}t \tag{23}$$

for quadrupole relaxation, and

$$J(\omega) = \tfrac{1}{2} \int_{-\infty}^{+\infty} < B_o(t') B_o(t' + t) > \exp(i\omega t)\, \mathrm{d}t \tag{24}$$

for dipolar relaxation.

These functions can be calculated with the aid of suitably chosen models for the molecular motion and for the character of the interaction; this will now be illustrated for the intramolecular dipolar relaxation of protons in H_2O and the quadrupole relaxation of deuterons in D_2O. If, for simplicity, we assume that for the dipolar interaction of protons in H_2O only the coupling with the other proton on the same molecule is important (which is, actually, a rather bad approximation; this mechanism accounts for approximately two-thirds of the observed relaxation rate), we see that the time dependence of the B_m is contained in the Y_{2m}, while the factor r^{-3} is constant, and is determined by molecular geometry. The arguments of the Y_{2m} specify the orientation of the proton - proton vector with respect to a laboratory-fixed coordinate system, whose z-axis is along the Zeeman field. Modulation occurs through molecular reorientation, assumed to obey a diffusion equation. In the most general case the diffusion is anisotropic, and this motion is only easy to evaluate in a molecule-fixed coordinate system, that has its axes along the principal axes of the diffusion tensor. If we distinguish quantities evaluated in this coordinate system by adding a prime, we have, by the rotation properties of irreducible tensor components

$$B_o\,(t) = \sum_{m=-2}^{2} D^{2*}_{0m}\,(\omega\,(t))\,B'_m \tag{25}$$

where the D's are elements of a Wigner rotation matrix; their argument $\Omega\,(t)$ describes the orientation of the molecular frame with respect to the laboratory frame at time t. Thus we have

$$< B_0\,(t')\,B_0\,(t'+t) > \; = \sum_{mm'} < D^{2*}_{0m}\,(\Omega\,(t'))\,D^{2*}_{0m'}\,(\Omega\,(t'+t)) > B'_m\,B'_{m'} \tag{26}$$

It has been shown that correlation functions of this type consist in the general case of a sum of five exponential decays 10); a considerable simplification is achieved if the rotational diffusion is isotropic. Then we may choose the primed coordinate system as having its z'-axis along the proton - proton vector, so that

$$B'_m = r^{-3}\,\delta_{0m} \tag{27}$$

and we need only the simplest of the rotation matrix elements, whose explicit form a given by

$$D^2_{00} = (4\pi/5)^{\frac{1}{2}}\,Y_{20} \tag{28}$$

so that

$$\begin{aligned} r^{-6} < D^2_{00}\,(t')\,D^2_{00}\,(t'+t) > &= (4\pi/5) < Y_{20}\,(t')\,Y_{20}\,(t'+t) > \\ &= \tfrac{1}{5} r^{-6} \exp\,(-\,t/\tau) \end{aligned} \tag{29}$$

where τ is the rotational correlation time for the second rank spherical harmonics.

The deuterons in D_2O possess a quadrupole moment, that couples to the field gradient that arises from the non-spherical electron density in the chemical bond. As a simplification we assume that the charge distribution in the bond has cylindrical symmetry. We choose a (primed) coordinate frame, fixed in the molecule, with the z'-axis along the bond. Clearly in this coordinate system the tensor F, given by Eq. (11), has only one non-zero component

$$F'_0 = \tfrac{1}{2}\,V_{z'z'} \tag{30}$$

It is customary in such cases to denote the field gradient by $eq \equiv V_{z'z'}$ so we have

$$< F_0\,(t')\,F_0\,(t'+t) > \; = \; < D^{2*}_{00}\,(\Omega\,(t'))\,D^{2*}_{00}\,(\Omega\,(t'+t)) > \tfrac{1}{4}(eq)^2 \tag{31}$$

where the Ω denote the orientation of the molecular z'-axis with respect to the laboratory frame; from the similarity of Eqs. (29) and (31) it is seen that molecular rotation has the same influence on intramolecular quadrupole and dipolar relaxation: for the case of isotropic rotational diffusion we have

$$< F_0(t') F_0(t'+t) > = \frac{1}{20}(eq)^2 \exp\left(-\frac{t}{\tau}\right) \tag{32}$$

The Relaxation Rates

In many instances it is found that the return to equilibrium of the nuclear magnetization after a disturbance is given by simple exponential decays[11)]

$$\begin{aligned} \frac{\mathrm{d}M_z(t)}{\mathrm{d}t} &= -\frac{M_z(t)-M_o}{T_1} \\ \frac{\mathrm{d}M_{xy}(t)}{\mathrm{d}t} &= -\frac{M_{xy}}{T_2} \end{aligned} \tag{33}$$

where T_1^{-1} and T_2^{-1} are called the longitudinal (or spin-lattice) and transversal (or spin-spin) relaxation rates; M_z and M_{xy} are the expectation values of the longitudinal and transversal (with respect to the Zeeman field) nuclear magnetizations, and M_o is the equilibrium value of M_z. Such equations are obtained for relaxation through pair-wise dipolar interactions between similar spins, with the relaxation rates given by[2, 3)]

$$\begin{aligned} T_1^{-1} &= \frac{2}{5} I(I+1)(\gamma^2 \hbar)^2 \left[J(\omega_o) + 4J(2\omega_o)\right] \\ T_2^{-1} &= \frac{2}{5} I(I+1)(\gamma^2 \hbar)^2 \left[\frac{3}{2}J(0) + \frac{5}{2}J(\omega_o) + J(2\omega_o)\right] \end{aligned} \tag{34}$$

where ω_o denotes the Larmor frequency, I the spin quantum number, and $J(\omega)$ is given by Eq. (24).

Such simple decays are also found[12)] for quadrupolar relaxation of spins with $I = 1$:

$$\begin{aligned} T_1^{-1} &= \frac{3}{2}(eQ/\hbar)^2 \left[J(\omega_o) + 4J(2\omega_o)\right] \\ T_2^{-1} &= \frac{3}{2}(eQ/\hbar)^2 \left[\frac{3}{2}J(0) + \frac{5}{2}J(\omega_o) + J(2\omega_o)\right] \end{aligned} \tag{35}$$

and for quadrupolar relaxation of all nuclei in the case $J(2\omega_o) = J(\omega_o) = J(0)$, commonly denoted as 'extreme narrowing':

$$T_1^{-1} = T_2^{-1} = \frac{3}{2}(eQ/\hbar)^2 \left[(2I+3)/I^2(2I-1)\right] J(0) \tag{36}$$

For quadrupolar relaxation of nuclei with $I > 1$, outside the extreme narrowing region, the return to equilibrium is more complicated: an example of this situation will be described shortly.

For the moment we restrict ourselves to quadrupolar relaxation in the extreme narrowing region. For the mechanism described in the derivation of Eq. (32) we have finally:

$$T_1^{-1} = T_2^{-1} = \frac{3}{40} (eqeQ/\hbar)^2 \,[(2I+3)/I^2\,(2I-1)]\,\tau \qquad (37)$$

where $(eqeQ/\hbar)$ is called the quadrupole coupling constant; in the solid and gas phases its value can be determined by other experimental techniques. For spherical ions in aqueous solution field gradients may arise from the electric dipoles (and higher multipoles) of the water molecules, and the charges on all other ions. Such relaxation mechanisms have been extensively studied in solutions of simple electrolytes[13, 14)]. A basic assumption in the theoretical description so far, has been that the motions of these charges with respect to the nucleus under consideration are mutually uncorrelated. Then of course the field gradient autocorrelation in a N - charge system equals N times the single - charge field gradient autocorrelation. The validity of these assumptions is subject of discussion, to which some attention will be paid in the introduction to Chapter IV.

To facilitate comparison of different relaxation mechanisms, we will use Eq. (37) as a *formal* expression, bringing the results derived by Hertz and coworkers to a similar form by defining

$$\tau \equiv J(0) \,/ < F^2(t') > \qquad (38)$$

Then their result[14)] for the relaxation rates caused by the point charges of the other ions can be expressed as

$$\tau = \frac{a^2}{40\,\pi\,D}\left(3\,\frac{1-(a/b)}{1-(a/b)^3} - 1\right) \qquad (39)$$

$$eq = 8\,\pi\,ze\left[\frac{N}{3V}\,(a^{-3} - b^{-3})\right]^{\frac{1}{2}} (1-\gamma_\infty)\,\frac{2\,\varepsilon + 3}{5\,\varepsilon} \qquad (40)$$

where a is the distance of closest approach, b is a measure for the thickness of the ionic cloud, D is the (average) diffusion coefficient, ze is the charge of the ions, N/V their number density, ε the dielectric constant, and $(1 - \gamma_\infty)$ is a factor to account for the shielding of the field gradient by the charge distribution of the ion under consideration.

For the effect of the electric water dipoles on the relaxation, we have as correlation time the rotational correlation time of the dipole in the hydration shell, and for the field gradient[14)]

$$eq = 2\,m\left(\frac{4\pi}{a'^5}\,\frac{N'}{V}\right)^{\frac{1}{2}} (1-\gamma_\infty)\,\frac{2\,\varepsilon + 3}{5\,\varepsilon} \qquad (41)$$

where $m = 1.85 \times 10^{-18}$ esu cm is the value of the water dipole, a' is the distance of closest approach, and N'/V the number density of the water-molecules.

To give an impression of the order of magnitude of the nuclear magnetic relaxation parameters of ^{23}Na, which has $I = 3/2$, in various systems, we have collected in Table I the relaxation rates, and the quadrupole coupling constants and correlation times derived from them by regarding Eqs. (37)

and (38) as formal definitions. Not too much significance should be attached to the individual values; they often have been obtained as crude estimates, and are meant merely as an illustration.

system	$eqeQ/h$	τ	T_1^{-1}	Ref.
crystal $NaCl \cdot 2H_2O$	1	–	–	a)
very dilute aqueous solution	0.75	8	18	b)
ion-ion contribution in 5 M NaCl solution	0.25	1	1	b)
Na-caprylate dissolved in caprylic acid	0.7	2×10^3	5×10^3	c)
NaCl in RNA-solutions	–	–	200	d)
NaCl in HEEDTA-solutions	4	10	600	e)
PAA solutions polyion contribution	0.85	20	70	f)
	MHz	psec	sec^{-1}	

Table I: Typical values of ^{23}Na nuclear magnetic relaxation parameters in various systems.

References:

a) H. Rockelmann and H. Sillescu, Ber. Bunsenges. Phys. Chem. **74** 1002 (1970)
b) H. Versmold, Dissertation, Karlsruhe 1970
c) B. Lindman and P. Ekwall, Kolloid Z. u. Z. Polymere **234** 1115 (1969) (Note: here the 'extreme narrowing' condition is not met. The value shown under T_1^{-1} is at $\nu_o = 16$ MHz.
d) T. L. James and J. H. Noggle, Proc. Nat. Acad. Sci. (USA), **62** 644 (1969)
e) T. L. James and J. H. Noggle, J. Am. Chem. Soc., **91** 3429 (1969)
f) This thesis, Chapter IV

Nonexponential relaxation of ^{23}Na

For spins $I > 1$, outside the extreme narrowing region, the return to equilibrium of the nuclear magnetization after a disturbance is no longer simply exponential; Hubbard [12)] has shown that for $I = 3/2$ the Eqs. (33) *et seq.* have to be replaced by

$$M_z(t) - M_o = M_o(\cos\vartheta - 1)\left[\frac{4}{5}\exp(-a_1 t) + \frac{1}{5}\exp(-a_2 t)\right]$$

$$M_{xy}(t) = M_o \sin \vartheta \left[\frac{3}{5} \exp(-b_1 t) + \frac{2}{5} \exp(-b_2 t)\right] \qquad (42)$$

Here ϑ is the angle through which the equilibrium magnetization has been suddenly rotated by the disturbance at time zero, and the coefficients a and b are given in terms of the spectral densities of Eq: (23) by

$$a_1 = 2\,(eQ/\hbar)^2\, J(2\,\omega_o) \qquad a_2 = 2\,(eQ/\hbar)\, J(\omega_o)$$

$$b_1 = (eQ/\hbar)^2\, [J(0) + J(\omega_o)] \qquad b_2 = (eQ/\hbar)^2\, [J(\omega_o) + J(2\,\omega_o)] \qquad (43)$$

Although a few reports have appeared describing a difference between transversal and longitudinal relaxation 15, 16), or a field-dependent line width 17) of ^{23}Na in liquid systems, no attempts seem to have been made to verify whether in these cases the predictions regarding the field-dependence of Eqs. (42) were obeyed; still, such information can support the hypothesis that the main relaxation mechanism is indeed quadrupole relaxation. In our studies of ^{23}Na nuclear magnetic relaxation in polyelectrolyte solutions, we found that in solutions of poly(methacrylic acid) at low degrees of neutralization the decay of the transversal magnetization was much more rapid than that of the longitudinal magnetization. Although we have not been able to find a molecular description to explain the phenomenon, it still has a certain interest to show that the relaxation indeed obeys Eqs. (42).

If the spectral densities do not change too rapidly from $\omega = 0$ to $\omega = 2\,\omega_o$ the simple Eqs. (33) are still approximately valid, with the expressions (35) for the relaxation rates, except that the numerical factor 3/2 has to be replaced by 2/5, to take into account the change of I from 1 to 3/2. Thus, if the relaxation is measured at two values ω_o and ω_o' of the Larmor frequency, that satisfy the condition $\omega_o' = \frac{1}{2}\omega_o$, the four relaxation rates are determined by the spectral densities at $\omega = 0$, $\omega = \frac{1}{2}\omega_o$, $\omega = \omega_o$ and $\omega = 2\,\omega_o$, and we may solve the equations to find these four spectral densities. Next, by iteration, a fit of the experimental data to the full Eqs. (42) can be made.

The reported results have been obtained on solutions of atactic poly(methacrylic acid) (PMA), that were prepared in the same way as the PMA samples described in Chapter V, except that the concentration was 0.52 mgeq/g.

Qualitatively the same nuclear magnetic relaxation behaviour was found for syndiotactic samples, and for a single sample of isotactic PMA at a degree of neutralization $\alpha = 0.15$. The measurement procedure was the same as that for ^{23}Na relaxation in poly(acrylic acid) solutions described in Chapter IV, except that at the time the free-induction decay lock was not yet available. For transversal relaxation $\frac{1}{2}\pi - \pi$ pulse sequences were used. The Larmor frequencies were 8 and 16 MHz. In fig. 1 it is shown how at degree of neutralization $\alpha = 0.05$ the transversal relaxations clearly are non-exponential, in fig. 2 the α-dependences of the quantities $J'(\omega) = (eQ/h)^2 J(\omega)$ are shown. All relaxation curves are very well described by these spectral densities, showing that the main nuclear magnetic relaxation mechanism is indeed the quadrupolar interaction. Un-

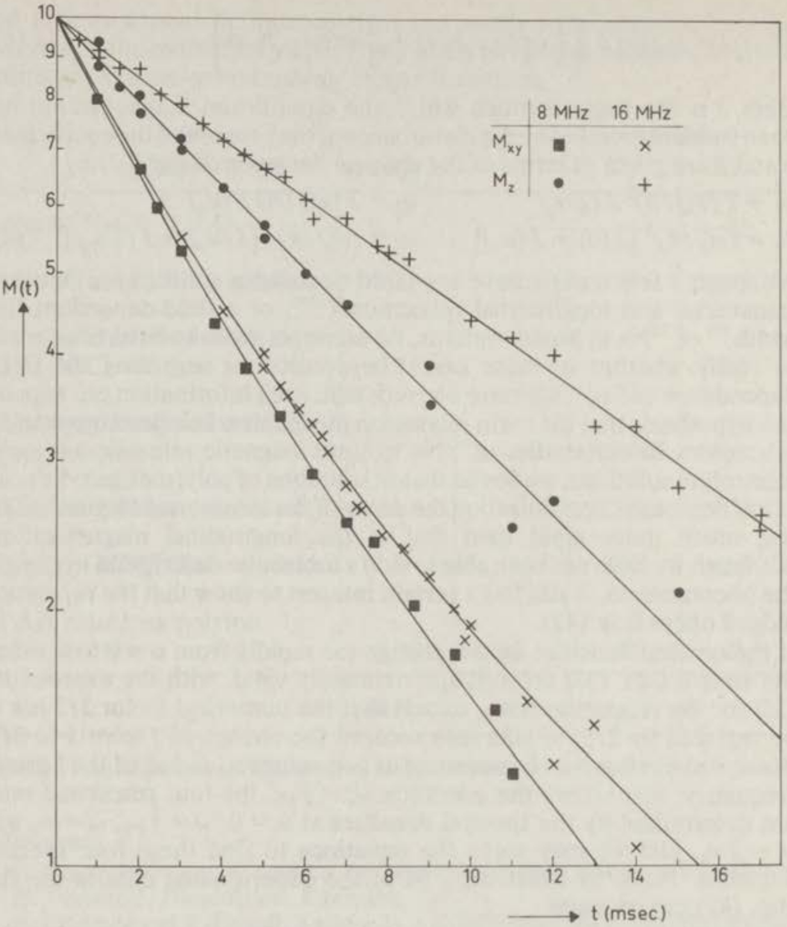

Fig. 1.
A semi-logarithmic plot of the decay of longitudinal and transversal nuclear magnetization of ^{23}Na in a poly(methacrylic acid) solution. Concentration: 0.52 mgeg./g. Degree of neutralization: 0.05. Molecular weight $M_v = 2.2 \times 10^5$. Solvent: D_2O.

fortunately we have not yet been able to develop a molecular interpretation of this very remarkable relaxation behaviour, and in the present work no further attention to these results will be given. We acknowledge the cooperation of G. Schoep (Kamerlingh Onnes Laboratory, Leiden), Dr. K. van Putte (Unilever Research, Vlaardingen) and Dr. I. D. Robb (Unilever Research, Port Sunlight) who put their equipment at our disposal during the early stages of the research reported in this section, and of W. F. Passchier of this Laboratory who wrote the computer program used in the iterative fitting procedure.

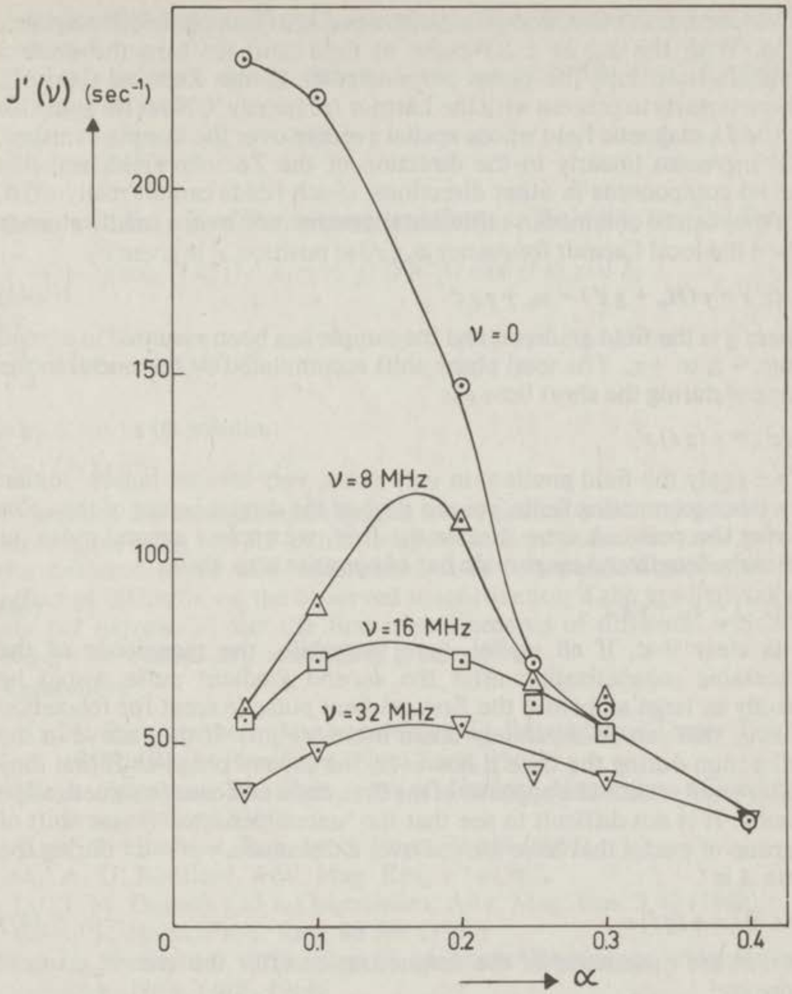

Fig. 2.
$J'(\nu) = (eQ/\hbar)^2\, J(\nu)$ as derived from ^{23}Na nuclear magnetic relaxation in poly(methacrylic acid) solutions with the aid of Eq. (42), *versus* degree of neutralization α. $\nu = (2\pi)^{-1}\omega$.
Concentration: 0.52 mgeq./g. Molecular weight $M_\nu = 2.2 \times 10^5$. Solvent: D_2O.

Selfdiffusion Measurements

The pulsed-field-gradient method[18, 19] of measuring selfdiffusion is based on the possibility of monitoring the position of a nucleus by its Larmor frequency in a magnetic field that is spatially dependent. We will describe here only the principle, referring to the original literature for a description of the actual experiment.

