THE FLOW PROPERTIES OF DILUTE POLYMER SOLUTIONS

by

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The phenomenon of drag reduction in dilute polymer solutions is of great interest to research workers. It is of considerable practical use, and a fundamental cause of the remarkable effects which are observed remains to be found. Much work has been done in recent years on the subject, but a study of the literature has revealed a need for detailed investigation of the hydrodynamic properties in the wall region of a drag-reducing fluid. Consequently, the methods available for the investigation of this region have been reviewed. An experimental technique involving the measurement of instantaneous mass transfer coefficients at an electrode flush with the solid wall was judged to be the most suitable for this application. The mass transfer coefficient has been found to fluctuate in a manner which reflects the level of turbulence in the wall region. It was hoped that any change in boundary layer turbulence consequent on the addition of polymer would result in some change in the form of the mass transfer fluctuations.

An apparatus was developed to carry out these measurements of fluctuating mass transfer coefficient at the wall of a cylindrical pipe. Its construction and operation are described in detail. Particular attention has been paid to minimising the effect of chemical and mechanical degradation on the polymer molecules, since this decreased the drag-reducing effectiveness of the solution.

The methods used for the analysis of the results are considered. It seemed that comparisons of normal and drag-reducing fluids based on the/
on the autocorrelation and spectral density function would yield
the best insight into the physical mechanism of drag reduction.
These techniques are reviewed in detail.

A series of experiments was carried out using concentrations
varying between 25 and 200 ppm, by weight of a high molecular weight
polyethylene oxide ("Polyox" WSR-301). Each run with polymer was
immediately preceded by a reference run (without polymer), which
could be used as a basis for comparison. Levels of drag reduction
(percentage decrease in friction factor) of up to 50% were obtained.
Several of the parameters associated with the mass transfer coeffi-
cient measurements were also found to change with the addition of
polymer. Both the mean mass transfer coefficient and the standard
deviation of the mass transfer fluctuations were reduced, while
the various time scales associated with the fluctuations were
increased. The presence of polymer seemed to have no effect on
the frequency distribution of the fluctuations, nor on their
forward speed (which crosscorrelation measurements revealed to be
of the same magnitude as the bulk velocity). However, there was
a reduction in the rate of decay of the eddies, reflecting an
increased stability along the pipe axis.

The observed results seemed to imply a model of boundary layer
turbulence in which the amplitude of the turbulent eddies was
reduced and their stability increased in the presence of polymer.
It was not possible at present to extend this model on a more
quantitative basis. Suggestions have been made for further work
which could be carried out with this end in mind.
ACKNOWLEDGEMENTS

The work for this project was carried out in the Department of Chemical Engineering at Edinburgh University. The author wishes to thank all who have given him help and advice during this period. In particular, thanks are due to Dr. D.H. Glass, for his considerable guidance and encouragement, and to the Science Research Council for the provision of a maintenance grant.

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NOMENCLATURE

Some symbols have been used to represent more than one quantity. This has only been done when common usage dictated such a duplication and there was no possibility of confusion. For example, "f" may represent "Friction Factor" or "Frequency" - it will be obvious from the text which application is intended.

\( a \) Constant \((\approx 0.5)\) in Equation 1.15
\( a \) Width of narrowest detail in spectrum (Hz.)
\( A \) Constant in Equation 1.13
\( A \) Surface area (of electrode) for mass transfer \( \text{m}^2 \)
\( B \) Spectrum bandwidth (Hz.)
\( C \) Concentration (kg. equiv./m.\(^3\).)
\( C_b \) Ferricyanide concentration in bulk electrolyte (kg. equiv./m.\(^3\).)
\( C_s \) Ferricyanide concentration at solid/liquid interface (kg. equiv. /m.\(^3\).)
\( d \) Pipe internal diameter (m.)
\( d \) Prefix denoting 'derivative of'.
\( D \) Number of delay loops (sampling program)
\( D \) Diffusivity of ferricyanide or ferrocyanide in electrolyte solution \( \text{m}^2./\text{S.} \)
\( D_o \) Diffusivity of ferricyanide or ferrocyanide in aqueous solution \( \text{m}^2./\text{S.} \)
\( D_m \) Effective molecular diameter (m.)
\( D_e \) Deborah number (dimensionless)
\( D_e^1 \) Modified Deborah number
\( DR \) Drag Reduction (%)
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<td>M</td>
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<td>Ma</td>
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<tr>
<td>Md</td>
<td>Microscale of turbulence (sec.)</td>
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<td>N</td>
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\( N_a \) Rate of mass transfer (kg. equiv./S.)