Let us consider a collection of nuclei in a perfectly homogeneous magnetic field. With the aid of a RF-pulse at time zero we turn the nuclear magnetization into the plane perpendicular to the Zeeman field $\mathbf{H}_o$, where it starts to precess with the Larmor frequency[6]. Next we apply for a time δ a magnetic field whose spatial average over the sample vanishes, that increases linearly in the direction of the Zeeman field, and that has no components in other directions. (Such fields cannot really exist, but they can be obtained in sufficient approzimation over a small volume). Then the local Larmor frequency $\omega_o(z')$ at position z' is given by

$$\omega_o(z') = \gamma(H_o + gz') = \omega_o + \gamma g z' \qquad (44)$$

where g is the field gradient, and the sample has been assumed to extend from $-z_o$ to $+z_o$. The total phase shift accumulated by the nuclei in the plane z' during the short time δ is

$$\varphi(z') = \gamma(g\delta)z' \qquad (45)$$

If we apply the field gradient in very short, very intense pulses, so that $\delta \rightarrow 0$ but $g\delta$ remains finite, we can neglect the displacement of the spins during the pulse. A time Δ after the first, we apply a second pulse, of the same length and magnitude but of opposite sign, thus

$$\omega_o(z'') = \omega_o - \gamma g z'' \qquad (46)$$

It is clear that, if all nuclei were immobile, the magnitude of the precessing magnetization after the second gradient pulse would be exactly as large as before the first gradient pulse (except for relaxation effects, that can be separately taken into account). If they move in the z-direction during the time Δ however, the second phase-shift that they suffer is not exactly the opposite of the first, and a net loss of magnetization results. It is not difficult to see that the 'uncompensated' phase shift of a group of nuclei that have moved over a distance $z = z' - z''$ during the time Δ is

$$\varphi(z, \Delta) = \gamma(g\delta)z \qquad (47)$$

so that the magnitude of the magnetization after the second gradient pulse is

$$M(g\delta, \Delta) = M(0) \int P(z, \Delta) \cos[\gamma(g\delta)z]\,\mathrm{d}z \qquad (48)$$

where the integration boundaries may be taken as $\pm\infty$, provided the dimension $2z_o$ of the sample is such that the probability $P(2z_o, \Delta)$ of a displacement $2z_o$ in time Δ is negligible. Assuming furthermore that P is an even function of z, and defining $k_z = -\gamma(g\delta)$ we can write

$$M(k_z, \Delta) = M(0) \int P(z, \Delta) \exp(-ik_z z)\,\mathrm{d}z \qquad (49)$$

Now, according to a general theorem on Fourier transforms[20], the second moment with respect to z of $P(z, \Delta)$, which is determined[21] by the selfdiffusion of the nuclei under consideration, is equal to $-(2\pi)^{-1}$ times the second derivate of $M(k_z, \Delta)/(M(0)$ with respect to k_z at $k_z = 0$. Therefore from a number of measurements of M at different k_z in the neighbourhood of $k_z = 0$ the value of the selfdiffusion coefficient can be obtained.

This can be more clearly shown if it is assumed that $P(z, \Delta)$ obeys a diffusion equation

$$\frac{\partial P}{\partial \Delta} = D \frac{\partial^2}{\partial z^2} P \tag{50}$$

then, with the aid of the inverse transform of Eq. (49), we find for M:

$$\int \frac{\partial}{\partial \Delta} M \exp(i k_z z) \,\mathrm{d}k_z = - \int D k_z^2 M \exp(i k_z z) \,\mathrm{d}k_z \tag{51}$$

or

$$\frac{\partial}{\partial \Delta} M = - D k_z^2 M \tag{52}$$

which has as its solution

$$\log [M/M(0)] = - \Delta D k_z^2 \tag{53}$$

In practice the main Zeeman field is never perfectly homogeneous, and techniques using two RF-pulses and two gradient pulses are used, where the detected signal is a 'spin echo'. It is also possible to derive the effect of diffusion on the observed magnetization if the gradient pulses are not narrow: in fact the first measurements of diffusion with spin echoes were made in a continuous gradient (22).

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CHAPTER IV

Nuclear Magnetic Relaxation of ^{23}Na in Polyelectrolyte Solutions

Introduction

Aqueous solutions of simple electrolytes have been extensively studied by NMR methods[1, 2]. Two rather different mechanisms have been proposed to explain the nuclear magnetic relaxation of alkali ions (all of which possess a quadrupole moment). Valiev and, independently, Hertz take the charges external to the ion (i.e. all the other ions and the water molecules) as the sources of the electric field gradients, that interact with the nuclear quadrupole moment to produce spin relaxation[3, 4]. Their model has been improved by Versmold[5] by the use of a Debye-Hückel, rather than an unscreened-Coulomb potential. Deverell considers the distortions of the electron cloud of the ion itself by short-range repulsive forces during a 'collision'. These points of view are referred to as the 'electrostatic' and the 'overlap' model respectively. The overlap model has been applied with some succes to the halogen resonances in aqueous alkali-halogenid solutions. Its applicability to the relaxation of the lighter alkali ions is uncertain. The theory focuses its attention on the magnitude of the field gradient, leaving the dynamics of the gradient fluctuations rather unspecified. Since our object is an investigation into the possibilities of nuclear magnetic relaxation to obtain information on the electrostatic interaction of a polyion and its counterions, we will apply the electrostatic model to this problem, and discuss our results within this framework.

There exists a pronounced difference between the formal development of a molecular theory of nuclear quadrupolar relaxation in molecules on one hand, and in simple spherical ions on the other. In the former case the electric field gradients originate within the molecule itself: there exists a frame of reference, attached to the molecule, in which the elements of the field-gradient tensor are time-independent. In solutions of simple electrolytes such a frame cannot be found: in any coordinate system the elements of the field-gradient tensor are time-dependent and average to zero.

In the case of polyelectrolyte solutions (to be specific: solutions of a weak polyacid, partially neutralized by sodium ions) we encounter a third possibility, not described so far in the litterature. Here the low molecular weight counterions are not surrounded by a time-averaged spherically symmetric distribution of opposite charges: the fact that the opposite charges are tied together by the polymer backbone prevents such an arrangement. Consequently, the situation can be described by a mixture of the above two models: the time-averaged distribution of counterions around a polyion gives rise to a field gradient of non-vanishing magnitude, whose *direction* is time dependent with respect to laboratory fixed axes. At the same time fluctuations in the average distribution give rise to field gradients that are modulated *both* in magnitude and in direction. In the present paper we stress the importance of the asymmetry of the average charge distribution; we checked our theoretical result by measurements on rather dilute solutions using concentrations where, in the case of simple non-associating electrolytes (e.g. the sodium halogenides), no major contribution of the fluctuations in the average charge distribution to the relaxation rate exists. The observed relaxation rates of sodium in polyelectrolyte solutions are four[6)] to ten[7)] times larger than in solutions of sodium halogenides of comparable concentration[8)].

In polyelectrolytes a pronounced asymmetry exists between the behaviour of the polyions and the low molecular weight counterions. The charged macromolecule is always at the centre of its own atmosphere and cannot be assumed to participate in the atmosphere of other ions on an equal footing. In the following we will assume the average charge distribution to be cylindrical, at least locally over lenghts of some tens of Å. For polyions of not too low charge density this should not be a severe approximation. Because of the lower symmetry of the charge distribution around a sodium ion in solutions of polyelectrolytes, as compared to simple electrolytes, it is possible to define a coordinate system, attached to the polymer, in which the field-gradient tensor at a fixed position has a non-zero time-average; fluctuations away from this average value are assumed to be small and short-lived, so that they do not give a significant contribution to the observed nuclear magnetic relaxation. It has to be noted that these deviations from the average charge distribution are the *only* ionic relaxation mechanism in simple electrolytes.

To give a quantitative description of the proposed mechanism, we will adopt the cylindrical cell model of polyelectrolyte solutions, which is now most widely used by workers in the polyelectrolyte field. Recently the subject has been reviewed by Katchalsky[9)]. It is assumed that a polyelectrolyte solution may be divided into 'cells', in the centres of which are the polymeric ions. The electrostatic repulsion between the polyions will lead to a homogeneous distribution of the macromolecular centres, so that an average interpolymer distance $2R$ may be attributed to the cell structure. For macroions of not too low charge density it is assumed that they are sufficiently stretched by electrostatic repulsion as to be ascribed a cylindrical symmetry, at least on a segmental scale. Then the polyion is represented as an uniformly charged rod of radius a, and the local counterion density within the cylindrical volume of radius R is connected to the local potential through Poisson's equation. As a consequence there is a radially directed electric field. We will consider only this 'static' field, and neglect the time-varying field that arises from the fact that the charge carriers are discrete particles, that perform a more or less random motion.

It has been argued on the basis of statistical-mechanical considerations[10)] that for high charge densities on the macroion, part of the counterions will 'condense' on the polyion: there is a sort of clustering about the polyion of these counterions[11)]. These condensed ions see the electric field of the unscreened polyion at a fairly small distance. Since the fraction of condensed ions is predicted to be considerable at high charge densities (approximately two-thirds for a fully charged vinylic polyelectrolyte) a marked increase in nuclear magnetic relaxation rate of the counterion upon raising the degree of neutralization is expected.

We have shown this effect to exist previously[6)]. Consistently, the ^{23}Na relaxation rate in polyphosphate solutions is found to be considerably larger than in low molecular weight phosphate solutions[7)].

The experimentally observed nuclear magnetic relaxation rates of alkali ions in aqueous solutions always contain a contribution from interaction of the nuclear quadrupole moment with the field gradients caused by the electric water dipoles. Although the molecular dynamics and dielectric properties of this process have as yet not been uniquely determined, – a discussion of the difficulties encountered has been given by Eisenstadt and Friedman[12)] –, the value of this contribution in solutions of simple electrolytes at low concentrations can be estimated from extrapolation of the observed relaxation rate to zero concentration of electrolyte. At finite concentrations, an experimental estimate of this solvent contribution is often made by assuming that it is proportional to the deuteron relaxation rate of D_2O in the same solution. Eisenstadt and Friedman[8)] have pointed out, however, that a plot of sodium relaxation rate at infinite dilution versus viscosity over temperature of the solvent, does not pass through the origin, while the same plot of the solvent relaxation rate does. That mobility of solvent and solute may depend quite differently upon concentration can be shown in RbI-solutions: here, solvent relaxation rate and reciprocal diffusion constant decrease upon increasing concentration[13)], while these quantities for the ions themselves increase[5, 14)]. From the observed increase of D_2O-relaxation rate upon increasing concentration and/or length of fatty acids and their salts in D_2O solution, Hertz and Zeidler[15)] concluded that the presence of non-polar groups on these molecules leads to an increased water structure. Specific interactions of water and polyelectrolyte-molecules have also been inferred from D_2O-relaxation rates[16)]. In view of these complications we will not attempt a calculation of the contribution of the water dipoles to the sodium relaxation rate, but rather consider it as an adjustable parameter, whose value can be deduced from the sodium relaxation rate at low degrees of neutralization.

In view of the above considerations, we will adopt the following model to explain the unexpectedly high nuclear magnetic relaxation rates of counterions in polyelectrolyte solutions:

A) The polyion is represented by a rigid rod of a certain radius *a*, and an uniform negative surface charge density. As seen from the laboratory coordinate system, this cylinder may perform any rotational or translational diffusion; but the conditions mentioned in B) – D) are assumed to be valid at any moment.

B) The position of the counterions with respect to the polyionic rod is represented by their equilibrium probability distribution, as given by the solution of the Poisson-Boltzmann equation with cylindrical boundary conditions. Fluctuations away from the equilibrium distribution are neglected.

C) The solvent is described by a hypothetical dielectric, viscous fluid with no molecular structure, but with dielectric and viscous properties like the macroscopic properties of water.

D) In the system, formed by A) - C), there moves a 'test particle' with nuclear spin 3/2. The motion of this particle through the solvent on an equipotential surface of the total charge distribution (A) plus (B) can be described by a diffusion equation with diffusion coefficient D; its ability to move perpendicular to such a surface is seriously hindered. We compute the nuclear spin relaxation rate of this 'test particle'.

Apart from these assumptions we will follow procedures that are common in the description of nuclear magnetic relaxation of diamagnetic ions in simple electrolytes.

Some features of this model can be more or less justified:

In A) and B) the total charge distribution is assumed to have cylindrical symmetry. The contribution to the relaxation rate of a certain nucleus from an electric point charge at a distance r decreases as r^{-6}; thus only a limited part of the charge distribution representing the polyion and its counterions will be important. Furthermore it will turn out that the fieldgradient autocorrelation in lost in 10^{-10} seconds, a time in which the nucleus diffuses over a distance of, say, ten Å. Thus the cylindrical symmetry only needs to exist on a time scale of 10^{-10} seconds, and for a part of the polymer of some tens of monomeric units. In connection with this it is of considerable interest to note that in polyphosphate solutions no dependence of the ^{23}Na relaxation rate on the degree of polymerization was found from roughly 60 monomeric units upwards 7).

In B) is stated that fluctuations in the average counteriondistribution are neglected; they can be assumed to cause relaxation rates of the same order of magnitude as in e.g. sodiumhalogenide solutions of the same concentration and can be neglected in the present case.

The assumptions C) on the solvent are made because we will try to estimate the value of the solvent contribution to the relaxation from experimental results, and not from theoretical considerations, so the molecular structure of the solvent will be of minor interest. A thorough theory of the influence of the dielectric properties of polar solvents on nuclear magnetic relaxation of diamagnetic ions is lacking at present 2).

The restriction on the motion of the 'test particle' in D) is taken to represent the difficulty a counterion has to escape from the polyion's atmosphere. This escape-time has been estimated to be $10^2 - 10^3$ times larger than the time required to travel the same distance on an equipotential surface. Furthermore, the radial displacement of the test-particle within the polyion's atmosphere does not change the direction of the field-gradient it experiences, so that this motion does not cause a *decay* of the field-gradient autocorrelation, but merely an *oscillation,* that is rapid compared to the decay-time. Therefore radial displacements within the polyion's atmosphere will not give significant contributions to the observed relaxation, while the time required to leave the atmosphere is estimated to be much longer than the correlation time for tangential motion in assumption D).

In the Discussion further remarks about the features of this model will be given.

Theoretical

The 'electrostatic model' of nuclear magnetic relaxation in electrolytes is patterned after that in ionic solids[3)]. We will follow the convention used by Hubbard[4)] and by Rose[17)] for the normalization of the irreducible representations of the field gradient tensor and the spinoperators. The molecular motion is taken to be invariant under rotations and fast with respect to the reciprocal of the Larmor frequency. The nuclear magnetic relaxation rates are then given by[4)]:

$$T_1^{-1} = T_2^{-1} = \frac{3}{2}\left(\frac{eQ}{\hbar}\right)^2 \frac{2I+3}{I^2\,(2I-1)}\, J_{oo}\,(0) \tag{1}$$

where

$$J_{oo}\,(\omega) = \tfrac{1}{2} \int_{-\infty}^{+\infty} < F_o\,(t)\, F_o\,(t+\tau) > \mathrm{e}^{i\omega\tau}\, \mathrm{d}\tau \tag{2}$$

and < > indicates an ensemble averaging. F_o is the irreducible component of the field-gradient that is invariant under rotations around the Zeeman field.

Let F'_o, $F'_{\pm1}$, $F'_{\pm2}$, be the irreducible components of the field-gradient tensor in a coordinate system that has Euler angles $(\alpha\beta\gamma)$ with respect to the magnetic-field fixed system; then:

$$F_o = \sum_{k=-2}^{2} D^{2*}_{ok}\,(\alpha\beta\gamma)\, F'_k \tag{3}$$

where D's are elements of a Wigner rotation matrix[17)].

The connection between irreducible and Cartesian components is:

$$F'_o = \tfrac{1}{2}\, V_{zz}$$

$$F'_{\pm1} = \mp\, (6)^{-\frac{1}{2}}\, (V_{zx} \pm i\, V_{zy}) \tag{4}$$

$$F'_{\pm2} = \tfrac{1}{2}\, (6)^{-\frac{1}{2}}\, (V_{xx} - V_{yy} \pm i\, 2\, V_{xy})$$

where the V_{ij} are second partial derivatives of the electric potential. If the field-gradient arises from point charges in a uniform continuous medium of dielectric constant ε, we will have to take into account contributions from the polarization of the medium by the point charge[3)] and from (anti-)shielding by the charge distribution of the ion under consideration[18, 19)]. Then the field-gradient tensor at a nucleus in $\boldsymbol{r}$, due to a point charge e in the origin is given by

$$V\,(\boldsymbol{r}) = (1-\gamma_\infty)\, \frac{2\varepsilon+3}{5}\, \nabla\, \nabla\, \frac{e}{\varepsilon\, r} \tag{5}$$

We call $(2\varepsilon + 3)/5\varepsilon$ the polarization factor P, and γ_∞ the shielding factor. It should be noted that in the case of polyelectrolyte solutions, the polarization effect is mainly due to orientation of water-dipoles in the hydration shell of the counterion by the electric field of the polyion. The correction accounts for the 'average amount' of orientation. Fluctuations away from this average orientation cause what we call the solvent contribution to the relaxation rate.

Contributions of different charges to the field-gradient are additive; however, if their positions are only known in the form of a probability function $\rho\ (r')$, care should be taken to exclude a small volume around the field point from the integration domain:

$$V\,(r) = (1 - \gamma_\infty)\ \varepsilon\, P\, \nabla\, \nabla \int_{r \neq r'} \frac{e\rho\,(r')}{\varepsilon\,|\,\boldsymbol{r}' - \boldsymbol{r}\,|}\,\mathrm{d}r' \qquad (6)$$

The integration extends over all sources, positive as well as negative, of the electric field.

We now specialize to the case that the distribution function ρ of the charges, which gives rise to the field-gradient, has cylindrical symmetry around certain axis z. The electric field in the 'hole' at $(r,\ \varphi,\ z)$ will be radially directed, and its magnitude E_h obeys Laplace's equations:

$$\frac{\partial E_h}{\partial r} + \frac{E_h}{r} = 0 \qquad (7)$$

At the boundary of the hole the magnitude of the electric field is continuous (while its derivate is not); thus we have, for a sufficiently small hole:

$$\frac{\partial E_h}{\partial r}\ (in\ hole) = -\frac{E_h}{r}\ (in\ hole) \approx -\frac{E_h}{r}\ (at\ boundary) = -\frac{E_r}{r}\ (at\ boundary) \qquad (8)$$

where E_r is the radial component of the macroscopie electric field, that is connected to the distribution function ρ by Poisson's equation. In this cylindrical case we get for Eqs. (4):

$$F_o = 0$$

$$F_{\pm 1} = 0 \qquad (9)$$

$$F_{\pm 2} = (6)^{-\frac{1}{2}}\ \frac{(1 - \gamma_\infty)\ \varepsilon\ P\ E_r}{r}\ \mathrm{e}^{\pm 2i\varphi}$$

If the ion, that bears the nucleus under consideration, is free to move in this coordinate system, modulation of the quadrupolar Hamiltonian occurs by changes in r as well as in φ. In general, however, changes in radial position will also affect the Coulomb energy of the ion. In polyelectrolyte solutions of non-vanishing concentration, the magnitude of the electric field passes through a minimum at a distance halfway between two macroions. A counterion in Brownian motion on a straight line between these two polyions, suffers loss of correlation of the field gradient in the average time it takes to escape from the potential well around the polyion. Motions on that straight line inside the potential well give rise only to oscillations on the autocorrelation function, that correspond to high frequencies in the power spectrum and will be neglected. It has been estimated[20)] that this escape time may be $10^2 - 10^3$ times larger than the time required to travel the same distance in a constant potential.

The tangential displacement causes loss of correlation after travelling about one radian; this time is thus always shorter than the correlation time for radial displacement. Therefore we will assume that the decay of the field-gradient correlation at a nucleus that is in (r_o, φ_o) at time $t = 0$, occurs wholly by changes in φ at constant r:

$$F'_{\pm 2}(0)\, F'_{\mp 2}(\tau) = \frac{1}{6}\left(\frac{(1-\gamma_\infty)\,\varepsilon\, P\, E_r(r_o)}{r_o}\right)^2 \exp\left(\pm 2\, i\,(\varphi_o - \varphi(\tau))\right) \tag{10}$$

Next we assume that the probability of a change $\Delta\varphi$ of φ during time τ is given by the probability of diffusional displacement along the arc $r_o \Delta\varphi$:

$$P(\Delta\varphi, \tau) = \tfrac{1}{2} r_o (\pi D \tau)^{-\frac{1}{2}} \exp\left(-(r_o \Delta\varphi)^2/4D\tau\right) \tag{11}$$

which leads to

$$\int\int P_o(\varphi_o) \exp(\pm 2 i \Delta\varphi)\, P(\Delta\varphi, \tau)\, \mathrm{d}\varphi_o\, \mathrm{d}\Delta\varphi = \exp(-4D\tau/r_o^2) \tag{12}$$

if the a priori distribution $P_o(\varphi_o)$ of nuclei has cylindrical symmetry. The interesting quantity, however, is the autocorrelation of the field gradient in the laboratory axes system. This is connected to the autocorrelation in the system that has its z-axis along the symmetry-axis of the field through Eq. (3). Obviously this symmetry-axis might rotate between times $t = 0$ and $t = \tau$. If this rotation is sufficiently slow, we may assume that the nucleus stays on an equipotential surface, whatever the motion of the field's symmetry axis is, and we may average over D's and F''s separately; then Eqs. (2) and (3) can be written:

$$J_{oo}(\omega) = \tfrac{1}{2} \int_{-\infty}^{+\infty} \sum_{k,k'} < D^{2*}_{ok}(t)\, D^{2*}_{ok'}(t+\tau) > < F'_k(t)\, F'_{k'}(t+\tau) > \exp(i\omega\tau)\, \mathrm{d} \tag{13}$$

In our application the changes in the arguments of D are connected to reorientations of the macroion; we take these not only to be sufficiently slow for Eq (13) to hold, but even to be so much slower than the changes in F that the D's become effectively time-independent:

$$< D^{2*}_{ok}(t)\, D^{2*}_{ok'}(t+\tau) > \approx < D^{2*}_{ok}(t)\, D^{2*}_{ok'}(t) > = \frac{1}{5}\delta_{kk'} \tag{14}$$

if all orientations of the symmetry-axis nave equal a priori probabilities. The averaging of $F_k F_{k'}$ in Eq. (13) is over r- and φ-coordinates. By use of Eqs. (10), (12) and (14) we get

$$J_{oo}(0) = \frac{1}{60D} (\varepsilon P (1-\gamma_\infty))^2 < E_r^2 >_r \tag{15}$$

where $< >_r$ indicates that the averaging only has to be taken over the radial probability function of the nuclei. Insertion of Eq. (15) into Eq. (1) gives, for spin 3/2

$$T_1^{-1} = \frac{1}{30}\left(\varepsilon\, P\,(1-\gamma_\infty)\,\frac{eQ}{\hbar}\right)^2 \frac{1}{D} < E_r^2 >_r \tag{16}$$

This equation expresses the observed relaxation rate as a weighted average over 'microscopic relaxation rates' that are propertional to E_r^2. This simple structure, of course, is due to the neglect of the radial displacement in Eq. (10).

On the basis of the cylindrical cell model for polyelectrolyte solutions we will compute $< E_r^2 >$ in two ways: first, using the analytical solution of the Poisson-Boltzmann equation as obtained by Fuoss, Katchalsky and Lifson[21] and second by using Manning's ion condensation concept[10]. For salt-free solutions of polyacid, partially neutralized by monovalent counterions, the macroscopic electric field at a distance r from the polyionic rod can be written as[21]:

$$\begin{aligned} E_r(r) &= E_r(a)\,\frac{a\,(1+\beta\coth(\beta\ln(R/a)))}{r\,(1+\beta\coth(\beta\ln(R/r)))} \\ E_r(R) &= 0 \\ E_r(a) &= -2\,\alpha\, e/b\varepsilon\, a \end{aligned} \tag{17}$$

where

α degree of neutralization

b distance between ionizable groups

a radius of polyionic rod

R radius of counterion-atmosphere

β a (real or imaginary) integration constant

The parameters R and β are given by

$$R = (\pi\, b\, N_p)^{-\frac{1}{2}} \tag{18}$$

where N_p is the monomer number density of the polyion in the solution and each monomer is supposed to carry one ionizable group, and

$$1-\beta^2 = \lambda\,(1+\beta\coth(\beta\ln(R/a))) \tag{19}$$

where

$$\lambda \equiv \alpha\, e^2/\varepsilon bkT \tag{20}$$

is the 'charge density parameter', central to all rod-like theories of polyelectrolyte solutions. From Poisson's equation it follows that the probability $P(r)$ to find a randomly chosen counterion at a distance between r and $r+\mathrm{d}r$ from the polyionic rod is given by

$$P(r) = \frac{\varepsilon b}{2e\alpha}\,\frac{\mathrm{d}}{\mathrm{d}r}(rE_r) \tag{21}$$

so that Eq. (16) becomes

$$T_1^{-1} = \frac{1}{15}\left(\varepsilon P\,(1-\gamma_\infty)\,\frac{eQ}{\hbar}\right)^2 \frac{b\varepsilon}{De\alpha}\int_{r=a}^{R} E_r^2\,\frac{\mathrm{d}}{\mathrm{d}r}(rE_r)\,\mathrm{d}r \tag{22}$$

By partial integration, using Eqs. (17) we get finally

$$T_1^{-1} = \frac{2}{45}\,(P\,(1-\gamma_\infty)\,eQ/\hbar)^2\left(\frac{\alpha e}{ab}\right)^2 \frac{1}{D}(1 - 2\int_0^y \frac{F(x)}{F(y)}\,\mathrm{d}x) \tag{23}$$

where

$$F(x) = (1 + \beta \coth \beta x)^{-3} \exp(2x) \tag{24}$$

and the concentration parameter $y = \ln (R/a)$.

This is the result for the relaxation rate of spin 3/2 nuclei in the counterioncloud of a polyelectrolyte, using the Poisson-Boltzmann equation.

Alternatively, we may use the ion-condensation concept: At charge densities characterised by $\lambda < 1$ the small ions are free to move around in the solution, and their average distance to the polyion may be large: consequently the electric field must be assumed negligeably small, and there is no contribution to the relaxation rate. For higher charge densities a fraction $(\lambda - 1)\lambda$ of the counterions 'condenses' on the line charge, - i.e. resides at an average distance d that is small compared to the Debye length [11]. These ions see the electric field of the unscreened line charge, as given by the third of Eqs. (17), with a replaced by d. The remaining ions are again free to move around and are assumed to contribute little to the observed relaxation rate. In this case the mean squared electric field may be estimated as:

$$< E_r^2 >_r = \frac{\lambda - 1}{\lambda} \left(\frac{2\,\alpha e}{\varepsilon b d} \right)^2 \quad \text{if } \lambda > 1 \tag{25}$$

and insertion into Eq. (16) gives

$$T_1^{-1} = \frac{2}{15} (P(1 - \gamma_\infty)\, eQ/\hbar)^2 \left(\frac{\alpha e}{bd} \right)^2 \frac{1}{D} \frac{\lambda - 1}{\lambda} \quad \text{if } \lambda > 1 \tag{26}$$

This equation clearly has the same structure as Eq. (23). Just as in simple electrolytes the effectiveness of a polyionic charge in producing spin relaxation is quadratic in the valence (degree of neutralization; the theory assumes infinitely long macromolecules, so there can be no molweight-dependence). An additional effect of increasing the polyion's charge shows up as a decrease of the mean distance of the nucleus to the polyion in Eq. (23), or, what amounts to the same, as an increase of the number of ions immediately surrounding the polyion in Eq. (26).

In order to facilitate the comparison of our result with that obtained in other cases, we may define a correlation time τ_c as

$$\tau_c = J_{oo}(0) \,/ < F_o^2(t) > \tag{27}$$

with $J_{oo}(0)$ given by Eq. (15). A similar result may be obtained for $< F_o^2(t) >$, via Eqs. (3), (9), (10), (12) and (14):

$$< F_o^2(t) > = \frac{1}{15} (\varepsilon P (1 - \gamma_\infty))^2 < (E_r/r)^2 >_r \tag{28}$$

Performing the radial averaging, with Eqs. (17) and (21), leads to

$$< F_o^2(t) > = \frac{4}{45} \left(P(1 - \gamma_\infty) \frac{\alpha e}{a^2 b} \right)^2 (1 - 4 \int_o^y \frac{f(x)}{f(y)} \mathrm{d}x) \tag{29}$$

where

$$f(x) = (1 + \beta \coth \beta x)^{-3} \exp(4x) \tag{30}$$

so Eq. (27) becomes:

$$\tau_c = \frac{a^2}{4D} \frac{1 - 2 \int_0^y F(x) / F(y) \, \mathrm{d}x}{1 - 4 \int_0^y f(x) / f(y) \, \mathrm{d}x} \tag{31}$$

This expression for τ_c offers a means to verify the validity of the assumption that the motion is fast with respect to

1) the Larmor frequency (Eq. (1))
2) the escape-time from the counterion-cloud (Eq. (10))
3) the polymer's rotational motion (Eq. (14))

When a simple electrolyte is added to the polyelectrolyte solution, Eq. (17) for the electric field is no longer valid. In view of the similarity of Eqs. (23) and (26) we attempt a description of this situation by using Manning's assumption[10)] that the number of condensed counterions is independent of added salt, if the latter is mono-monovalent. For our purposes we will also require that it has no significant influence on the solvent structure[1, 2, 8, 12)]. In that case we might use a 'two state model'[22)]: the nucleus is either inside the polyion-atmosphere, and relaxes as if the added salt were absent, or it is outside, and relaxes as if the polyion were absent. Using the same estimate as before for the lifetime of an ion in the polyion-atmosphere[20)] we find the equation for the 'fast exchange' - case to be applicable:

$$(T_1^{-1})_{obs} = P_1 \, (T_1^{-1})_p + P_2 \, (T_1^{-1})_s \tag{32}$$

where $P_{1,2}$ are the probabilities that the nucleus is inside resp. outside the polyion cloud, and $(T_1^{-1})_p$ and $(T_1^{-1})_s$ are the relaxation rates in absence of the simple salt, resp. absence of the polyion.

This would be another 'additivity rule', as have been found for the osmotic and activity coefficients, and, recently, for the diffusion coefficient[33)].

Experimental.

Poly(acrylic acid) (PAA) was synthezised and fractionated as described before[23)]. The viscosity averaged molecular weight of PAA was 1.39×10^6. NaOD solution was prepared by dissolving freshly cut sodium in D_2O in a nitrogen atmosphere. D_2O was obtaind from Merck 2919 (99.75%). The D_2O solution of PAA was obtained by dissolving PAA in D_2O, freeze drying and redissolving in D_2O. This procedure was repeated three times. Deuterium solutions of PAA at different degrees of neutralization were prepared by adding calculated quantities of NaOD solutions to weighted amounts of D_2O solutions of PAA and adjustment of the concentration by adding calculated quantities of D_2O. Final sample volumes were 1.5 cm³ approx.

All operations involving the D_2O solutions were performed in a dry box. Solutions containing different quantities of added salt were prepared by opening the sample tube and adding progressively more NaCl. Added quantities were determined by weight.

We used D_2O as a solvent rather than H_2O because it is expected that the sodium relaxation rates are proportional to the viscosity of the pure solvent [12)]. The effect is thus predicted to be larger in D_2O-solutions than in H_2O-solutions. We prepared some solutions in H_2O and verified that this was actually the case.

Measurements of spin-lattice relaxation rates of ^{23}Na were made on a Bruker pulsed -NMR spectrometer, using $\pi - \frac{1}{2}\pi$ sequences. The magnet was a Varian high-resolution type, operated at 14.21 kG, with a Varian flux stabiliser and a Bruker proton free-induction decay lock. Signal/noise improvement was achieved by using phase-sensitive detection and by accumulating signals in a Varian C-1024 time-averager. Heights of signals were measured on an external oscilloscope, connected to the analog outputs of the C-1024. No sample-temperature control was attempted; but the magnet cooling water was thermostatted at 31 °C approximately, and the room at 20 °C. Sample temperature was measured to be 23 °C approx. For some samples it was verified that longitudinal and transversal relaxation times were equal, within experimental accuracy.

The integrals in Eqs. (23) and (29) were evaluated numerically, by converting them to sums, and summing over 100 intervals of equal length. The range of the parameters was: λ from 1 in 0.2 increments to 3 and y from 1.4 in 0.2 increments to 3. For the special case $\lambda = y/(1+y)$ Eq. (24) simplifies to $F(x) = x^3 (1+x)^{-3} \exp(2x)$ and the integral can be expressed in terms of the exponential integral $\mathrm{Ei}(x)$, which is well tabulated. We verified that downward extrapolation of our computed values yielded the correct result.

Results

In fig. 1 the expression $Y(\lambda) = \lambda^2 (1 - 2 \int_0^y F(y)\,\mathrm{d}x)$ is plotted as function of λ for two values of the concentration parameter y. It is to be noted that, once a value for the radius a has been chosen, an increase of y by one unit corresponds to a sevenfold dilution. The shape of the curve is seen not to be very sensitive to the y value chosen.

The experimental relaxation rates of the ^{23}Na nuclei in heavy water solutions of partially neutralized poly(acrylic acid) are shown in fig. 2. Three regions may be distinguished: from zero neutralization to $\alpha = 0.1$ the relaxation rate increases, then it is approximately constant to $\alpha = 0.3$, and for higher degrees of neutralization it increases rapidly.

In our earlier report on sodium relaxation in H_2O-solutions of poly (acrylic acid) [6)] these regions did not show up as distinctly as in the present case. The number of experimental points was less, and no points were taken below α = 0.1. Experimental accuracy too has slightly improved since. As can be seen from fig. 2 a satisfactory agreement

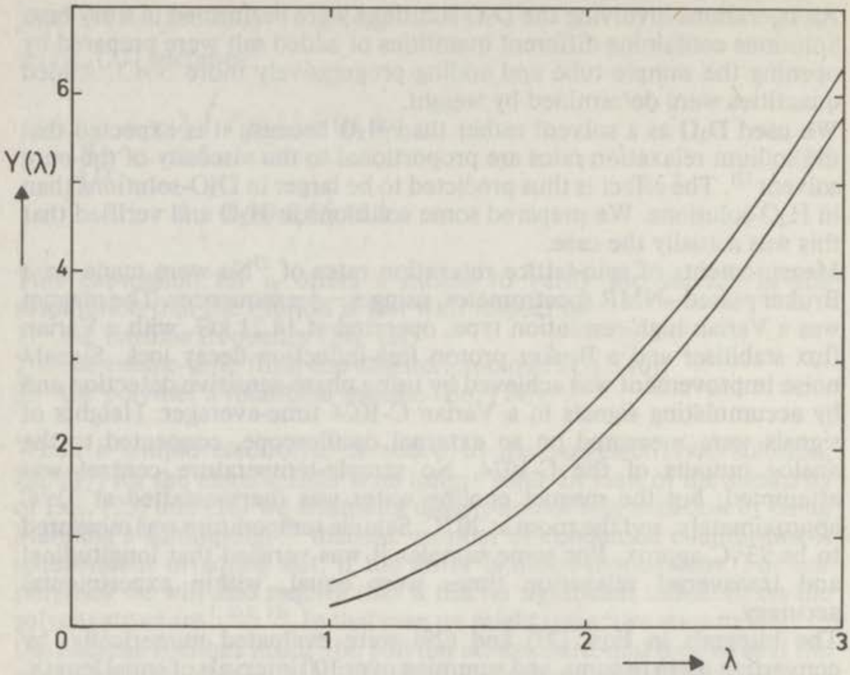

Fig. 1.
The expression $Y(\lambda) = \lambda^2 (1 - 2 \int_0^{\lambda} F(x) / F(y)\,\mathrm{d}x)$ with $F(x)$ defined in Eq. (24), that gives the dependence of the relaxation rate on the charge parameter λ (cf. Eq. (23)) as a function of λ for two values of the concentration parameter y. Upper curve: $y = 1.4$. Lower curve: $y = 3.0$.
The lower curve represents a 25-fold dilution with respect to the upper curve.

between the earlier and the present results is obtained if the correction for changing viscosity is applied.

We believe the first region to be associated with conformational changes in the macromolecule, from (nearly) uncharged to a more or less extended charged rod. The most rapid change of diffusion constants of the counterions[24, 25)] and, – in the case of poly(methacrylic acid) –, also of the polyion[26, 27)], with neutralization occurs in this α-region. Both changes in correlation time (by a slowing down of the motion) or in the magnitude of the field-gradient (by an increasing polarization factor) may play a part in the observed increase of the relaxation rate. Which one is the most important is not clear at the moment; we are continuing our relaxation studies in this α-region.

The plateau-value of 35 $\sec^{-1}$, that is reached in the second region, is thought to be characteristic of the solvent contribution to the relaxation

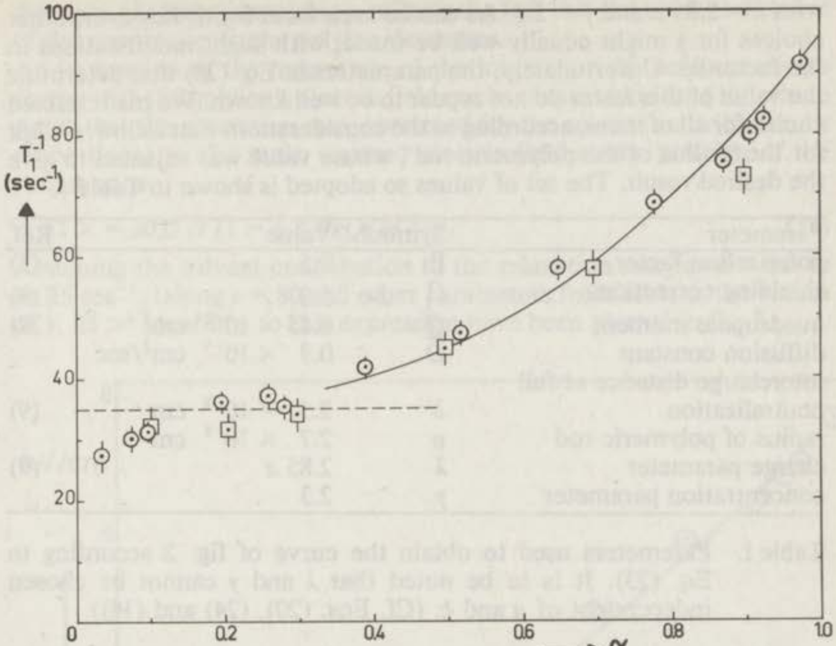

Fig. 2.
Spin-lattice relaxation of sodium nuclei in 0.3 N poly(acrylic acid) solutions as a function of the degree of neutralization α.
Circles: experimental results in D_2O solutions.
Squares: experimental results in H_2O solutions, multiplied by the D_2O/H_2O viscosity ratio (1.25).
(The error bars are estimated from reproducibility.)
Dashed line: assumed constant value for the contribution of the water dipoles to the observed relaxation rate.
Solid line: The assumed water contribution plus the ion-cloud contribution computed according to Eq. (23) with the parameter-values of Table I. (See also Eq. (33).)

rate of the counterions in the presence of the, more or less, extended form of the polyion. The relaxation rate of ^{23}Na in D_2O at infinite dilution is 21 sec^{-1} [12]. This seems to indicate that the presence of the polyion has a definite effect upon the hydration shell of the counterion, for example by lowering the effective dielectric constant, thus increasing the polarization factor.

The third region comprises the degrees of neutralization where 'ion condensation' is thought to occur. The experimental points are well described by

$$T_1^{-1} = 35 + 93\,\alpha^2 \left(1 - 2\int_0^{y} F(x) / F(y)\,\mathrm{d}x\right) \qquad (33)$$

with $\lambda = 2.85\ \alpha$ and $\gamma = 2.3$. As can be seen from fig. 1, however, other choices for γ might equally well be made, with slight modifications in the factor 93. Unfortunately, the parameters in Eq. (23) that determine the value of this factor do not appear to be well known. We made a fixed choice for all of them, according to the considerations that follow, except for the 'radius of the polymeric rod', whose value was adjusted to give the desired result. The set of values so adopted is shown in Table 1.

Parameter	Symbol	Value	Ref.
polarization factor	P	0.5	(2)
shielding correction	$(1-\gamma_\infty)$	5.8	(19)
quadrupole moment	Q	0.15×10^{-24} cm^2	(28)
diffusion constant	D	0.9×10^{-5} cm^2/sec	
intercharge distance at full neutralization	b	2.5×10^{-8} cm	(9)
radius of polymeric rod	a	2.7×10^{-8} cm	
charge parameter	λ	$2.85\ \alpha$	(9)
concentration parameter	γ	2.3	

Table I. Parameters used to obtain the curve of fig. 2 according to Eq. (23). It is to be noted that λ and γ cannot be chosen independent of a and b. (Cf. Eqs. (20), (24) and (18)).

For the quadrupole moment of ^{23}Na the older literature gives 0.11 ± 0.01 barn, while a recent tabulation[28)] gives 0.14 − 0.15 barn. A recent computation of $(1-\gamma_\infty)$ gives[19)] the value 5.78, instead of the previously used value of 5. Both these quantities have tended to increase with time, so we use the most recent values.

The macroscopic diffusion constant of counterions in polyelectrolyte solutions is strongly α-dependent[24, 25)]. At full neutralization it is less than half the value at $\alpha = 0$. For dilute solutions this latter value agrees well with the infinite-dilution value in NaCl-solutions[29)] which is 1.33×10^{-5} cm^2/sec at 25 °C in H_2O. Viscosity correction gives 1.08×10^{-5} cm^2/sec in D_2O. This should be the upper limit for the diffusion constant D appearing in Eq. (23). We performed some preliminary diffusion measurements on the sodium ions in our samples with $\alpha > 0.3$ by the pulsed-field-gradient method[30)]. These results extrapolated linearly to 0.9×10^{-5} cm^2/sec at zero neutralization.

The model parameters a and b are of course only rough descriptions of the structure of the polyelectrolyte under study. We take b equal to the monomeric length of vinylic polymers (2.5 Å) and consider a as an adjustable parameter, whose value should turn out to be a few Å.

Using these parameters in the computation of the correlation time according to Eq. (31) gives

$\tau = 2.5 \times 10^{-11}$ sec at $\alpha = 0.35$

$\tau = 2.1 \times 10^{-11}$ sec at $\alpha = 1$.

These values are somewhat larger than the correlation time for the solvent contribution in simple electrolytes, which is 8 psec[2)] The slight decrease of ι upon increasing α reflects the fact that the average distance of the counterion to the polyion decreases.

An impression of the magnitude of the interaction of the counterion's charge with the polyion's electric field can be obtained via Eq. (16), which states that the relaxation rate, corrected for the solvent contribution, is proportional to the mean squared electric field at the position of the counterions

$$< E_r^2 > = 30D\,(\varepsilon\,(1-\gamma_\infty)\,PeQ/\hbar)^{-2}\,T_1^{-1} \tag{34}$$

Assuming the solvent contribution to the relaxation rate for $\alpha > 0.3$ to be 35 $\sec^{-1}$; taking $\varepsilon = 80$ and other parameters from table 1, the values of $< E_r^2 >^{\frac{1}{2}}$ according to this expression have been plotted in fig. 3.