\( P \) Pressure (N./m.\(^2\)).

\( \rho R \) Pressure-drop manometer reading (cm.).

\( R \) Constant in Eqn. 1.3

\( R \) Gas constant

\( R_o \) Limiting value (zero concentration) of \( R \) in Eqn. 1.3

\( R_e \) Reynolds number (dimensionless)

\( R_c \) Resistance of electrolytic cell (Ohms.)

\( R(j) \) Autocorrelation function (lag \( j \))

\( S \) Electrode separation (m.)

\( S(f) \) Spectral density function (frequency \( f \))

\( \overline{S}(f) \) Smoothed spectral density function

\( S_k \) Skewness of sampled electrode signal (dimensionless)

\( S_k \) Skewness of fluctuations in mass transfer coefficient (dimensionless)

\( S_h \) Schmidt number (dimensionless)

\( Sh \) Sherwood number (dimensionless)

\( t \) Time, time delay (sec.)

\( t_1 \) Molecular relaxation time (Zimm) (sec.)

\( t_o \) Time for autocorrelation (or cross-correlation) to fall to zero (sec.)

\( t_c \) Time for cross-correlation function to reach a maximum (sec.)

\( T \) Record length (sec.)

\( T \) Temperature (\(^0\)R)

\( T_o \) Reference Temperature (\(^0\)R)

\( u \) Point velocity (m./S.)

\( \overline{u} \) Mean velocity (m./S.)

\( u_t \) Friction velocity (m./S.)

\( u^+ \) Dimensionless velocity
\( v_c \) Convection velocity (m./S.)

\( w(t) \) Lag window

\( w_t(t) \) Tukey lag window

\( W(f) \) Spectral window

\( W_t(f) \) Tukey spectral window

\( W_p(f) \) Parzen spectral window

\( x \) Axial distance (m.)

\( x_i \) Value of \( i \)th sample

\( \bar{x} \) Mean sample value

\( y \) Radial distance (m.)

\( y^+ \) Dimensionless radial distance

\( z \) Circumferential distance (m.)

\( z^+ \) Dimensionless circumferential distance

\( a \) Experimental constant in Eqns. 1.5 and 1.14

\( \gamma \) Parameter in Eqn. 1.12

\( \delta \) Parameter in Eqn. 1.12

\( \Delta \) Prefix denoting 'partial derivative of'

\( \Delta \) Prefix denoting 'differential'

\( \Delta \) Sampling interval (sec.)

\( \varepsilon \) Eddy diffusivity

\( \mu \) Viscosity (kg./m.S.)

\( \mu_s \) Solvent viscosity (kg./m.S.)

\( \mu_o \) Viscosity at reference temperature (kg./m.S.)

\( [\mu] \) Intrinsic solution viscosity (kg./m.S.)

\( \nu \) Kinematic viscosity (m\(^2\)/s.)

\( \nu \) No. of degrees of freedom
\[ \pi \]
\[ \rho \] Density \((\text{kg./m}^3)\)
\[ \sigma_x \] Standard deviation of sampled signal
\[ \sigma_k \] Standard deviation of fluctuations in mass transfer coeff. \((\text{m./S.})\)
\[ \sigma_v \] Standard deviation of fluctuations in voltage \((\text{V.})\)
\[ \sigma_i \] Standard deviation of fluctuations in current \((\text{A.})\)
\[ \tau \] Shear stress \((\text{kg./m.S}^2)\)
\[ \tau_w \] Wall shear stress \((\text{kg./m.S}^2)\)
\[ \tau_{ws} \] Solvent wall shear stress \((\text{kg./m.S}^2)\)
\[ \tau_{wp} \] Polymer solution wall shear stress \((\text{kg./m.S}^2)\)
CHAPTER ONE