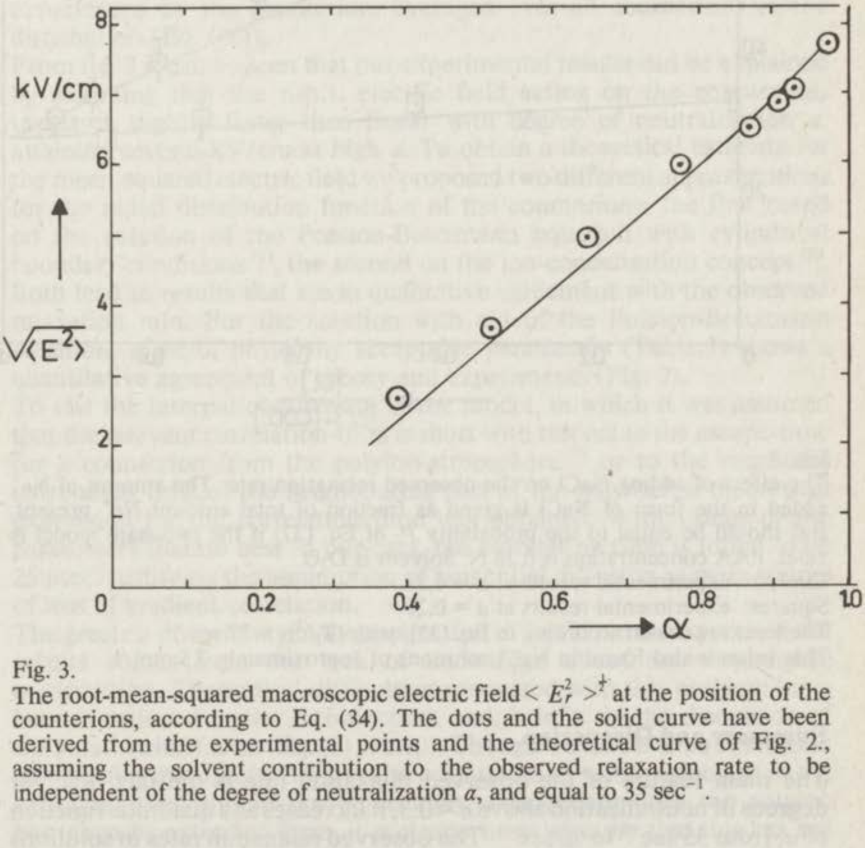

Fig. 3.
The root-mean-squared macroscopic electric field $< E_r^2 >^{\frac{1}{2}}$ at the position of the counterions, according to Eq. (34). The dots and the solid curve have been derived from the experimental points and the theoretical curve of Fig. 2., assuming the solvent contribution to the observed relaxation rate to be independent of the degree of neutralization α, and equal to 35 $\sec^{-1}$.

The effect of adding NaCl to a polyelectrolyte solution on the ^{23}Na relaxation rates is shown in fig. 4. It is seen that within experimental accuracy Eq. (32) is satisfied, with $(T_1^{-1})_s = 27$ $\sec^{-1}$. The increase of

30 percent with respect to the 'infinite dilution value' is also found in NaCl-solutions of approximately 3.5 mol/l [5].

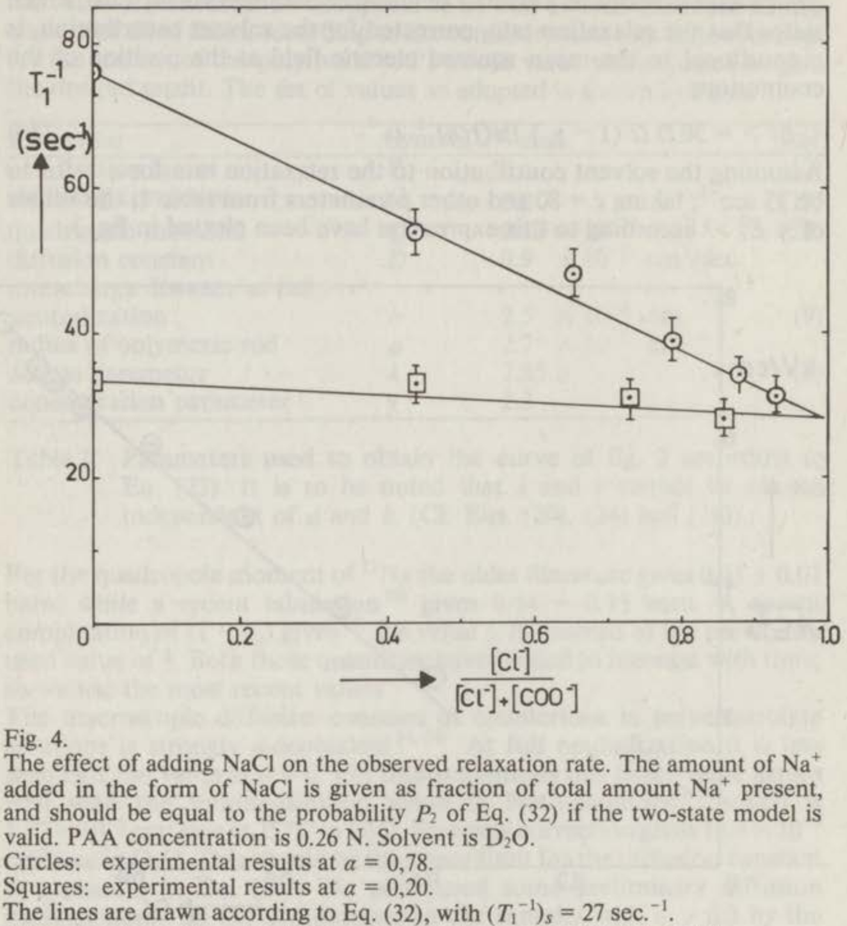

Fig. 4.
The effect of adding NaCl on the observed relaxation rate. The amount of Na^+ added in the form of NaCl is given as fraction of total amount Na^+ present, and should be equal to the probability P_2 of Eq. (32) if the two-state model is valid. PAA concentration is 0.26 N. Solvent is D_2O.
Circles: experimental results at $\alpha = 0,78$.
Squares: experimental results at $\alpha = 0,20$.
The lines are drawn according to Eq. (32), with $(T_1^{-1})_s = 27$ sec.$^{-1}$.
This value is also found in NaCl-solutions of approximately 3.5 mol/l.

Summary and Discussion.

The main feature of the observed relaxation rate is the fact that, for degrees of neutralization above $\alpha = 0.3$, it increases as a quadratic function of α, from 35 sec^{-1} to 90 sec^{-1}. The observed relaxation rates in solutions of simple electrolytes of this concentration [5, 8, 12] do not exceed 30 sec^{-1}, so it is clear that the main relaxation mechanism in our case should be due to a feature that is absent in simple electrolytes: it does not seem reasonable to ascribe the relaxation to fluctuations in the ionic charge distribution, or to changes in dynamical or dielectrical properties of the solvent, which are the main mechanisms in simple electrolytes[2)].

As a most fundamental difference between simple electrolytes and polyelectrolytes we have the symmetry of the time-averaged charge distribution around a (small) ion. In solutions of polyelectrolytes of sufficient charge density this symmetry is generally assumed to be lower than spherical[9)], so that the time-averaged field-gradient at a fixed position relative to the polyion, is not zero. We developed an expression for the relaxation rate due to this 'static' field-gradient, under the assumption that the distribution of charges has cylindrical symmetry, and that the field-gradient correlation is lost by the tangential motion of the ion in the cylindrical field. Without additional assumptions about the radial distribution function of the charges, the relaxation rate is found to be proportional to the squared magnitude of the electric field experienced by the counterion, averaged over all counterions in the distribution (Eq. (16)).

From fig. 3 it can be seen that our experimental results can be explained by assuming that the r.m.s. electric field acting on the counterions increases slightly faster then linear with degree of neutralization α, attaining several kV/cm at high α. To obtain a theoretical estimate for the mean-squared electric field we proposed two different approximations for the radial distribution function of the counterions; the first based on the solution of the Poisson-Boltzmann equation with cylindrical boundary conditions[21)], the second on the ion-condensation concept[10)]. Both lead to results that are in qualitative agreement with the observed relaxation rate. For the solution with aid of the Poisson-Boltzmann equation, a set of physically acceptable parameters (Table I) shows a quantitative agreement of theory and experiments (Fig. 2).

To test the internal consistency of the model, in which it was assumed that the relevant correlation-time is short with respect to the escape-time for a counterion from the polyion-atmosphere[20)] or to the rotational correlation time of the neighbouring part of the polymer, a theoretical expression for the correlation time was obtained. With values of the parameters that do best fit our data, the correlation time is found to be 25 psec, justifying the assumption of tangential diffusion as main source of loss of gradient correlation.

The greatest uncertainty in the application of Eq (23) to our experimental results comes from our lack of knowledge about the waterdipole contribution. Theoretical difficulties connected with this problem have been mentioned in the Introduction, and, briefly, in the discussion of the polarizarion factor (Eq. (5) et seq.). Though we take it to be a plausible assumption that fluctuations in the orientation of watermolecules in the hydration shell should not be strongly α-dependent once the polyion has taken its extended form, it is clearly unsatisfactory that this has not been experimentally established.

This situation may possibly be remedied by using ^{7}Li instead of ^{23}Na as the counterion nucleus. Woessner, Snowden and Ostroff[31)] have shown that in H_2O-solutions of LiCl the ^{7}Li nuclei relax partially by magnetic dipole interactions with the solvent protons. In our case it may be expected that the correlation time for changes in the orientation of the Li-proton vector in the hydration shell varies with α in the same way as the correlation time for the field-gradient reorientation. (The translational contributions might be different, but are of less importance.) For the less concentrated solutions (up to 2 molar) the results of Woessner et al. in H_2O and D_2O might be related by

$$(T_1^{-1})_{H_2O} = 2.1\,(T_1^{-1})_{D_2O} \tag{35}$$

judging from their Fig. 1.; which suggests that correlation times for both mechanism are proportional. We will shortly be performing measurements of ^{7}Li relaxation rates in polyelectrolyte solutions, both in H_2O and D_2O. By putting the water-dipole contribution proportional to the difference in relaxation rates in the two solvents, we hope to be able to make a better-founded correction for the water contribution than was done in Eq. (33). It has to be remarked, that even if the water contribution is a (not too fast) changing function of α, a reasonable fit for the polyion contribution according to Eq. (23) can still be obtained.

Compared to the uncertainty in the contribution of the solvent to the observed relaxation rate, the neglect of relaxation due to fluctuations in the charge distribution can be expected to be of minor importance. Inclusion of this contribution in the theory would require the solution of a complicated diffusion problem [20]), and does not seem feasible at the moment.

In spite of these uncertainties, we believe to have shown that use of the Poisson-Boltzmann equation, that has been succesfully applied to thermodynamical problems, gives correct results for this nuclear relaxation problem as well. This may appear strange at first sight, but by inspection of Eq. (16) it becomes clear what is the source of this success: the relaxation rate is determined by the magnitude of the electric field, that is *static* in a reference frame attached to the polymer; the time-dependence of the interaction arises from diffusion of the nucleus under consideration through this field. Apparently the effect of this static field is large enough to dominate the observed relaxation behaviour. The success of the cylindrical cell model in the present case further supports the idea that the remarkable properties of polyelectrolytes have to be attributed to the asymmetry in the total ionic charge distribution.

The most promising extension of the present research seems to be in the direction of polyelectrolytes neutralized by mixtures of mono- and divalent counterions. It is expected from numerical solutions of the Poisson-Boltzmann equation [32]) that the monovalent ions will be driven away from the polyion. Following the same type of reasoning that led to Eq. (32) we expect the relaxation rate of the monovalent ions to decrease, when their number fraction decreases. The relaxation rate for both types of nuclei may be computed along the lines of the present paper, computing the mean squared electric field by numerical means, instead of from the analytical Eq. (17).

The nuclear magnetic relaxation of co- and counterions in polyelectrolytes will be most directly dependant upon details in the ion-distribution. This feature will make NMR studies of these ions, - though admittedly unsensitive on a concentration scale -, the most sensitive means, seen in Å, hitherto used in studies of the polyion's atmosphere.

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APPENDIX I: Time of escape from a potential well

In the theoretical part of the preceding chapter, between the Eqs. (9) and (10) a result of Lifson and Jackson is quoted, concerning an estimate for the average time it takes for a counterion to escape from the potential well around a polyion. For sake of completeness, we will derive here an estimate of this same quantity, based on a model that H. A. Kramers has developed 1) for calculating the rate of chemical reactions by considering a particle that is caught in a potential hole, and which, by the shuttling action of Brownian motion, can escape over the potential barrier.
He considers an ensemble of one-dimensional systems, consisting of a single particle caught in a potential hole of the type sketched in Fig. 1.

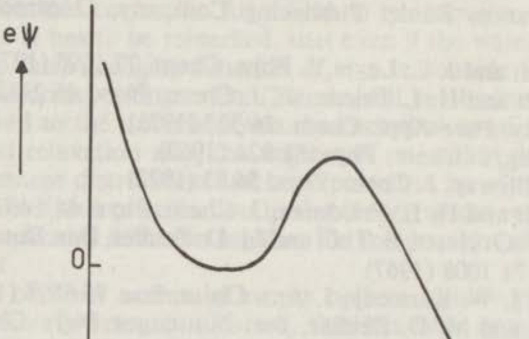

Fig. 1.
The potential field considered
by Kramers.

The barrier is supposed to be large compared to *kT*, and all particles are initially at *A*. Due to the large barrier between *A* and *B*, the equilibrium distribution (with a non-zero number of particles in *B*) will be attained slowly, by a quasi-stationary diffusion current of particles from *A* to *B*. The starting point is the Smoluchowski diffusion equation, for the rate of change of the probability *w(r)* to find the particle at *r*:

$$\frac{\partial w}{\partial t} = \nabla \cdot \left(\frac{kT}{m\beta} \nabla w + \frac{w}{m\beta} \nabla (e\,\psi) \right)$$

$$= D \nabla \cdot (\nabla w + w \nabla \varphi) = -\nabla \cdot j \qquad (1)$$

where $\varphi = e\,\psi/kT$, $-\nabla\,(e\,\psi)$ is the force acting on the particle, β is the friction constant and D the diffusion constant. A stationary diffusion current **j** obeys the law

$$j = constant \tag{2}$$

and thus, in a notation appropriate to the one-dimensional system under consideration

$$\begin{aligned} j &= -D\left(\frac{\partial w}{\partial r} + w\,\frac{\partial \varphi}{\partial r}\right) \\ &= -D\exp(-\varphi)\,\frac{\partial}{\partial r}\,(w\exp\varphi) \end{aligned} \tag{3}$$

Using the fact that j is independent of r, and integrating from A to B:

$$j\int_A^B \exp(\varphi)\,\mathrm{d}r = D\,w\exp\varphi\,\Big|_B^A \tag{4}$$

For the case in which we are interested, $w(B) \approx 0$, so that, defining the zero of the potential at A:

$$j = D\,w\,(A)\left[\int_A^B \exp(\varphi)\,\mathrm{d}r\right]^{-1} \tag{5}$$

The largest contribution to the integral in the denominator comes from the region near C; its actual value depends on the shape of the barrier, especially at the top. The probability $w(A)$ to find a particle in a small volume near A depends on the shape of the hole near A. Kramers considers various possibilities. We will simplify the model considerably by assuming a rectangular-barrier type of potential, as shown in Fig. 2. Since φ_c is assumed to be much larger than unity, the largest contribution to the integral in Eq. (5) comes from the region between a and b; furthermore we take $(b - a) \approx b$, so that

$$\int_A^B \exp\varphi\,\mathrm{d}r \approx b\exp\varphi_c \tag{6}$$

We take the probability $w(A)$ to find the particle near position A in the well as uniform over the interval (0, a), so that $w\,(A) = 1/a$. Then the rate of escape (the rate at which particles initially caught in the well (0, a) arrive at b) is given by

$$\frac{1}{\tau} = j = D\,(a\,b)^{-1}\exp(-\varphi_c) \tag{7}$$

The average time τ_o required for particles starting at $r = 0$ to arrive at b in absence of the barrier is of the order b^2/D, and we have finally

$$\frac{\tau}{\tau_o} \approx \frac{a}{b}\exp(\varphi_c) \tag{8}$$

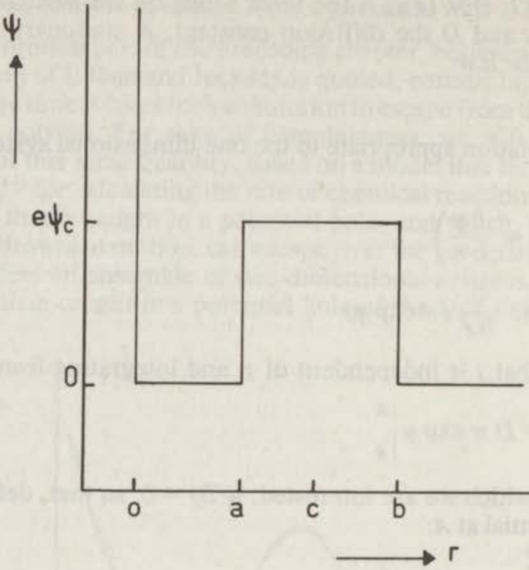

Fig. 2.
A simple square well
and square Barrier.

To apply this estimate to the entrapment of small ions in the electrostatic field of polyions, we estimate, from numerical solutions of the Poisson -Boltzmann equation [2], the values of the parameters as: $a/b \approx 10^{-1} - 10^{-2}$, and $\varphi_c \approx 7 - 9$, so that $\frac{\tau}{\tau_o} \approx 10 - 10^3$.

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APPENDIX II: Nuclear Magnetic Relaxation of ^{23}Na in mono/divalent counterion clouds

In the Discussion of the preceding Chapter it was stated that in counterion clouds consisting of mono and divalent ions, the relaxation rate of the monovalent ions should decrease as their number fraction decreases because the electrostatic interaction of the polyion with the divalent ions is much stronger than with the monovalent ions. We will work out this statement somewhat further, starting from Eq. (16) of the preceding Chapter:

$$T_1^{-1} = \frac{1}{30}\left[\varepsilon\, P\,(1-\gamma_\infty)\; eQ/\hbar\right]^2 D^{-1} < E_r^2 >_r$$

and using the ion-condensation model for the monovalent ion. We consider a solution of a polyelectrolyte, where a fraction f of the acid groups is neutralized by sodium hydroxide, and the remaining fraction $(1-f)$ by some divalent hydroxide.

If the divalent ions are merely condensed, and not bound to the polymer, the mean-squared electric field at the position of the monovalent ions can be expressed as (see Eq. (25) of this Chapter)

$$< E_r^2 >_r = f'\,(2\,e/\varepsilon\, b\, d)^2 \qquad \text{(II 1)}$$

where f' denotes the fraction of the monovalent ions that is condensed. The monovalent ions will condense if $2.85\, f > 1$ (in the case of vinylic polyions) and the fraction of condensed counterions in that case is given by

$$f' = 1 - 0.35\, f^{-1} \qquad \text{(II 2)}$$

and the expression for the relaxation rate becomes

$$T_1^{-1} = \frac{2}{15}\left[P\,(1-\gamma_\infty)\; eQ/\hbar\right]^2 D^{-1}\,(1-0.35\, f^{-1})\;(e/bd)^2 \quad \text{if } f > 0.35 \qquad \text{(II 3)}$$

If, on the other hand, it is assumed that all divalent counterions are really bound to the polyacid groups, thus lowering the charge of the polyion, we have for the nuclear magnetic relaxation rates of the monovalent ion by strict analogy with Eq. (26):

$$T_1^{-1} = \frac{2}{15}\left[P\,(1-\gamma_\infty)\; eQ/\hbar\right]^2 D^{-1}\,(1-0.35\, f^{-1})\, f^2\,(e/bd)^2 \quad \text{if } f > 0.35 \qquad \text{(II 4)}$$

So, in principle the measurement of the nuclear magnetic relaxation of the monovalent ion can give information about the status of the divalent ion. This of course should show up also in the nuclear magnetic relaxation of the divalent ion, but unfortunately most of them have a too low NMR sensitivity to be of practical interest in the magnetic fields attainable with iron-core magnets.

We performed some preliminary measurements on ^{23}Na spin-lattice

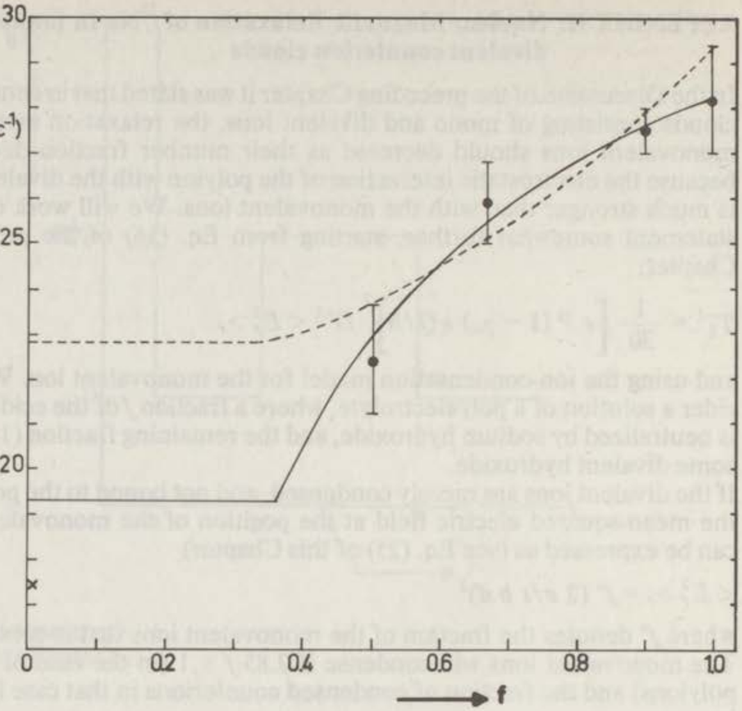

Fig. (II 1): ^{23}Na spin-lattice relaxation in H_2O solutions of poly(styrenesulphonic acid) neutralized by sodium and barium hydroxide, as a function of the charge fraction of Na^+ f. Dashed curve: binding model (Eq. (II 4)) with assumed water contribution to the relaxation rate of 22.8 sec^{-1}, and a fitted value for the average distance d of 11.2 Å. Full curve: condensation model (Eq. (II 3)) with water-contribution 18.3 sec^{-1} and $d = 9.2$ Å. Polyion concentration 2×10^{-2} N.
The value of the nuclear magnetic relaxation rate in dilute solutions of simple salt is indicated by the cross at lower left.

relaxation in H_2O solutions of the strong acid poly(styrenesulphonic acid), fully neutralized by mixtures of sodium hydroxide and barium hydroxide. The polyacid concentration was 2×10^{-2} N, its molweight $M_v = 1.15 \times 10^5$, and the sample volumes 3 cm^3; the experimental method and equipment were the same as described in the preceding Chapter, except that instead of the C-1024 the digital boxcar system described in Chapter II was used, and no measurements of transversal relaxation have been made up to now. The results at four values of f (the fraction of acid groups that is neutralized by sodium) are shown in the figure, with error bars estimated from scatter in the single relaxation curves and/or the reproducibility of the slope of the relaxation curves. It is perhaps illustrative to mention that the four points shown are derived from 10^6 individual measurements of nuclear magnetization, obtained in a net measuring time of 80 hours. The lines shown are visual fits to Eqs. (II 3) and (II 4), treating the water-contribution to the relaxation rate and the average distance *d* as adjustable parameters. The water contribution in the case of the 'bindingmodel' seems fairly high: from measurements on sodium relaxation rates in H_2O solutions of poly(acrylic acid) (see Ref. (6) of preceding Chapter) one gets the impression that the water contribution increases roughly linearly with concentration, at a rate of approximately 20 percent per 0.1 *N*; the fitted value in the case of the 'condensation-model' is in good agreement with this estimate.

By increasing the number of experimental data, we hope to be able to distinguish between the binding- and condensation-models for the divalent ion; the data obtained so far seem to favor the condensation model.

CHAPTER V

Solvent Nuclear Magnetic Relaxation in Polyacid Solutions.

Introduction

Several papers have been published on nuclear magnetic relaxation in aqueous solutions of macromolecules: mostly proteins[1–7], and some synthetic polymers[8, 9]. In a few cases the difference in relaxation behaviour between H_2O and D_2O solutions is discussed; for serum albumin solutions this has been done by Kimmich and Noack[5, 6].

The general approach is to distinguish between water molecules in the hydrated phase and those in the non-associated phase, and to describe the observed relaxation rate as some average over the relaxation rates in these two phases. Little attention has been paid to the facts that the amount of protons or deuterons incorporated in the acid groups of the polymer changes with the degree of neutralization and that, at constant degree of neutralization, such incorporation may have quite different effects on the observed relaxation for deuterons and protons. In the former case the electron-distribution in the chemical bond interacts with the nuclear quadrupole moment to produce relaxation, and the magnitude of the interaction can be expected to be of the same order as in e.g. D_2O[18]. In the latter case there is no quadrupole moment and relaxation can occur through magnetic interactions only. From structural considerations these interactions can be expected to be much smaller than e.g. in H_2O. In both cases modulation of the interaction occurs through reorientation of the acid-group, and/or chemical exchange. The reorientational motion of an acid group attached to a polymer should in general be anisotropic; thus the efficiency of the relaxation process will depend on the geometry of the molecule, or molecular group[11–14].

If chemical exchange is slow with respect to the reorientational correlation times, but fast with respect to the relaxation times in the water molecules and in the acid groups, the observed relaxation rate is a weighted average of the relaxation rates in these two environments[16]. The effect of the presence of the polyion on the motion of the solvent molecules can be studied by solvent-diffusion measurements. Again the observed self-diffusion will be an average over the different environments; if the molar fraction of acid groups is low (e.g. 0.01) the observed self-diffusion will be essentially equal to the solvent diffusion, since the polymer diffusion constant is smaller than the solvent diffusion constant[10]. It is to be expected that the proportionality between translational and rotational diffusion, that exists for the pure solvent, will also hold for sufficiently dilute solutions.

A study of solvent relaxation in aqueous poly-electrolyte solutions as a function of the degree of neutralization should therefore comprise measurements of H_2O and D_2O relaxation, as well as self-diffusion of at least one solvent. In the case of slowed-down reorientation in a hydration shell, the H_2O and D_2O relaxation should show approximately the same behaviour, after correction for the solvent-intermolecular relaxation in H_2O by means of the observed self-diffusion. If deuteron relaxation in COOD-groups is important, the dependence of the H_2O and D_2O results on the degree of neutralization should be markedly different. The observed D_2O relaxation rates can be corrected for the contribution of the water molecules through the observed diffusion coefficients, in order to obtain the relaxation rates in a COOD-group.

In the present communication we will show that COOD-group formation is an important relaxation mechanism for deuterons in D_2O solutions of poly(acrylic acid).

Although small effects due to hydrated watermolecules cannot be excluded, it will be shown that the main features of the deuteron relaxation are due to the presence of COOD-groups.

A simple theory for the solvent relaxation rate adequately explains the experimental results with no reference to the hydrated water at all. Conversely, no information on the reorientational freedom of hydrated water may be obtained from the present experiments.

Theoretical.

For nuclear magnetic relaxation of deuterons, which have a spin $I = 1$, the interaction of the nuclear quadrupole moment with the electric field gradient arising from the non-spherical symmetry of the electron distribution in the chemical bond, is the most important relaxation mechanism. We will assume that the electron distribution has cylindrical symmetry and that relaxation occurs through, in general anisotropic, diffusional reorientation of the bond axis with respect to the Zeeman field; in that case the deuteron relaxation rates are given by 11–14).

$$T_1^{-1} = \frac{3}{8}\left(\frac{eqeQ}{\hbar}\right)^2 \frac{1}{5}\sum_{i=-2}^{2} c_i\,\tau_i\left[(1+\omega_o^2\tau_i^2)^{-1} + 4\,(1+4\,\omega_o^2\tau_i^2)^{-1}\right] \qquad (1)$$

$$T_2^{-1} = \frac{3}{8}\left(\frac{eqeQ}{\hbar}\right)^2 \frac{1}{5}\sum_{i=-2}^{2} c_i\,\tau_i\left[\frac{3}{2} + \frac{5}{2}(1+\omega_o^2\tau_i^2)^{-1} + (1+4\omega_o^2\tau_i^2)^{-1}\right] \qquad (2)$$

where $eqeQ/h$ is the quadrupole coupling constant 15) and ω_o the Larmor frequency. The coefficients c_i and the correlation times τ_i are given as function of the principal values of the rotational diffusion tensor and the orientation of the bond axis with respect to the diffusion tensor principal axes in Table I.

In the general case of totally anisotropic rotation, the relaxation rates are described by five Lorentzian functions, containing five independent parameters: D_x, D_y, D_z, ϑ and φ. For axially symmetric rotation the terms with $i = \pm 1$ and the terms with $i = \pm 2$ can be taken together; resulting in three Lorentzian functions with three independent parameters: $D_\perp$, $D_{/\!/}$ and ϑ. For spherically symmetric rotational diffusion only one Lorentzian function is left, containing one parameter D; the coefficients c_i in this case sum up to unity.

i	c_i	τ_i^{-1}
-2	$3x^2y(1-y)$	$D_x + D_y + 4D_z$
-1	$3x(1-x)(1-y)$	$D_x + 4D_y + D_z$
0	$\frac{1}{4}[(1-p^2)^{\frac{1}{2}}(2-3x) +$ $+ (3)^{\frac{1}{2}} px(1-2y)]^2$	$2(D_x + D_y + D_z - \Delta)$
$+1$	$3x(1-x)y$	$4D_x + D_y + D_z$
$+2$	$\frac{1}{4}[p(2-3x) +$ $+ (3-3p^2)^{\frac{1}{2}} x(1-2y)]^2$	$2(D_x + D_y + D_z + \Delta)$

Table I: the coefficients and correlation times in Eqs. (1) and (2). The symbols in the table are defined as:

$$x = \sin^2\vartheta,\ y = \sin^2\varphi,\ \ p = \left(\tfrac{3}{4}\right)^{\frac{1}{2}} (D_x - D_y)\,(3\,\Delta\,(D_z - D_s) + 2\Delta^2)^{-\frac{1}{2}}$$

$$D_s = \tfrac{1}{3}(D_x + D_y + D_z),\ \Delta = [(D_x - D_y)^2 + (D_z - D_x)\,(D_z - D_y)]^{\frac{1}{2}}$$

D_x, D_y, D_z are the principal values of the diffusion tensor; ϑ and φ are the polar, resp. azimuthal angle of the bond with respect to the diffusion-tensor principal axes.

In the present case we wish to apply the theory to relaxation of deuterons in a COOD-group attached to a polymer; surely we should not treat the whole macromolecule as a rigid body, undergoing diffusional reorientation. As an approximation, a chain segment of appropriate length might be chosen as the 'rigid body', while the presence of the rest of the polymer reflects itself in the *values* that the rotational diffusion constants of this 'rigid body' do assume. Because of the variety of possible conformations in a given configuration for such a chain segment, there is also variety of possible angles ϑ and φ. Therefore it is not to be expected that a molecular interpretation for the experimentally determined values of these angles can be given; still we feel their use as rather formal than molecular parameters, justified. To a certain extent the same precautions hold for the interpretation of the experimentally determined correlation times; these, however, are *always* 'ensemble-properties', not uniquely related to molecular geometry.

Experimentally, it is found that the 'extreme narrowing' condition is not met: i.e. at least one of the five correlation times in Table I is of the order of the inverse Larmor frequency. From the definitions it can be shown that no correlation time is longer than τ_o:

$$\tau_o \geqslant \tau_i \qquad i = -2, -1, 1, 2 \tag{3}$$

To simplify the description of the frequency dependence of the relaxation rates we will assume that only one correlation time, τ_o, is of the order of the inverse Larmor frequency, while the four other correlation times are much shorter

$$\omega_o \tau_o \approx 1,\ \omega_o \tau_i \ll 1 \qquad i = -2.\ -1, 1, 2 \tag{4}$$

From inspection, it can be seen that this is the case if one of the diffusion constants, - D_z, say - is much larger than the other two:

$$D_z \gg D_x,\ D_z \gg D_y$$

If these conditions are met, we may use for c_i and τ_i of Eqs. (1) and (2) the approximate expressions shown in Table II. It can be seen that if ϑ

i	c_i	τ_i^{-1}
-2	$3x^2y\,(1-y)$	$4D_z$
-1	$3x\,(1-x)\,(1-y)$	D_z
0	$\frac{1}{4}\,(2-3x)^2$	$3\,(D_x + D_y)$
$+1$	$3x\,(1-x)\,y$	D_z
$+2$	$\frac{3}{4}\,x^2\,(1-2y)^2$	$4D_z$

Table II: Approximate expressions for the coefficients and correlation times in Eqs. (1) and (2), for the case that $D_z \gg D_x$ and $D_z \gg D_y$. The symbols in the table are defined in the same way as in Table I.

equals the 'magic angle', the coefficient c_o vanishes, and there is no contribution from the slow reorientations to the relaxation rate.

From the assumption (4) we can collect the four frequency-independent terms in Eqs. (1) and (2):

$$\sum_{i \neq 0} c_i \tau_i = [4\,(c_1 + c_{-1}) + c_2 + c_{-2}]/4D_z = 3x\,[15\,(1-x) + 1]/16D_z \tag{5}$$

The frequency-independent part is seen to vanish for $x = 0$ ($\vartheta = 0$) and to be maximal if $x = 8/15$ ($\vartheta = 47°$).

The full expressions for the relaxation rates become, under the assumption $D_z \gg D_x$, $D_z \gg D_y$:

$$T_1^{-1} = \frac{3}{160}\left(\frac{eqeQ}{\hbar}\right)^2 \left[45\,x\,[15(1-x)+1]\,\tau_z + (2-3x)^2\,\tau_{xy} \times [(1+\omega_o^2\,\tau_{xy}^2)^{-1} + 4\,(1+4\omega_o^2\,\tau_{xy}^2)^{-1}]\right] \tag{6}$$

$$T_2^{-1} = \frac{3}{160}\left(\frac{eqeQ}{\hbar}\right)^2 \left[45\,x\,[15(1-x)+1]\tau_z + (2-3x)^2\,\tau_{xy} \times [\frac{3}{2} + \frac{5}{2}\,(1+\omega_o^2\,\tau_{xy}^2)^{-1} + (1+4\omega_o^2\,\tau_{xy}^2)^{-1}]\right] \tag{7}$$

where $\tau_z = (6D_z)^{-1}$, $\tau_{xy} = (3D_x + 3D_y)^{-1}$, $x = \sin^2\vartheta$

If the deuteron can be in either of two environments, 1 and 2, and the exchange between the two is fast, the observed relaxation rate is given by[16]:

$$(T_{1,2}^{-1})_{obsvd} = p_1\,(T_{1,2}^{-1})_1 + p_2\,(T_{1,2}^{-1})_2$$

where $p_{1,2}$ are the probabilities to find the deuteron in each of these environments.

In the present case, a deuteron is either in a COOD-group, where the relaxation rates are given by Eqs. (6, 7) or in a D_2O molecule, in which case we assume its relaxation rate to be proportional to the reciprocal of the diffusion coefficient D.

The expressions for the observed relaxation rates become:

$$(T_{1,2}^{-1})_{\mathrm{obsvd}} = \frac{2X_1}{2X_1 + X_2}\,\frac{D_o}{D}\,(T_{1,2}^{-1})_o + \frac{X_2}{2X_1 + X_2}\,(1 - \alpha')\,(T_{1,2}^{-1})_{\mathrm{COOD}} \qquad (8)$$

where the index o indicates the pure solvent, $(T_{1,2}^{-1})_{\mathrm{COOD}}$ is given by Eqs. (6, 7), α' is the degree of neutralization and X_1 and X_2 indicate the molar fractions of D_2O molecules and PAA-monomers respectively.

Experimental.

Atactic Poly(acrylic acid) (PAA) was synthezised and fractionated as described before[19]. The viscosity averaged molecular weight of PAA was 1.39×10^6 for the D_2O solutions and 0.43×10^6 for the H_2O solutions. Atactic Poly (methacrylic acid) (PMA) was synthesized and fractionated as described before[20]. The viscosity averaged molecular weight of PMA was 0.22×10^6. NaOD solution was prepared by dissolving freshly cut sodium in D_2O in a nitrogen atmosphere; D_2O solution was obtained by dissolving PAA or PMA in D_2O, freeze drying and redissolving in D_2O. This procedure was repeated three times.

Deuterium solutions of PAA at different degrees of neutralization were prepared by adding calculated quantities of NaOD solutions to weighted amounts of D_2O solutions of PAA and adjustment of the concentration by adding calculated quantities of D_2O. Deuterium solutions of PMA at different degrees of neutralization were prepated by adding calculated quantities of fully neutralized PMA solutions to weighted amounts of unneutralized PMA solutions of the same concentration. PAA solutions in H_2O were prepared in the same way as the PMA solutions; the conventional freeze-pump-thaw cyclus was repeated four times and the sample tubes were sealed off in a helium atmosphere. The H_2O reference sample was treated similarly. Final sample volumes were 1.5 cm^3 approx. All operations involving the D_2O solutions were performed in a dry box.

Relaxation rates were measured on a Bruker pulsed-NMR spectrometer, using $\pi - \frac{1}{2}\pi$ sequences for the longitudinal and $\frac{1}{2}\pi - \pi$ or CP-GM (when necessary) sequences for the transversal relaxation. The magnet was a Varian high-resolution type, operated at 14.21 kG max.

Solvent proton relaxation was measured with such a time interval between the π and $\frac{1}{2}\pi$ pulses that there was no contributions from the polymer protons (except the proton of the acid group) to the measured signal.

Diffusion coefficients were measured with a Bruker pulsed gradient apparatus in a home made liquid thermostated probe head at 25 °C; the attenuation of the spin echo was measured as a function of the gradient magnitude. All diffusion coefficients were measured relatively to a standard D_2O sample (Merck 2919).

Results.

In order to test the proposed mechanism for deuteron relaxation in heavy water solutions of poly-electrolytes, we measured solvent proton relaxation rates and deuteron relaxation rates and selfdiffusion-coefficients in poly (acrylic acid) solutions. This polymer was chosen because of its lack of a sharp conformational transition, to which the remarkable behaviour of deuteron relaxation rates in some other poly-electrolyte solutions has been related[8].

It is well known that spin-echo determinations of selfdiffusion coefficients are considerably less accurate than tracer measurements; on the other hand they are much easier to perform. For the concentration range of interest we found that our results may be represented by

$$(D_o - D)/D = (p - q\,(1 - \alpha'))\,X_2 \qquad (9)$$

where $p = 23$ and $q = 15$ with an estimated accuracy of ten percent. In Fig. 1 we have plotted D_o/D as function of α' at $X_2 = 6.10 \times 10^{-3}$; the point-dash line has been drawn according to Eq. (9). It has to be remarked that in the determination of the coefficients p and q also measurements at other values of X_2 (up to 0.02) have been taken into consideration; therefore the line shown does not represent a least-squares fit to the experimental results of this figure only.

In the same figure we show the proton and deuteron relaxation rates in poly(acrylic acid) solutions, relative to their values, as measured in the pure solvent:

$(T_{1,2}^{-1})_o = 2.4 \ \text{sec}^{-1}$ for D_2O

$(T_{1,2}^{-1})_o = 0.30 \ \text{sec}^{-1}$ for H_2O

It is seen that, at low degrees of neutralization, the relative deuteron relaxation is much faster than the relative proton relaxation, while at high α' the protons relax slightly faster than the deuterons. Both nuclei relax faster than would be expected from the change in diffusion coefficients only, except the deuterons at full neutralization.

The long-dashed line is a least-squares fit through the five H_2O relaxation points, each point being the average of the measured T_1^{-1} and T_2^{-1}, which differed five percent at most. The $\alpha' = 0$ point lies on a probably significant distance from this line; still the difference is rather small and we will not try to give a molecular interpretation. The faster increase with α' of the H_2O-line with respect to the diffusion line may be due to an increasing dipole-dipole coupling between solvent and polymer-protons. We have not tried to identify this mechanism (this could be done e.g.

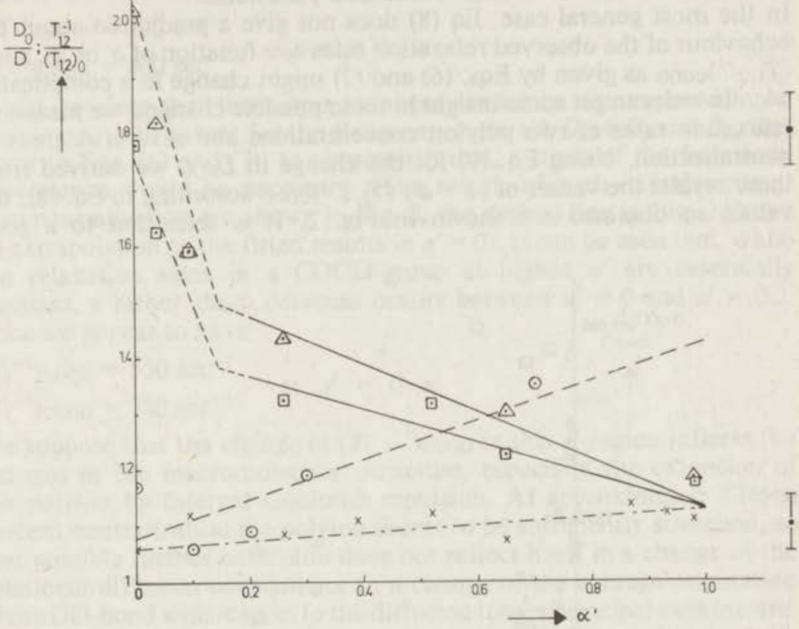

Fig. 1.
Relaxation rates T_1^{-1} and T_2^{-1}, and inverse self-diffusion coefficient D^{-1} in poly-(acrylic acid) solutions, relative to their values in the pure solvent, as function of the degree of neutralization α'.
□ longitudinal, and △ transversal relaxation; × self-diffusion for deuterons in D_2O-solutions of PAA. $M_v = 1.39 \times 10^6$ $X_2 = 6.10 \times 10^{-3}$ $\nu_o = 9.21$ MHz
⊙ average of longitudinal and transversal relaxation for solvent protons in degassed H_2O-solutions of PAA. $M_v = 0.43 \times 10^6$ $X_2 = 5.30 \times 10^{-3}$ $\nu_o = 9.49$ MHz.

by fully deuterating the polymer, as has been done by Willenberg and Sillescu[17] for the benzene-PMMA system); the main goal of the H_2O measurements was to test the assumption of a relaxation process acting on the water molecule as a whole, as has been used in the case of poly-(methacrylic acid) solutions[8]. The full lines for $\alpha' > 0.2$ have been derived from results shown in Fig. 2; their meaning will be clear from the discussion in the next paragraph. The extrapolation to $\alpha' = 0$ has been derived from fig. 3; the short-dashed lines have been drawn as an aid to the eye: we do not wish to suggest that the relaxation rates really do decrease linearly in this region.