LITERATURE SURVEY

1.1 Introduction

The remarkable reduction of friction factor in turbulent flow obtained by the addition of very small quantities of certain high molecular weight polymers to a flowing solvent was first observed by Toms in 1948\(^{(1)}\). It has since become known as The Toms Effect. In recent years much research has been carried out in attempts to predict the optimum conditions for the effect, and to determine the mechanism by which it occurs. Because the effect is so disproportionately large (reductions of friction factor by as much as 40\% may be achieved by the addition of as little as 10 ppm. by weight of a suitable polymer), it is interesting both from academic and economic points of view. It is of academic importance because the polymer must grossly modify some hydrodynamic characteristic of the fluid to produce such a large change in friction factor, although this is achieved without any significant change in the bulk properties of the fluid (density, viscosity, surface tension, etc.). Precisely what fluid characteristic is modified, and how this is brought about, is not yet fully understood. Research has also been directed towards correlating and predicting the conditions under which drag reduction is most effective, since, as well as throwing light on the mechanism of the effect, this may enable more economic use to be made of drag-reducing polymers.

The two main ways in which the effect may be utilised are in the reduction of the/
the reduction of the pressure drop of fluids in pipelines (and hence of the pumping costs) and in the reduction of the skin friction of bodies moving in fluids (Gadd, ²). The former application includes the reduction of drag in oil pipelines, water and sewer systems, fire-fighting hoses, irrigation sprinklers and washing sprays, and the increase of flow velocity in the fracturing process of petroleum production operations (Patterson et al.,³). Skin friction reduction may be utilised to reduce the power requirement for ships, submarines or hydrofoils, the reduction usually being obtained by the ejection of polymer solution from the vessel hull.

As the effect takes place at the interface between a solid and a liquid, it seems likely that a profitable area of investigation would be the boundary layer of the fluid. The structure of the boundary layer, even in strictly Newtonian fluids, is still a matter of some conjecture, but it is clear that motions within the boundary layer play an important part in the transfer of momentum from the bulk of the fluid to the solid wall. It is this transfer of momentum which produces the pressure loss in a pipe, or the drag on a body moving through a fluid. Thus it seems likely that, as the polymer molecules reduce the pressure-loss or drag to such a large extent, they may well have some effect on the boundary layer motions. The extension of methods used for the investigation of the Newtonian boundary layer to observe the boundary layer in non-Newtonian drag-reducing flow would seem to be a profitable avenue of research.

The phenomenon/
The phenomenon of drag reduction will now be discussed in greater detail.

1.2 Drag Reduction

1.2.1 The Toms Effect

As mentioned above, the Toms Effect was first observed in 1948(1). Little further work on the subject was reported until 1961, since when there have been many publications, including several review articles (2, 3, 4, 5, 6). It can be seen from a bibliography included in (4) that over 140 articles on the general subject of drag reduction were published in 1966 alone, and this rate of production continues unabated at the present time. This survey cannot, by nature of its brevity, be regarded as comprehensive, and the reader seeking further information is recommended to consult the review articles mentioned above and the bibliographies therein.

In general, the polymers which are effective in drag reduction are essentially linear in structure, having few, or no, side chains. This was established by Hoyt and Fabula (7) using drag reduction measurements on a rotating-disk apparatus for a wide range of synthetic and naturally-occurring polymers in dilute aqueous solution. Merrill et al. (8) made drag reduction measurements with dilute solutions of five species (differing in molecular weight) of polyisobutylene (PIB) and five of polyethylene oxide (PEO). For the same number of monomer units in the main chain, a greater quantity of PIB was required to produce the same amount of drag reduction. Thus, since PEO is the more flexible of the two polymers, molecular flexibility assists drag reduction.
In addition, the concentration excess of PIB required to produce the same amount of drag reduction was much greater for species with the same molecular weight than for species with the same number of monomer units. It was, therefore, concluded that the number of monomer units in the main chain, rather than molecular weight, was the important factor in drag reduction. It was also found, for either polymer, that, as chain length was increased, the concentration (relative to the critical concentration, at which the polymer molecules would theoretically be in dense spheroidal packing) required for a given amount of drag reduction decreased.

The other constituent of the drag-reducing solution is the solvent. Hershey and Zakin found that polyisobutylene was twice as effective a drag-reducing agent in cyclohexane as in benzene. Cyclohexane is a "good" solvent, in which polymer-solvent interactions are favoured over polymer-polymer interactions and the polymer molecules are relatively extended. Benzene, however, is a "theta" solvent, in which neither sort of interaction is favoured. It was, therefore, concluded that polymer expansion, aided by a "good" solvent, increases drag-reducing effectiveness.