From the difference in relative proton and deuteron relaxation rates at zero neutralization it is quite clear that the dominant relaxation process is *not* a hindered of slowed-down rotation of the water molecule as a whole: in that case the relative proton spin-spin relaxation rate should be 1.7 approximately, since in pure H_2O about two-thirds of the relaxation rate is due to rotational ('intramolecular') motions.

In the most general case, Eq (8) does not give a prediction about the behaviour of the observed relaxation rates as a function of α' or X_2, since $(T_{1,2}^{-1})_{COOD}$ as given by Eqs. (6) and (7) might change in a complicated way. In order to get some insight in these possible changes, we measured relaxation rates at two polyion concentrations and several degrees of neutralization. Using Eq. (9) for the change in D_o/D we derived from these results the values of $(1 - \alpha')(T_{1,2}^{-1})_{COOD}$ according to Eq. (8); the values so obtained are shown in Fig. 2. It is seen that to a good

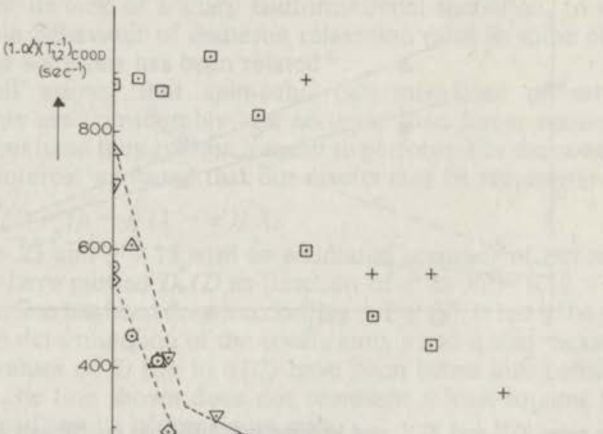

Fig. 2.
Deuteron relaxation rates in a COOD-group times $(1 - \alpha')$, as derived from the observed relaxation rates by Eqs. (8) and (9) for D_2O-solutions of poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) as a function of degree of neutralization α', at $\nu_o = 9.21$ MHz.
⊙ longitudinal, and △ transversal relaxation for PAA;
$M_v = 1.39 \times 10^6$, $X_2 = 6.10 \times 10^{-3}$
◈ longitudinal, and ▽ transversal relaxation for PAA;
$M_v = 1.39 \times 10^6$, $X_2 = 11.2 \times 10^{-3}$
⊡ longitudinal, and × transversal relaxation for PMA;
$M_v = 0.22 \times 10^6$, $X_2 = 10.8 \times 10^{-3}$
The bar shown at $\alpha' = 0.43$ corresponds to ± 5% deviation in the raw data for that point. The lines are described in the text.

approximation $(T_{1,2}^{-1})_{\text{COOD}}$ is independent of concentration for the solutions studied: at zero and eighty percent neutralization it was verified that this independence extends to at least $X_2 = 0.02$ Furthermore for $\alpha' > 0.2$ we have, from a least-squares fit represented by the full lines,

$$\left.\begin{array}{l}(T_1^{-1})_{\text{COOD}} = 290\ \text{sec}^{-1}\\ (T_2^{-1})_{\text{COOD}} = 400\ \text{sec}^{-1}\end{array}\right\}\quad \text{for } \alpha' > 0.2$$

It will be clear that these two numbers cannot be decomposed in an unique way into values for the three parameters ϑ, $D_x + D_y$ and D_z, that occur in Eqs. (6) and (7); to accomplish that, a study of the frequency dependence would be necessary. (The results of such experiments at zero neutralization are shown in Fig. 3; the dashed line in Fig. 2 shows an extrapolation to the fitted results in $\alpha' = 0$). It can be seen that, while the relaxation rates in a COOD-group at higher α' are essentially constant, a rather sharp decrease occurs between $\alpha' = 0$ and $\alpha' = 0.2$, since we appear to have

$$\left.\begin{array}{l}(T_1^{-1})_{\text{COOD}} = 550\ \text{sec}^{-1}\\ (T_2^{-1})_{\text{COOD}} = 780\ \text{sec}^{-1}\end{array}\right\}\quad \text{at } \alpha' = 0$$

We suppose that the change in $(T_{1,2}^{-1})_{\text{COOD}}$ in this α'-region reflects the changes in the macromolecular structure, especially the extension of the polyion by internal Coulomb repulsion. At approximately fifteen percent neutralization the polyion seems to be sufficiently stretched, so that possible further extension does not reflect itself in a change of the rotational diffusion constants or in a change of the average orientation of the OD-bond with respect to the diffusion tensor principal axes system. As an illustration we have also plotted some results for poly(methacrylic acid) solutions. Diffusion results in these samples could be represented by Eq. (9) with $p = 29$ and $q = 23$ The value of $(T_2^{-1})_{\text{COOD}}$ at zero neutralization was found to be $14 \times 10^3\ \text{sec}^{-1}$, some twenty times faster than in poly(acrylic acid). The discussion of the proton and deuteron relaxation data in poly(methacrylic acid) solutions will be the subject of a separate communication.

In Fig. 3 the frequency-dependence of the observed relaxation rates at different Larmor frequencies for a PAA sample with $\alpha' = 0$ are shown. The difference between T_1 and T_2 is seen to be rather small, but systematic. A unique fit to Eqs. (6) and (7) (with the aid of Eqs. (8) and (9)) is not possible: the lines drawn correspond to *both* of the following sets of parameters-values:

$$eqQ/h = 200\ \text{kHz}\quad 3(D_x + D_y) = 1.1 \times 10^8\ \text{sec}^{-1}\quad 6D_z = 4\ \ \times 10^{10}\ \text{sec}^{-1}\quad \vartheta = 37°$$

or

$$eqQ/h = 200\ \text{kHz}\quad 3(D_x + D_y) = 5.9 \times 10^7\ \text{sec}^{-1}\quad 6D_z = 7\ 7 \times 10^9\ \text{sec}^{-1}\quad \vartheta = 41°$$

The choice for eqQ/h in the COOD-group has been based on its values in the gas and solid phases of formic acid, which are 260 kHz and 160 kHz respectively [18]. Since both sets of parameters give the same results, there exist no doubt many others that fit the data; the sets given correspond to 'extreme values' in the sense that, to obtain a reasonable fit one

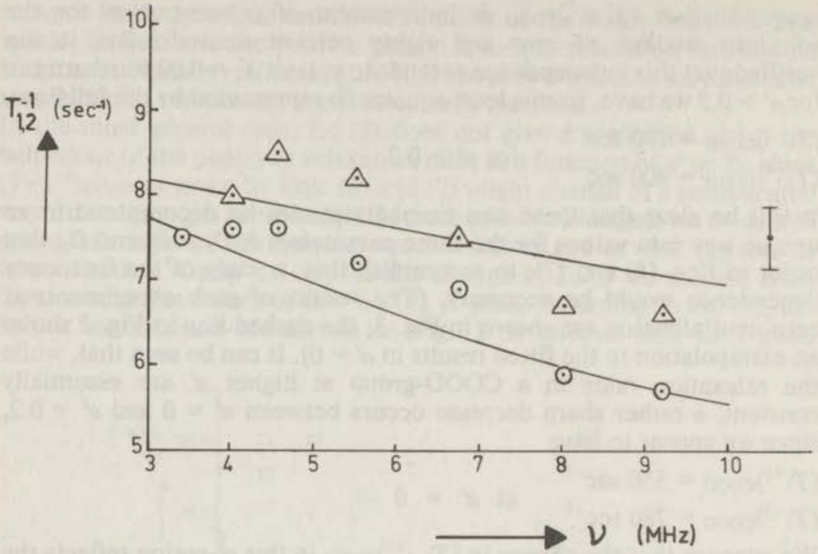

Fig. 3.
Observed deuteron relaxation rates in a poly(acrylic acid) (PAA) solution at zero neutralization as a function of Larmor frequency ν.
△ T_2^{-1} ⊙ T_1^{-1}; PAA, $M_V = 1.39 \times 10^6$, $X_2 = 11.2 \times 10^{-3}$.
The lines represent a fit to Eqs. (6) and (7), as explained in the text. The bar shown at the extreme right shows ± 5% variation on this scale.

always has:

$5.9 \times 10^7 \text{ sec}^{-1} \leq 3\ (D_x + D_y) \leqq 11 \times 10^7 \text{ sec}^{-1}$

$7\ 7 \times 10^9 \text{ sec}^{-1} \leqq 6\, D_z$

The r.m.s. deviation of the experimental points from the solid lines is 0.4 sec^{-1}, or approximately 5%. The maximum deviation is 9 percent.

Discussion.

The essential experimental result is in our opinion the fact that the deuterium relaxation is a monotonously decreasing function of α', while the reciprocal of the deuterium self-diffusion coefficient and the proton relaxation rate both behave as (weakly) increasing functions of α'. Knowing that the quadrupole interaction in COOD and in D_2O will be of the same magnitude, while there is no intramolecular dipole-dipole relaxation for the proton in a COOH-group possible, we come to be conclusion that the formation of COOD-groups is the main enhancement process in this case and that the difference in relaxation rate between water, associated with the polymer and non-associated water, is a small one.

To describe the deuteron relaxation in a polyacid group, we used Huntress' treatment of relaxation by anisotropic diffusional reorientation, modified to allow for one correlation time that is long compared to the reciprocal of the Larmor frequency. The geometrical parameters occuring in this theory cannot be easily derived from molecular structure, because of the variety of possible conformations; but the coefficients c_i that contain them (see tables I and II) can assume only limited values: this offers a, - be it modest -, test for the fitted value of the quadrupole interaction. In poly(acrylic acid) solutions the frequency dependence of the deuteron relaxation rates is only slight and a unique fit of theory and experiment is not possible; however, if a reasonable estimate for the magnitude of the quadrupole interaction is made, allowed values for the coefficients c_i are found, and our estimates for the correlation times agree with the values of rotational correlation times of other polymers in aqueous solution 21).

We also believe that in PMA-D_2O there is the same COOD-group effect; because when one uses the experimental results of Glasel 8) and his 'associated water formulae' one calculates an unrealistic low fraction of associated watermolecules (only approx. 0.5 watermolecules per PMA-monomer).

As result of the domination of the COOD-groups on the deuterium relaxation rate it is not possible to examine the influence of the conformation of a polyelectrolyte on the association of watermolecules by measuring the deuterium relaxation rate in D_2O solutions of polyelectrolytes as a function of pH.

For such an investigation it is necessary to use H_2O as solvent, and if possible deuterate the polymer, because of the insensitivity of the proton relaxation rate for COOH-group formation.

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APPENDIX: 'Bound' and 'free' counterions

The presentation of the preceding Chapter has been directed mainly towards clarifying some errors in a previous treatment of deuteron relaxation in D_2O solutions of polyelectrolytes. It may be worthwile to comment briefly on the connection of the results of this Chapter with those of Chapter IV. We have just shown that in D_2O solutions of a weak polyacid, that is not fully ionized, the nuclear magnetic relaxation of deuterons in COOD groups is governed by the slow reorientation of the polymer in solution. The deuteron in such a group is covalently bound, and may be considered as a perfect example of a truly bound counterion with a nuclear quadrupole moment. So we can say that the binding of such a counterion immediately shows up as an increase in its nuclear magnetic relaxation rates, the main reason for this interaction *not* being the forming of the bond itself, but the fact that the reorientational motion of this bond is very slow.

Going back to the ion-condensation model for sodium-polyacrylate solutions (see Chapter IV, discussion preceding Eq. (25)), we are now in a position to conclude that such ion-condensation does not involve association of sodium ions to specific carboxylic groups for a time that is at least of the order of 10^{-8} second, since from the data collected in Table I of Chapter III we can expect that the quadrupole coupling constant in such cases will be at least a few hundred kHz, leading to relaxation rates of several hundreds per second, contrary to what is observed.

CHAPTER VI

Electrical and mass transport in polyelectrolyte solutions

Introduction

Since the famous experiments of Huizenga, Grieger and Wall [1, 2], some twenty-five years ago, it has been known that the transport behaviour of small ions in polyelectrolyte solutions is greatly influenced by the presence of the polyion. Up to now, explanations of the observed diffusion and electrophoresis have been based on the assumption of an 'associated', 'bound' or 'condensed' fraction of counterions. The foundations for this type of theories were laid by the conclusion of Huizenga et al. that *'the exchange* (i.e. of radiolabeled and unlabeled ions) *is rapid but not infinite'*. In a series of important papers, Gottlieb [3-5] has shown that the experimental results which led them to this conclusion were a result of electroosmotically induced solution flows through the glass frit in their transference cell. Thus we will in the following assume that on the time scale of a diffusion or transference experiment there exists only one type of counterion and one type of polyion, since no 'binding' of the two occurs on a comparable time scale.

After the successfull application of the ion-condensation concept [6, 7] (which has been shown [8] to be an asymptotic result of the Poisson-Boltzmann equation) to thermodynamic problems, it has also been applied to transport phenomena, with the additional assumption that the condensed ions give no contribution to the observed transport quantities. It is important to realize that condensed ions in a thermodynamic sense are something else than bound ions in the transport sense. In the latter case the time scale of the binding is of crucial importance to its effect on the transport properties, while in the former case it is only the time-averaged distribution that matters. If 'bound' is defined as 'moving together' for some time of interest, than 'condensed' means simply 'being together' at a certain moment.

Instead of in terms of association it is preferable to speak in terms of time-correlation between the velocities of the different particles. Some years ago Mazo [10] has pointed out that the existence of such correlations in colloidal micelles can be derived from experimental data on micellar diffusion and electrophoresis; up to now his ideas appear not to have been applied to macromolecular polyelectrolytes. In the following we will extend his treatment to include the diffusion constant and mobility of the counterion, and discuss the implications of our results for the usual treatment of conductivity and electrophoresis in polyelectrolyte solutions.

Static Fluctuations

In the sequel it will be necessary to have an expression for the mean squared fluctuation of the number of particles under consideration in a given volume. Now it has to be realized that at all practical concentrations the behaviour of polyelectrolyte solutions is strongly non-ideal, in the sense that the osmotic coefficient is smaller than unity. This can also be expressed by saying that, even at high dilution, there persists a strong correlation between the positions of the counterions, imposed by the Coulombic attraction of the polyion. On the other hand, the positions of different polyions, as represented by the position of their center of mass, are much less correlated, since their mutual Coulombic interaction is weak, due to screening by the counterion cloud.

We will therefore consider the equation of state for the counterions to contain an osmotic coefficient, while that for the polyions is given by the ideal law[11]:

$$\begin{aligned} \pi_c\, V &= \varphi\, N_c kT \\ \pi_p\, V &= N_p\, kT \end{aligned} \tag{1}$$

and the total osmotic pressure π of the solution is given by $\pi = \pi_c + \pi_p$. Now, if we consider a sufficiently large volume, the mean-squared fluctuation of the number of particles in that volume is given by[12]

$$\overline{\Delta N^2} = -\frac{kTN^2}{V^2}\left(\frac{\partial V}{\partial p}\right)_{N,T} \tag{2}$$

Thus we have

$$\begin{aligned} \overline{\Delta N_c^2} &= \frac{N_c}{\varphi} \\ \overline{\Delta N_p^2} &= N_p \end{aligned} \tag{3}$$

The Diffusion Coefficients

For a system of particles that is in thermal equilibrium (no macroscopic concentration- or temperature-gradients) it is usually found that, for sufficiently long times Δt and sufficiently large distances ΔR, the second moment $\overline{\Delta R^2}$ of the displacement of the particles in time Δt is given by

$$\overline{\Delta R^2} = 6\, D\, \Delta t \tag{4}$$

where D is called the (self-)diffusion coefficient[13].
The correlationfunction-expression for D is given by[14]

$$D = \lim_{\varepsilon \to 0} \frac{1}{3\,\overline{\Delta N^2}} \sum_{i,j=1}^{N} \int_0^\infty \mathrm{e}^{-\varepsilon t} < \dot{\boldsymbol{R}}_i\,(0) \cdot \dot{\boldsymbol{R}}_j\,(t) > \mathrm{d}t \tag{5}$$

where we considered an ensemble of open systems of volume V, containing on the average N particles with velocity vectors $\dot{\boldsymbol{R}}_i\,(t)$. The brackets indicate an ensemble average, and the limit $\varepsilon \to 0$ should formally be taken after the integration over all times. Since we will not try to actually compute the time-integrals, we will not bother about this rather theoretical question and delete this limiting procedure in the following.

It should be stressed at this point that the more familiar form of the above equation

$$D = \frac{1}{3} \int_0^\infty < \dot{R}(0) \cdot \dot{R}(t) > \mathrm{d}t \tag{6}$$

is clearly valid only for systems of ideal (non-interacting) particles, and cannot be expected to hold for counterion diffusion.

For large particles with internal degrees of freedom, the diffusion equation will hold for the center-of-mass motion. Of course it depends on the observational technique whether this is really the measured quantity; this however should be the usual case.

The Electrical Conductivity

If a solution containing two kinds of ions is subjected to an electric field **E**, we may, by suitable techniques, observe separately the current densities $\mathbf{j}_+$, due to the positive ions, and $\mathbf{j}_-$, due to the negative ions. Observations can be made of the time-integrals of these currents (i.e. the net amount of charge transported by each charged species), or of the average velocity that the respective particles acquire in the external field (i.e. their average mobility). In both cases an average over the contributions of *all* particles of the observed species is obtained; so if we measure the amount of a radiotracer that is transported in a given time, we see the number-averaged contributions of all forms of hydratation, complexation or association to which the radiotracer species lends itself; *mutatis mutandis* the same holds for the boundary velocity in a 'moving boundary' experiment.

Now, if we have two kinds of charge carriers: the first bearing q_c units of positive unit charge e, and the second bearing q_p units of negative charge $-e$; their average number in a certain volume V, which is part of an open system, being N_c, resp. N_p, then:

$$\begin{aligned} j_c &= \frac{q_c\, e}{V} \sum_{i=1}^{N_c} \dot{R}_{c_i} \\ j_p &= -\frac{q_p\, e}{V} \sum_{i=1}^{N_p} \dot{R}_{p_i} \end{aligned} \tag{7}$$

Usually there is a linear relation between the current density and the applied field; for an isotropic system:

$$j_{c,\,p} = \sigma_{c,\,p}\, E \tag{8}$$

where σ is called the conductivity.

The Hamiltonian of this system of charges in the electric field is given by

$$H = -\left(\sum_{i=1}^{N_c} q_c\, e\, R_{c_i} - \sum_{i=1}^{N_p} q_p\, e\, R_{p_i} \right) \cdot E \tag{9}$$

Thus, according to the lineair-response theory the conductivities are given by [15]

$$
\begin{aligned}
\sigma_c &= \frac{e^2}{3\,kTV} \sum_{i,j=1}^{N_c} \sum_{k=1}^{N_p} \int_0^\infty < q_c\, \dot{R}_{c_i}(0) \cdot (q_c\, \dot{R}_{c_j}(t) - q_p\, \dot{R}_{p_k}(t) > \mathrm{d}t \\
\sigma_p &= \frac{e^2}{3\,kTV} \sum_{i,j=1}^{N_p} \sum_{k=1}^{N_c} \int_0^\infty < q_p\, \dot{R}_{p_i}(0) \cdot (q_p\, \dot{R}_{p_j}(t) - q_c\, \dot{R}_{c_k}(t)) > \mathrm{d}t
\end{aligned}
\tag{10}
$$

and the total specific conductivity of the solution is $\sigma = \sigma_c + \sigma_p$.
(For these time integrals we also neglected a limiting procedure, slightly different from that in the expression for the diffusion constant.)
Now transport numbers are simply given by

$$
\begin{aligned}
t_c &= \frac{\sigma_c}{\sigma_c + \sigma_p} \\
t_p &= \frac{\sigma_p}{\sigma_c + \sigma_p}
\end{aligned}
\tag{11}
$$

and electrical mobilities by

$$
\mu_c = \frac{\sigma_c}{\dfrac{N_c\, q_c\, e}{V}} \qquad \mu_p = \frac{\sigma_p}{\dfrac{N_p\, q_p\, e}{V}}
\tag{12}
$$

(here defined as positive quantities).

Relations between Electrical and Mass Transport.