The concentrations of drag-reducing solutions are so small (of the order of a few parts per million by weight) that the bulk properties of the fluid (density and viscosity) are scarcely affected. For example, the viscosity of a 50 ppm solution of polyethylene oxide was found to be only 2.7%. (Merill et al.,) greater than that of the solvent. The solutions appear clear to the eye/
the eye (Lumley,\textsuperscript{5} ), any cloudiness being the result of incomplete dissolution of the polymer or of the presence of impurities. They sometimes have a slightly soapy feel, although to what physical property this may be attributed is not clear.

Most of the polymers effective in drag reduction are susceptible to degradation. This is a reduction in the apparent molecular weight of the polymer caused by chemical or mechanical scission, and results in a decrease in the drag-reducing effectiveness of the solution. Lumley\textsuperscript{(4)} has stated that degradation and different solution characteristics caused by different methods of preparation are the main reasons for the considerable amount of contradictory drag reduction data. Degradation is so important in any experimental situation that it is considered separately (section 1.2.2). Different methods of preparation of polymer solutions may lead to differing degrees of homogeneity or entanglement, and may even (by degradation) change the molecular weight of the polymer.

Molecular entanglements (agglomerations) are always present initially in the polymer solution. If the solution is allowed to rest these virtually disappear, but there is evidence\textsuperscript{(10, reported in 5)} that they reappear under the influence of turbulent straining.

Gadd\textsuperscript{(2)} has cited a number of phenomena in addition to drag reduction, which may be observed in drag-reducing solutions. Some drag-reducing additives were found to reduce the free turbulence in a jet remote from a wall. However, this did not seem to occur in very dilute solutions (below 10 ppm in the case of the polyethylene oxide, 'Polyox' WSR301) which are still effective in reducing drag, or in jets which are not initially laminar\textsuperscript{(2)}. 
Another effect which seems to require a certain minimum polymer concentration is the reduction of the frequency of eddy shedding from a fine wire, as measured by a downstream sensing element (Gadd, 11). At 'Polyox' concentrations less than 10 ppm there was no effect, but at concentrations in excess of 20 ppm the frequency was halved.

In addition, solutions of some additives display filament formation on pouring once a certain concentration has been exceeded (30 ppm in the case of 'Polyox'). While water breaks into droplets on pouring, these polymer solutions have been found to form long hair-like filaments, which descend unbroken (2). Although the explanation for this behaviour is not known, Lumley (4) has suggested that the resistance of the solution to the droplet-forming instabilities to which Newtonian liquids are subject may be due to some change in the structure of the thin shear layer on the outside of the fluid filament under the influence of intense straining. Measurements of the intrinsic viscosity of drag-reducing solutions reported in (5) have shown that the intense axisymmetric strain in a filament may produce extreme extension of the polymer molecules. This would result in extremely high local values of the intrinsic viscosity of the solution, and a consequent stabilisation of the filament.

It has also been found by Gadd (12) that measured normal stress differences in dilute (less than 100 ppm) polymer solutions differ considerably for solutions which exhibit the same amount of drag reduction. These normal stress differences demonstrate the non-Newtonian/
non-Newtonian character of the drag-reducing solutions, since there are no such differences in stress in Newtonian fluids (in which the pressure acts equally in all directions).

The overall conclusion resulting from the measurement of these secondary effects in drag-reducing solutions is that the physical properties of such solutions do not follow a common pattern. It is thus difficult to explain turbulent drag reduction in terms of a generalised form of the stress relations for Newtonian fluids which takes account of the non-Newtonian character of the solutions.

One common factor between drag-reducing polymer solutions seems to be that they all display viscoelastic effects at higher concentrations (2, 5, 6). However, this does not seem to be an essential feature of all forms of turbulent drag reduction, since it has been reported (3) that drag reduction takes place in soap solutions and suspensions of fine solid particles as well as in polymer solutions. Although it remains to be shown that polymer and suspension drag reduction take place by the same mechanism, the latter is of obvious economic importance, since the suspended particles are not susceptible to degradation, give drag reduction at relatively low velocities, and do not permanently contaminate the liquid.