The sums over particles in the above equations in principle run over a macroscopic volume of the solution under study. As stated under 'Static Fluctuations' we consider the different polyion-domains as non-interacting, so there is no correlation of the motion of any particle (be it *c* or *p*) in domain *A* with the motion of any particle in domain *B;* then our sums reduce to N_p partial sums over individual polyion-domains. This point of view finds experimental support in the fact that observed transport coefficients [1, 2, 16] vary only slightly with concentration for concentrations of a few times 10^{-2} *N* (this variation might be due only to 'excluded volume'-effects).
Now, if we consider a polyion consisting of *P* monomeric units and bearing aP negative charges, contained in a volume V'; denote by the index *c* an at random chosen ion from the aP monovalent counterions belonging to the polyion-domain, while the index *i* runs over all (including *c*) aP counterions; we get:

$$D_c = \frac{\varphi}{3} \int_0^\infty < \sum_i \boldsymbol{R}_i\,(0) \cdot \boldsymbol{R}_c\,(t) > \mathrm{d}t$$

$$D_p = \frac{1}{3} \int_0^\infty < \dot{\boldsymbol{R}}_p\,(0) \cdot \dot{\boldsymbol{R}}_p\,(t) > \mathrm{d}t \tag{13}$$

$$\sigma_c = \frac{e^2}{3\,k\,T\,V'}\,\alpha\,P \int_0^\infty < \dot{\boldsymbol{R}}_c\,(0) \cdot (\sum_i \dot{\boldsymbol{R}}_i\,(t) - \alpha\,P\,\dot{\boldsymbol{R}}_p\,(t)) > \mathrm{d}t$$

$$\sigma_p = \frac{e^2}{3\,k\,T\,V'}\,\alpha\,P \int_0^\infty < \dot{\boldsymbol{R}}_p\,(0) \cdot (\alpha\,P\,\dot{\boldsymbol{R}}_p\,(t) - \sum_i \dot{\boldsymbol{R}}_i\,(t)) > \mathrm{d}t \tag{14}$$

Here P is the number of monomers in the volume V'; if we take the polymer concentration as being given as C monomer equivalents/unity volume, we may put

$$e^2\,P\,/\,k\,T\,V' = F^2\,C\,/\,R\,T \tag{15}$$

Now we define the following three integrals:

$$I_{cc} = \frac{1}{3} \int_0^\infty < \sum_i \dot{\boldsymbol{R}}_i\,(0) \cdot \dot{\boldsymbol{R}}_c\,(t) > \mathrm{d}t$$

$$I_{cp} = I_{pc} = \frac{1}{3} \int_0^\infty < \dot{\boldsymbol{R}}_c\,(0) \cdot \dot{\boldsymbol{R}}_p\,(t) > \mathrm{d}t = \frac{1}{3\,\alpha P} \int_0^\infty < \sum_i \dot{\boldsymbol{R}}_i\,(0) \cdot \dot{\boldsymbol{R}}_p\,(t) > \mathrm{d}t$$

$$I_{pp} = \frac{1}{3} \int_0^\infty < \dot{\boldsymbol{R}}_p\,(0) \cdot \dot{\boldsymbol{R}}_p\,(t) > \mathrm{d}t \tag{16}$$

then

$$D_c = \varphi\, I_{cc}$$

$$D_p = \quad I_{pp} \tag{17}$$

$$\sigma_c = \frac{F^2}{RT}\,C\alpha\,[I_{cc} - \alpha P I_{pc}]$$

$$\sigma_p = \frac{F^2}{RT}\,C\alpha\,[\alpha P I_{pp} - \alpha\,P I_{pc}] \tag{18}$$

Comparison with experimental data

In principle, each of these four transport coefficients can be independently determined, as well as the osmotic coefficient. If they were all known, this system of four equations would contain three unknowns, and the present decription could be rigorously tested. Unfortunately there exists, as far as we are aware, no polyelectrolyte for which all coefficients have been measured.

For sodium-poly(acrylate) solutions, at least D_c, φ, σ_c and σ_p have been determined, so we may solve for the three integrals.

Kern [17] has measured the osmotic pressure of poly(acrylic acid) solutions over a fairly wide range of concentrations; he describes his data for φ by

$$\varphi = 0.832 \, \frac{K}{K + \alpha} \tag{19}$$

where K depends on concentration; its value at the concentrations of interest in the present work was obtained by graphical interpolation of Kern's data.

Huizenga et al. determined the diffusion coefficient[2] of sodium counterions in poly(acrylic acid) solutions relative to that in a dilute solution of NaCl; denoting the latter value by D_o, we define

$$f' = \frac{D_c}{D_o} \tag{20}$$

where, according to Mills[18], $D_o = 1.33 \times 10^{-5}\ \mathrm{cm^2 sec^{-1}}$.

They also determined[1] the increase q_1 in equivalents of sodium ion and q_2 in equivalents of polymeric anion in the anode compartment of a transference cell upon the passage of N_e equivalents of electricity; and the specific conductivity κ of their solutions. In terms of these experimental quantities, the 'two charge-carrier' assumption of the present theory means that we should have

$$- q_1 + \alpha q_2 = N_e \tag{21}$$

If this condition is fulfilled we can find the integrals I_{xy} from the experimental data: defining an additional quantity D_k by

$$\kappa = \frac{F^2}{RT} C \alpha D_k \tag{22}$$

we may write

$$I_{cc} = \frac{f' D_o}{\varphi} \tag{23}$$

$$PI_{pc} = \frac{1}{\alpha} I_{cc} + \frac{1}{\alpha} D_\kappa \frac{q_1}{N_e} \tag{24}$$

$$PI_{pp} = PI_{pc} + \frac{1}{\alpha} D_\kappa \frac{\alpha q_2}{N_e} \tag{25}$$

The experimental data used have been collected in Table I; the values of the three integrals are shown in Fig. 1. A few data are seen to be inconsistent with the 'two charge-carrier' model, but generally the relation (21) is well obeyed.

A remarkable feature is the monotonic and rather drastic decrease of the polyion self-diffusion coefficient with increasing α. If P is taken equal to 1000, as did the original authors (footnote 10 of Ref.[2]) we find for the $1.5 \times 10^{-2}\ N$ solutions:

$D_p = 2 \times 10^{-7}\ \mathrm{cm^2 sec^{-1}}$ at $\alpha = 0.10$

$D_p = 0.5 \times 10^{-7}\ \mathrm{cm^2 sec^{-1}}$ at $\alpha = 0.98$

	a	D_κ	q_1/N_e	$a q_2/N_e$	f'	φ	I_{cc}	PI_{pc}	PI_{pp}	f''	n	I_{pc}/I_{pp}
$C = 1.51 \times 10^{-2}\,N$	0.096	2.16	− 0.489	0.387	0.92	0.567	2.16	11.5	20.2	0.80	0.6	0.57
	0.240	1.74	− 0.354	0.624	0.79	0.383	2.74	8.85	13.4	0.60	1.1	0.66
	0.413	1.48	− 0.171	0.862	0.62	0.276	2.99	6.63	9.72	0.55	1.2	0.68
	0.617	1.19	0.172	1.14	0.51	0.207	3.28	5.65	7.85	0.35	1.5	0.72
	0.816	0.988	0.380	1.34	0.39	0.167	3.11	4.27	5.89	0.32	1.3	0.73
	0.979	0.962	0.467	1.34	0.38	0.144	3.51	4.04	5.36	0.26	1.6	0.75
$C = 3.78 \times 10^{-2}\,N$	0.096	1.80	− 0.475	0.348	0.88	0.584	2.00				0.5	
	0.240	1.59	− 0.396	0.568	0.71	0.404	2.34	7.13	10.9	0.65	0.8	0.65
	0.413	1.37	− 0.145	0.777	0.59	0.294	2.67	5.98	8.56	0.45	1.0	0.70
	0.617	1.12	0.111	1.06	0.49	0.223	2.92	4.93	6.85	0.35	1.2	0.72
	0.816	0.950	0.229	1.23	0.41	0.180	3.03	3.98	5.41	0.35	1.3	0.74
	0.979	0.820	0.323	1.12	0.38	0.156	3.24				1.4	
		$\times 10^{-5}$ cm^{2}sec^{-1}					$\times 10^{-5}$ cm^{2}sec^{-1}					
See Eq.		(22)	(21)		(20)	(19)	(23)	(24)	(25)	(29)	(27)	

TABLE I: Experimental data on electrical and mass transport in poly(acrylic acid) solutions, and the values of the correlationfunction integrals derived from them.

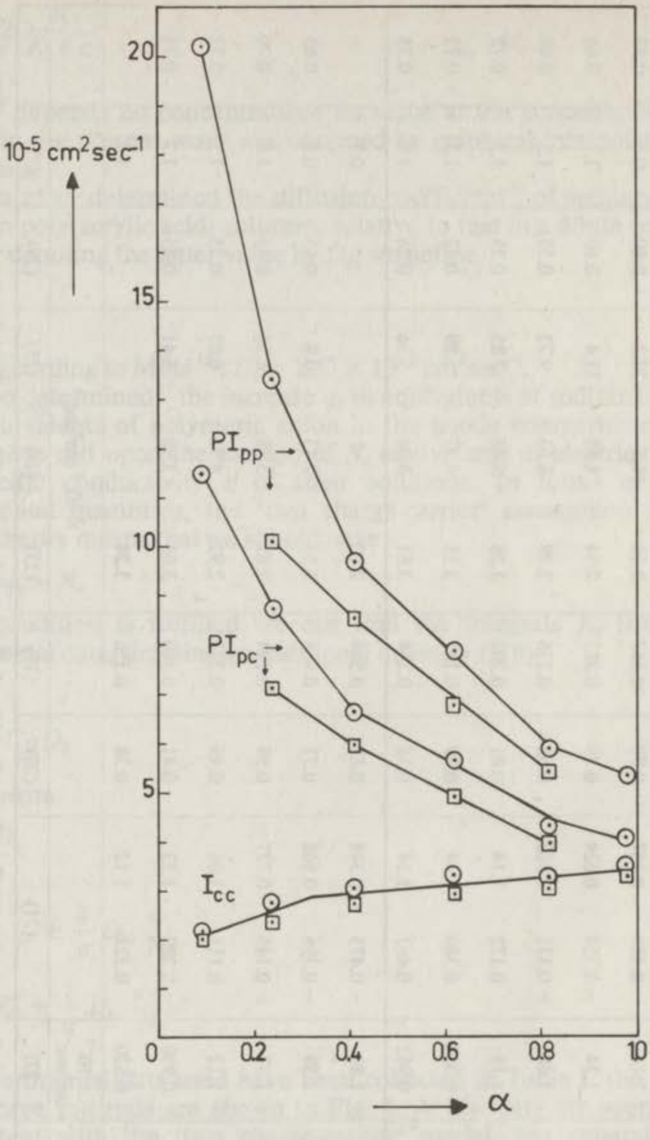

Fig. 1:
The values of I_{cc}, PI_{pc} and PI_{pp}, computed according to Eqs. (23) - (25) from the data in references 1) 2) and 10) for electrical and mass transport coefficients in poly(acrylic acid) solutions as a function of degree of neutralization *α*.
Squares: concentration is $1.51 \times 10^{-2}\,N$
Circles : concentration is $3.78 \times 10^{-2}\,N$

This behavior seems in contradiction with that found by Kedem and Katchalsky[19] and by Kern and Anderson[20] for poly(methacrylic acid); their measurements however were made in a macroscopic gradient of polyelectrolyte concentration. We have recently performed measurements of the selfdiffusion coefficient of poly(acrylic acid) by the pulsed-field-gradient spin-echo method[21]: these results[22], although obtained at a higher concentration, lower P and higher temperature, seem to confirm those presented here.

The time-integral of the counterion-polyion velocity crosscorrelation shows a similar decrease: the ratio to the polyion velocity autocorrelation integral increases slightly with α as shown in Fig. 2, and the value of this ratio is high: 0.66 at $\alpha = 0.24$ and 0.75 at $\alpha = 0.98$. Approximately the same values of this ratio were determined by Mazo[10] from data on diffusion and electrophoresis of micelles of sodium dodecyl sulfate.

From figure 1 it can be seen that I_{cc} increases with α. In principle I_{cc} contains an autocorrelation plus crosscorrelation terms:

$$I_{cc} = \frac{1}{3} \int < \dot{\boldsymbol{R}}_c\,(0) \cdot \dot{\boldsymbol{R}}_c\,(t) > \mathrm{d}t + \frac{1}{3} \sum_{i \neq c} \int < \dot{\boldsymbol{R}}_c\,(0) \cdot \dot{\boldsymbol{R}}_i\,(t) > \mathrm{d}t \tag{26}$$

and experimental data might be described by changes in the autocorrelation and/or the crosscorrelation.

From the fact that I_{cc} is larger than D_o it seems reasonable to conclude that the crosscorrelation does really contribute to I_{cc}, since it is difficult to imagine that the velocity autocorrelation time of a small ion in a polyelectrolyte could be longer than in a dilute solution of a simple electrolyte. Additional support for this idea can be found in the fact that, at higher degrees of neutralization, the root-mean-squared electric field that acts on the counterions increases fairly rapidly[23]. This will no doubt impose increasing difficulty on independent motions of the counterions. (This suggestion that the diffusion constant increases if the counterions are 'more tightly bound' may sound somewhat strange to those accustomed to the usual association theories). On the other hand it is known[16] that the observed diffusion is independent of P, so that only a limited number of terms can contribute to the crosscorrelation. A lower limit n for this number may be estimated from a comparison of crosscorrelation and autocorrelation, if it is assumed that the latter is approximately equal to D_o:

$$n = \frac{I_{cc}}{D_o} - 1 = \frac{f'}{\varphi} - 1 \tag{27}$$

It is seen in Figure 2 that n is always a small number, in accord with the assumption that only a few ions contribute to the crosscorrelation.

The most astonishing of the transport properties of polyelectrolyte solutions is no doubt the fact that for $\alpha > 0.4$ we appear to have $\alpha P I_{pc} > I_{cc}$ so that the conductivity σ_c becomes negative; it is stressed in the present treatment that the conductivity σ_p contains this same quantity $\alpha P I_{pc}$ as a diminishing term.

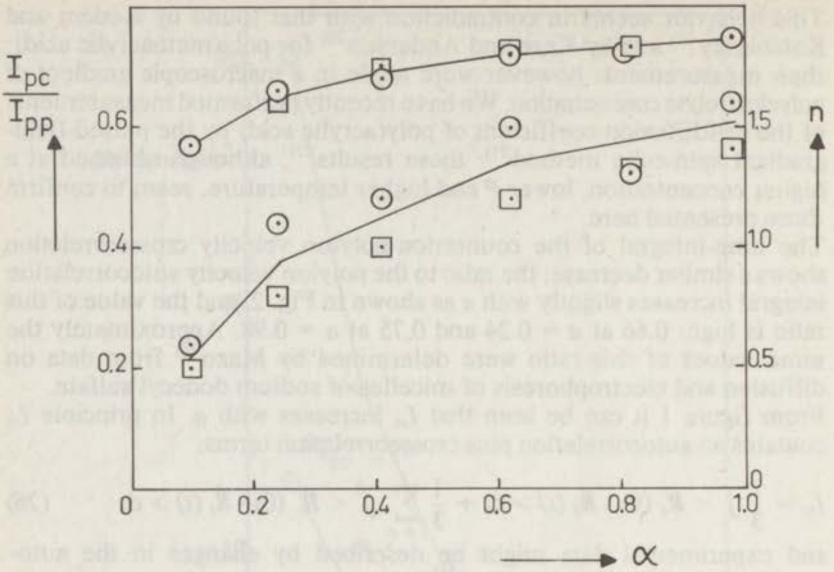

Fig. 2:
Lower curve and right-hand scale: The correlation parameter *n* according to Eq. (27).
Upper curve and left-hand scale: The correlation parameter I_{pc}/I_{pp}, computed from the data in Table I.
Squares: concentration is 1.51×10^{-2} *N*
Circles : concentration is 3.78×10^{-2} *N*

Comparison with existing theories

It has been usual[24)] to consider σ_c as the sum of two contributions, one proportional to D_o, and the other proportional to σ_p:

$$\sigma_c = \frac{F^2}{RT}\, C\alpha\, [I_{cc} - \alpha P I_{pc}]$$

$$= \frac{F^2}{RT}\, C\alpha\, [f'\, D_o - \{\alpha P I_{pc} - (1-\varphi)\, I_{cc}\}] \tag{28}$$

If we define a proportionality factor f'' by:

$$(1 - f'') = \frac{P I_{pc} - \dfrac{1-\varphi}{\alpha}\, I_{cc}}{P I_{pp} - P I_{pc}} = \frac{\dfrac{q_1}{N_e} + f'\, \dfrac{D_o}{D_\kappa}}{\dfrac{\alpha\, q_2}{N_e}} \tag{29}$$

we get:

$$\sigma_c = \frac{F^2}{RT} C \alpha f' D_o - (1 - f'') \sigma_p \tag{30}$$

or, using equivalent ionic conductances:

$$\lambda_c = f' \lambda_c^o - (1 - f'') \lambda_p \tag{31}$$

(These are defined as

$$\kappa = C_+ q_+ \lambda_+ + C_- q_- \lambda_- \tag{32}$$

where C is concentration in moles/unity volume and q the number of charges on the respective ions.)
It may be seen from Figure 3 that there is a rather large (> ten percent) and systematic difference between the f'' so computed and the f'.

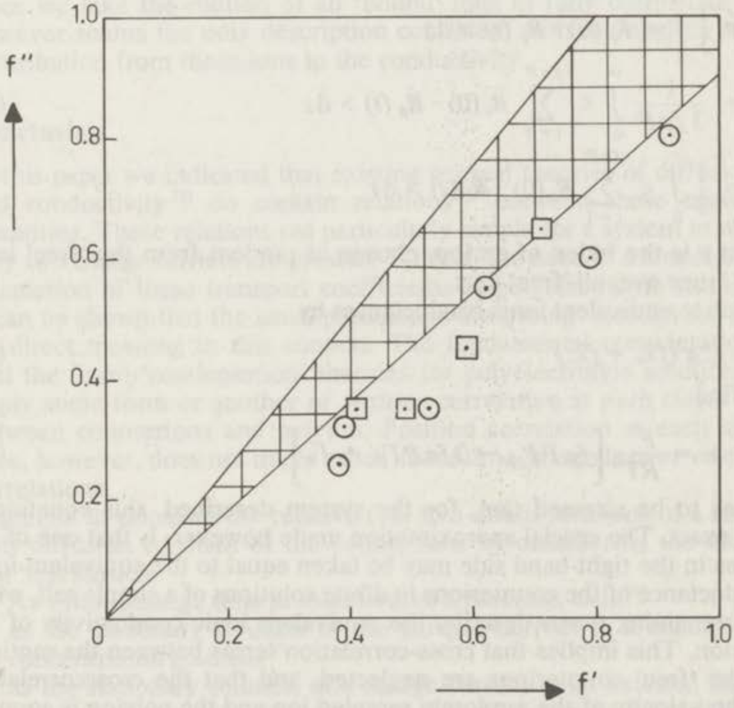

Fig. 3:
The relation between the association parameters f' according to Eq. (20) and f'' according to Eq. (29). The cross-hatched area shows ± ten percent deviation from $f' = f''$, as required by the usual association theories.
Squares: concentration is $1.51 \times 10^{-2}\,N$
Circles : concentration is $3.78 \times 10^{-2}\,N$

The poor agreement between the 'association factors' f'' and f' leads us to the conclusion that the charge transport in polyelectrolyte solutions does *not* in general obey an equation of the type

$$\Lambda = f' \, (\lambda_c^o + \lambda_p) \tag{33}$$

where $f' = D_c / D_o$; this seems to be answer to the question of Manning25) as to the validity of the physical picture underlying the derivation of this equation. It is usually arrived at as follows:

Instead of a system consisting of αP counterions of charge e and one polyion of charge $-\alpha P e$, one considers a system of $f \alpha P$ counterions, and one polyion of charge $-\alpha f P e$. If we write the expression for the total conductivity of such a system

$$\sigma_t' = \frac{F^2}{RT} C \alpha \, \{f^2 \alpha P I'_{pp} - 2 f^2 \alpha P I'_{pc} + f I'_{cc}\} \tag{34}$$

where

$$I'_{pp} = \frac{1}{3} \int_0^\infty < \boldsymbol{R}_p(0) \cdot \boldsymbol{R}_p(t) > \mathrm{d}t$$

$$I'_{pc} = \frac{1}{3 f \alpha P} \int_0^\infty < \sum_{i=1}^{f \alpha P} \dot{\boldsymbol{R}}_i(0) \cdot \dot{\boldsymbol{R}}_p(t) > \mathrm{d}t \tag{35}$$

$$I'_{cc} = \frac{1}{3} \int_0^\infty < \sum_{i=1}^{f \alpha P} \boldsymbol{R}_i(0) \cdot \boldsymbol{R}_c(t) > \mathrm{d}t$$

Here c is the index of an ion, chosen at random from the 'free' ions, and i runs over all 'free' ions.

Going to equivalent ionic conductances by

$$\sigma_t' = C \alpha \, (f \lambda_+ + f \lambda_-) \tag{36}$$

we find

$$\lambda_+ + \lambda_- = \frac{F^2}{RT} \left[f \alpha P I'_{pp} - 2 f \alpha P I'_{pc} + I'_{cc} \right] \tag{37}$$

It has to be stressed that, for the system described, this equation is still exact. The crucial approximation made however, is that one of the terms in the right-hand side may be taken equal to the equivalent ionic conductance of the counterions in dilute solutions of a simple salt, while the remaining terms describe the equivalent ionic conductivity of the polyion. This implies that cross-correlation terms between the motions of the 'free' counterions are neglected, and that the crosscorrelation of the velocity of the randomly sampled ion and the polyion is counted twice in the conductivity of the polyion (or, which is not an improvement, is neglected). Next we consider the expression for the counterion self-diffusion in this system. A fraction $(1 - f)$ of them is tightly bound to the polyion for a time that is long compared to the polyion-velocity autocorrelation time, and the fraction f moves freely, without mutual correlation. Furthermore no crosscorrelations are assumed between the motions of the 'free' and the 'bound' counterions.

The expression for the diffusion coefficients becomes

$$D = \frac{1}{3\Delta N^2}\left[\sum_{i,j=1}^{faP}\int_0^{\infty} < \dot{\boldsymbol{R}}_{c_i}(0)\cdot\dot{\boldsymbol{R}}_{c_j}(t) > \mathrm{d}\,t\right.$$

$$\left. + \sum_{i,j=faP}^{aP}\int_0^{\infty} < \dot{\boldsymbol{R}}_{c_i}(0)\,\dot{\boldsymbol{R}}_{c_j}(t) > \mathrm{d}\,t\right]$$

$$= \frac{1}{\Delta N^2}\left[faPD_o + \{(1-f)\,aP\}^2\,D_p\right] \tag{38}$$

Then the usual assumption is that the term containing D_p may be neglected with respect to the term containing D_o; this assumption may not be justified, since PD_p might well be of the order of magnitude of D_o.

This computation of the diffusion constant is, of course, a 'worst case' since we take the motion of all 'bound' ions as fully correlated; this however seems the only description consistent with the neglect of the contribution from these ions to the conductivity.

Conclusion

In this paper we indicated that existing general theories of diffusion[14)] and conductivity[15)] do contain relations[10)] between these transport quantities. These relations are particularly simple for a system in which only two charge carriers are present. Without the need of a model-based calculation of these transport coefficients in polyelectrolyte solutions, it can be shown that the usual parameters describing 'association' have no direct meaning in this context. The fundamental consideration is that the usual 'condensation' theories for polyelectrolyte solutions do imply some form or another of *position* correlation at *each single* time between counterions and polyion. Position correlation at each single time, however, does not imply much about time-integrals over velocity-correlations.

Attempts to calculate the relative (i.e. to a dilute solutions of a simple salt) diffusion constant of the counterions by considering the motion of a 'test particle'

a) As a first-passage time problem out of a potential well[26)]

b) as the stationary solution of the particle current in a macroscopic concentration gradient[27)]

c. as the stationary solution of a charge current in an external field[28)]

give always incomplete results, since they all consider the motion of the 'test particle' in a static environment, thus neglecting all velocity-crosscorrelations.

The best way to describe the transport coefficients is thus simply to reduce them to the correlation-function integrals, and compare their relative magnitude. We did so for the experimental results of Huizenga et al.[1, 2)], using osmotic data of Kern[17)]. Since polyion self-diffusion data are lacking we cannot rigorously test the validity of our description; but we have been able to show that the usual assumption of a 'bound' fraction in the treatment of conductivity and electrophoresis data is not generally justified.

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CHAPTER VII

Selfdiffusion of poly(acrylate) anions in aqueous solutions

Introduction.

Of the four (solute) electrical and mass transport coefficients, viz. two self-diffusion coefficients and two mobilities, in polyelectrolyte solutions without added salt, the polyion selfdiffusion-coefficient has seldom been investigated. For poly(glumatic acid) it has been shown that the helix-coil transition shows up by a sharp decrease in the selfdiffusion coefficient upon going from low to high pH [1]. So it might be suspected that the gradual changes in conformation of a weak polyacid upon titration reflect themselves in the diffusion coefficient as well. Furthermore, a measurement of the polyion diffusion is of interest since it may be shown that the four transport coefficients are not independent [2].

The radiotracer method, that has been successfully applied to studies of counterion selfdiffusion in polyelectrolytes [3, 4, 5, 6] is less suitable for measurements of polyion diffusion, because of preparative requirements. The spin-echo method, and in particular the pulsed-fieldgradient variant [7, 8] can be more easily applied. Diffusion measurements by the spin-echo method are based on the possibility to record the instantaneous positions of the nuclei by their Larmor frequencies in a magnetic field that is spatially dependent. If a nucleus changes its Larmor frequency by diffusional motion through the magnetic field, the net effect is a 'randomization' of the final Larmor frequencies with respect to their starting values, resulting in a net loss of transversal magnetization of the sample, as detected by a decreasing amplitude of the spin-echo.

If the molecules have internal degrees of freedom, and contain more nuclei of the same species, for such observation times as are experimentally accessible, the observed motion is the center-of-mass motion of the nuclei in the molecule. In principle the diffusion of charged particles in a fluid in a magnetic field is impeded by the presence of the field [9]; in practice the effect can be neglected.

Experimental.

a. method

For a full description of the method, and of the relations between the experimental quantities and the desired diffusion coefficient we refer to the original papers [7, 8]. In our experiments a commercially available RF-pulse spectrometer and pulsed-fieldgradient unit (Bruker Physik) were used. We employed the conventional $\frac{1}{2}\pi - \pi$ RF-pulse sequence, with gradient pulses after the first and second RF-pulses. Since it was generally not easy to obtain exact equality of the gradient pulses for more than two or three consecutive pulse-bursts, use was made of the finding by Tanner [10) that, if the second pulse is nearly but not exactly equal to the first, the observed echo is displaced and attenuated in such a way that the locus of its maximum is the shape of the echo in the correctly-compensated case. So, by slowly varying the amplitude of the second gradient pulse this locus can be written on the screen of a variable-persistence oscilloscope, and subsequently its maximum measured.

The fieldgradient was produced by two coils in an approximate anti-Helmholtz configuration; their inner and outer radii are 17 and 24 mm respectively; in mounted position they extended from 13 mm to 20 mm from the midplane. These coils are cemented to a plexiglas housing, in which the RF-coil is mounted. Shielding of the RF-coil is by a piece of flexible printed-circuit foil, into which a meander-like pattern has been etched, so as to minimize eddy currents. The printed-circuit foil is bent into a cylinder, and cemented into the plexiglas housing.

A provision is made to pump a thermostatting fluid around and through the RF-coil; this provision was not used in the present investigation, since turbulences in the coolant caused vibrations of the RF-leads, that gave rise to instabilities of the echo. In blank runs temperature fluctuations were found to be ± 0.5 °C; the average temperature was 30 °C approximately.

The current to the coil is delivered by a heavy current-pulsed, voltage-stabilised power supply. The stabilised output voltage is 25 V, and the total load resistance (coils plus emitter resistors in the current passgate) is 0.81 Ohm. As measured *in situ,* the inductance of the load is quite high: approximately 250 μH . So, when the passgate is driven into conduction, the current through the coils rises exponentially with a time-constant of 360 μs towards a final current of 31 A. At the moment that the preset value of the current is attained, the regulating action of the passgate starts, and the current is kept at the preset value until the end of the gradient pulse. The preset value of the current in the second pulse can be fine-regulated in order to balance the two gradient-pulses. The current through the coils is monitored by a fast sampling voltmeter that, during the gradient pulse, senses the voltage drop across the emitter.resistor of one of the passgate transistors. Its reading in quiescent condition is therefore proportional to the value of the gradient current just before turn-off.

We performed our measurements at 55 MHz in a Varian 3601-1 magnet with fluxstabilisation. Apparently the pulsed-fieldgradient was symmetrical enough so as not to be sensed by the fluxstabiliser. This magnet has an airgap of only slightly more than 4 cm, thus the gradient-coils were very near to the pole-faces. In such an arrangement the magnetic fieldgradient's rise- and falltimes can be substantially larger than the corresponding times for the current, and the deviation of the field-gradient's time-dependence from the ideal rectangular shape may be worse than it was for the current. Then, strictly speaking, the formulae derived for attenuation of the echo by diffusion in the case of rectangular pulses, are no longer valid.

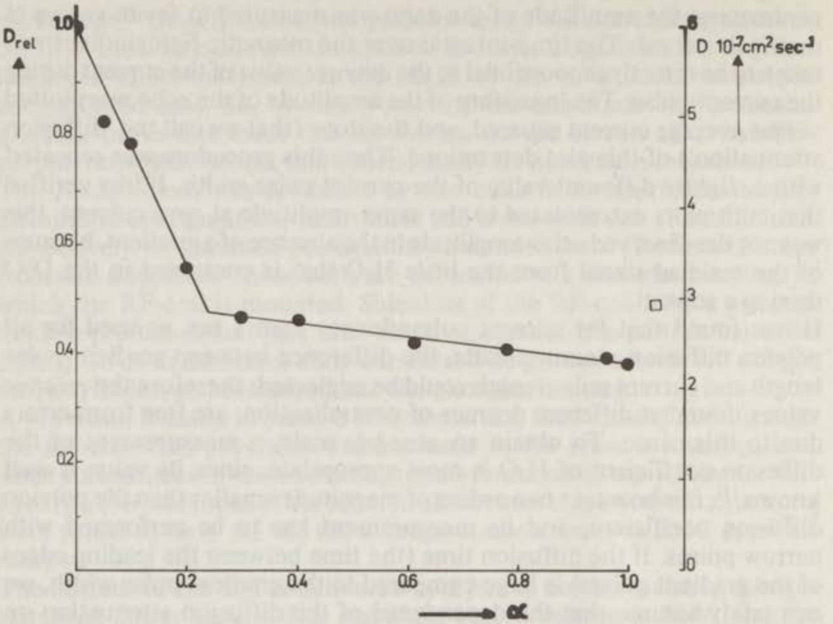
We therefore adapted the following procedure to measure the diffusion constants of the poly(acrylate) ion: Using constant values for all timing parameters, the amplitude of the echo was measured at seven values of the final current. The time-integral over the magnetic-fieldgradient was taken to be directly proportional to the *average* value of the current during the current-pulse. The logarithm of the amplitude of the echo was plotted versus average current squared, and the slope (that we call the 'diffusion attenuation') of this plot determined. Then this procedure was repeated with a slightly different value of the current pulse width. It was verified that both plots extrapolated to the same amplitude at zero current; this was not the observed echo-amplitude in the absence of a gradient, because of the residual signal from the little H_2O that is contained in the D_2O used as a solvent.

It was found that for current pulses longer than 1 ms, as used for all polyion diffusion measurements, the difference between gradient pulse length and current pulse length could be neglected: therefore the *relative* values, found at different degrees of neutralization, are free from errors due to this cause. To obtain an *absolute* scale, a measurement of the diffusion coefficient of H_2O is most appropriate, since its value is well known [11)]; it is however two orders of magnitude smaller than the polyion diffusion coefficient, and its measurement has to be performed with narrow pulses. If the diffusion time (the time between the leading edges of the gradient pulses) is large compared to the gradient pulse width, we can safely assume that the dependence of the diffusion attenuation on the diffusion time will not be seriously altered by the imperfect shape of the narrow gradient pulses. The ratio of the diffusion coefficients of two different samples, measured with different diffusion times, but otherwise identical settings, will then be determined by the ratio of the diffusion attenuations and the ratio of the diffusion times.

Because of fast transversal relaxation it was not possible to measure the diffusion of the polyions with the aid of narrow pulses; therefore it was decided to make an intermediate calibration on a sample with a small diffusion constant, but with a sufficiently slow transversal relaxation so that its diffusion constant might be determined with the same settings as used for the polyions on one hand, and with narrow pulses but a long diffusion time on the other hand. A sample of glycerol was found to be useful for this purpose. Next a H_2O sample was measured with the same narrow pulses, but a much shorter diffusion time (that was, however, still long compared to the gradient pulse width). Then we can find the diffusion coefficient of the glycerol used with respect to that of H_2O from the measurements with the narrow pulses, and with respect to the polyions from the experiments with the long pulses.

b. materials

The solutions of poly(acrylic acid) in D_2O at different degrees of neutralization, without added salt, were prepared as described previously [12)], except that a fraction with a viscosity averaged molecular weight of 4.6×10^4 was used, and that the concentration in the present investigation was 0.5 *N*.



The relative selfdiffusion coefficient of poly(acrylic acid) ions of different degrees of neutralization *α*. $M_v = 4.6 \times 10^4$, solvent is D_2O, and temperature 30 °C approximately.
The square shown at right is the selfdiffusion of glycerol in a reference sample, shown on the same relative scale, from which, by comparison with H_2O, the absolute scale at right has been derived.

The glycerol used was Merck 4094 from a fresh bottle; it was used without drying.
The H_2O used was tap water, to which some $CuSO_4$ had been added to increase the relaxation rates.

Results

The relative values of the selfdiffusion coefficient of the poly(acrylate) ion at different degrees of neutralization, for a 0.5 *N* solution of a sample with $M_v = 4.6 \times 10^4$ in D_2O are shown in the figure. Plotted on the same scale is the glycerol reference sample, from which, by comparison with a H_2O sample, the absolute scale shown at right has been derived. The error in the relative values, as estimated from reproducibility, are thought to be ten percent, while the error in the calibration may be somewhat larger. The value taken for the H_2O diffusion coefficient was $2.66 \times 10^{-5}\,cm^2sec^{-1}$. This was arrived at by multiplying Simpson and Carr's data[13)] by 1.08, in order to obtain agreement between their value at 25 °C and the value of $2.31 \times 10^{-5}\,cm^2sec^{-1}$, considered by Mills[11)] to be the best at this temperature. According to Simpson and Carr's data, a ten percent

variation in the H_2O diffusion coefficient results if the temperature is varied by 4 °C.
The instrument settings used in the various runs are shown in the table: we estimate the coil factor in our set-up to be 14 G cm^{-1} A^{-1}.

Experiment repeat time	400	800	400	ms
Time between RF-pulses	12	100–140	12	ms
Time between gradient current pulses	12.2	190–260	12.2	ms
Length of gradient current pulses	2–3.5	0.5	0.5	ms
Average gradient current	9–18	9–18	2–12	A

Table: Experimental settings used in determinations of the selfdiffusion coefficients. The first column pertains to the polyion-runs and a glycerol reference run. The second column gives parameters for the intermediate calibration of glycerol, and the third the calibration run on H_2O.

Attempts to determine the selfdiffusion coefficient of the fully neutralized polyion in a sample with $M_v = 2.6 \times 10^5$ were unsuccessfull; apparently its value was more then three times lower than that shown in the figure. To measure this would have necessitated a much longer distance between RF-pulses: this could not be achieved because of poor signal-to-noise ratios due to transversal relaxation. The selfdiffusion coefficient of sodium counterions in 0.5 *N* solutions of fully neutralized poly(acrylic acid) of $M_v = 4.6 \times 10^4$, 2.6×10^5 and 1.4×10^6 in D_2O were by the same method as above, but with use of the thermostatting facility at 25 °C, found to be equal within experimental accuracy. Using as a calibration data of Mills[14] for tracer diffusion of $^{22}NaCl$ in H_2O, the common value was found to be 5.7×10^{-6} $cm^2 sec^{-1}$. Independence of counterion diffusion of the polyion's molecular weight has also been found by Pefferkorn and Varoqui[6].

Discussion.

The steep slope of the curve between zero and twenty percent neutralization is clearly due to the uncoiling of the polyion upon increase of its charge. It is interesting to note that an accompanying change in the rotational diffusion of the acid group has been derived from deuteron nuclear magnetic relaxation in D_2O solutions of poly(acrylic acid)[15]. At higher charge the hydrodynamic resistance of the polyion still seems to increase monotonically, but not nearly as fast. At substantially lower polyion concentrations a similar behavior of the polyion selfdiffusion constant upon increasing neutralization has been derived[2] from Huizenga, Grieger and Wall's data on electrical transport and counterion diffusion.

There is a large qualitative and quantitative difference between the present results and the diffusion coefficient of poly(methacrylic acid) solutions in a concentration gradient $^{16, 17)}$. In the latter case, the diffusion is mainly determined by the concentration gradient of the small ions, who tend to drag along the polyions with them. This also explains the independence of molecular weight that has been found in these experiments. The molecular weight dependence of the electrical conductivity $^{18)}$ is probably connected to $^{2)}$ our finding that the polyion's selfdiffusion coefficient depends on its molecular weight.

Of course the high concentrations used in the present investigation make a comparison with other results difficult; it is to be expected, that the sensitivity of this type of measurement may be increased by something like an order of magnitude, bringing it more or less on the concentration scales used in transport measurements that involve some form of refractive-index monitoring.

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Samenvatting

In dit proefschrift wordt aangetoond dat metingen met behulp van spin echo technieken (ter bepaling van longitudinale en transversale kernspinrelaxatie snelheden, en van de kern-zelfdiffusie coëfficiënt) duidelijke informatie kunnen geven over de aard van de interactie tussen polyionen en hun tegenionen. De kernspinrelaxatie snelheden van ^{23}Na in oplossingen van gedeeltelijk geneutraliseerd poly(acrylzuur) met en zonder toegevoegd zout, en van poly(styreensulfonzuur) geneutraliseerd met mengsels van natrium en barium hydroxide, kunnen beschreven worden met het ioncondensatie model. Hier wordt een „gecondenseerd" ion gedefinieerd als een ion dat het electrisch veld ondervindt van de onafgeschermde lijnlading. In het geval van één soort tegenionen en geen toegevoegd zout kunnen de resultaten ook kwantitatief bevredigend beschreven worden op basis van de Poisson-Boltzmann vergelijking met cylindrische randvoorwaarden. Het kernspinrelaxatiegedrag van een werkelijk „gebonden ion" waarvan de kern een quadrupoolmoment heeft, vertoont duidelijke kenmerken, zoals blijkt uit metingen aan het „tegenion" deuterium in oplossingen van gedeeltelijk geneutraliseerd poly(acrylzuur) in zwaar water.
De theoretische samenhang van vier transportgrootheden, te weten de zelfdiffusie coëfficiënten en mobiliteiten van polyion en tegenion, wordt aangetoond. Uit literatuurgegevens voor drie van deze grootheden kan de vierde, te weten de polyion zelfdiffusie coëfficiënt, worden afgeleid. De zo gevonden afhankelijkheid van deze grootheid van de neutralisatiegraad wordt kwalitatief bevestigd door metingen van deze zelfdiffusie coëfficiënt met de spin echo methode.

Naar gebruik volgt hier een overzicht van mijn studie.
In 1961 legde ik het eindexamen Gymnasium *β* af aan het Sint Franciscus College te Rotterdam, waar Drs. P. van Vianen natuurkunde en Drs. A. P. Th. Overeem OFM scheikunde doceerde. In datzelfde jaar begon de studie aan de Rijksuniversiteit te Leiden, waar ik het candidaats examen natuurkunde en wiskunde met scheikunde (letter d') in november 1964 aflegde. Gedurende het kalenderjaar 1965 werd de studie om verschillende redenen onderbroken; in januari 1966 kwam ik bij de magnetische resonantiegroep van Prof. Dr. N. J. Poulis in het Kamerlingh Onnes Laboratorium, om de protonspin relaxatie in mengsels van H_2 en HD in de vloeibare en vaste fase te bestuderen.
Vanaf mei 1967 assisteerde ik Dr. T. O. Klaassen bij een onderzoek naar antiferromagnetische lineaire ketens, tot aan mijn doctoraal examen natuurkunde in november 1968.
Daarna vertrok ik naar de groep van Dr. J. C. Leyte op de afdeling Physische Chemie III in het Gorlaeus Laboratorium, om onderzoek te doen aan polyelectrolyten met behulp van kernspinresonantie. De spin echo apparatuur waarmee het in dit proefschrift beschreven werk is gedaan, arriveerde in juni 1970. Vanaf juli 1969 tot december 1973 was ik in dienst van de Stichting voor Scheikundig Onderzoek in Nederland; voor en na die tijd van de Rijksuniversiteit.
Dit proefschrift zou niet geworden zijn wat het is, zonder de veelsoortige hulp van Ina Zuiderweg.

STELLINGEN

I

De bewering van Schurr dat de door hem gegeven uitdrukking voor de Fouriercomponenten van de tegenion-tegenion Coulomb energie divergeert voor grote golfgetallen, is onjuist.
J. M. Schurr, Biopolymers **10** 1371 (1971)

II

De observatie van Headley dat de door hem waargenomen kernspinrelaxatie van ^{23}Na in met een NaCl-oplossing doordrenkte porcelein monsters beschreven kan worden met eenvoudige exponentiële vervalcurven, is inconsistent met de door hem gevonden relaxatiesnelheden.
L. C. Headley, J. Appl. Phys. **44** 3118 (1973).
A. Abragam, The Principles of Nuclear Magnetism (Clarendon, Oxford 1961) p. 314.

III

Het verdient aanbeveling de magnetische ordening van protonspins in $Mg(OH)_2$ te onderzoeken.
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IV

Het is op eenvoudige wijze mogelijk een mechanisch en thermisch stabiel gekruiste-spoelenpaar voor gebruik in kernspinresonantie te vervaardigen door de zendspoel niet, zoals gebruikelijk, in een Helmholtz-configuratie uit te voeren, maar als een stelsel van langs een cylinderoppervlak lopende draden, verdeeld zoals aangegeven door Mascart en Joubert.
E. Mascart en J. Joubert, Leçons sur l'electricité et le magnétisme (Corbeil, 1886) tome 1, § 357.

V

Bij de bepaling van het 'core polarization' - hyperfijn veld van de d-electronen uit de temperatuurafhankelijkheid van Knight shift en susceptibiliteit in overgangsmetalen, mag de Coulomb- en exchange-enhancement van de susceptibiliteit niet verwaarloosd worden.
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VI

De interpretatie door Vitagliano et al. van hun transportexperimenten aan oplossingen van poly(Na-acrylaat) met de 'bewegende-grensvlak'-methode is inconsistent met hun aanname dat zij een zuiver elektrisch transportverschijnsel bestuderen.
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VII

De door Beckerman gegeven omschrijving van het door hem gehanteerde begrip 'action' is uit natuurkundig standpunt onbevredigend.
B. Beckerman, Dynamics of Drama (Knopf, New York 1970).