The first feature of the drag reduction phenomenon itself is that it occurs only in turbulent flow (6). Hershey and Zakin (9) have shown the existence of a second type of drag reduction, in which the laminar flow regime was extended beyond its normal limit. However, this is merely a delay in laminar-turbulent transition, and no drag-reduction was observed in fully turbulent flow beyond the transition point in these cases.
Turbulent friction factor measurements in pipe flow of dilute polymer solutions by Elata et al. (13) and others, have shown that drag reduction occurs only at Reynolds numbers in excess of a certain (onset) value. The onset Reynolds number increased with increasing pipe diameter (for the same polymer concentration), and was found to decrease with increasing polymer concentration (Figure 1.1(a)). However, the onset wall shear stress, \( \tau_w \) was found to be independent of pipe diameter for a given polymer solution. Further research by Virk and co-workers (14, 15) showed that this onset wall shear stress could be predicted in terms of a shear (friction) velocity at the wall, \( u_t \), given by

\[
\frac{D_m u_t}{\tau_w} = 0.015 + 0.005 \quad \text{Equation 1.1}
\]

where

- \( D_m \) = effective molecular diameter
- \( u_t \) = friction velocity = \( \sqrt{\tau_w/\rho} \)
- \( \nu \) = solution kinematic viscosity
- \( \tau_w \) = wall shear stress
- \( \rho \) = solution density

and wall shear stress \( \tau_w = \frac{d\Delta P}{4\Delta x} \) \( \text{Equation 1.2} \)

where \( \Delta P \) is the pressure drop along a length, \( \Delta x \), of pipe of diameter \( d \).

Once the onset wall shear stress has been exceeded, the drag reduction (at a given flow rate) is proportional to the polymer concentration \( (c) \), provided the solution remains dilute (5).

Thus/
\[
\frac{\tau_{ws} - \tau_{wp}}{\tau_{ws}} = R \times C \quad \text{Equation 1.3}
\]

where
- \( \tau_{ws} \) = solvent wall shear stress
- \( \tau_{wp} \) = polymer solution wall shear stress at the same flow rate.

\( R_0 \), the limiting value of \( R \) for zero concentration, is known as the intrinsic drag reduction, and depends only on flow rate and polymer chain length.

A different approach to the prediction of the amount of drag reduction attainable entails modification of the friction factor equation relating \( 1/\sqrt{f} \) and \( \text{Re}\sqrt{f} \) which may be obtained from the law-of-the-wall velocity profile. Modification is achieved by the addition of a term incorporating a dimensionless number, \( \text{De} \), the Deborah number, which reflects the ratio of polymer relaxation time to a characteristic flow time of the fluid.

\[
\text{De} = u_t^2 t_1 / \nu \quad \text{Equation 1.4}
\]

where
- \( u_t \) = friction velocity
- \( t_1 \) = polymer relaxation time (Zimm theory)\(^{(13)}\)
- \( \nu \) = kinematic viscosity.

The equation obtained by Elata et al.\(^{(13)}\) gives good agreement with drag-reduction data for different polymer concentrations.

\[
\frac{1}{\sqrt{f}} = 2.0 \log_{10}(\text{Re}\sqrt{f^1}) - 0.8 + \frac{\alpha}{\sqrt{8}} \log_{10}(\text{De}) \quad \text{Equation 1.5}
\]

where
- \( f^1 \)/
\[ f^1 = \text{Blasius friction factor} \]
\[ \text{Re} = \text{Reynolds number} \]
and \( \alpha \) is an experimentally determined constant, proportional to the polymer concentration (13).

In terms of \( f \), the Fanning friction factor (= \( f^1 / \mu \)), this becomes (Figure 1.2).

\[
\frac{1}{\sqrt{f}} = 1.0 \log_{10}(\text{Re} \sqrt{T}) - 0.40 + \frac{\alpha}{\sqrt{2}} \log_{10}(\text{De})
\]

Equation 1.6

The amount of drag reduction does not increase indefinitely with increasing polymer concentration, but reaches a maximum value (for fixed Reynolds number) at a friction factor given by (Figure 1.2)

\[
\frac{1}{\sqrt{f}} = 19.0 \log_{10}(\text{Re} \sqrt{T}) - 32.4
\]

Equation 1.7

This equation was found by Virk et al. (16) to correlate well the maximum drag reduction data from all available sources. Although much of the data was for the system polyethylene oxide/water, the asymptote defined by equation 1.7 represents an upper bound to all dilute polymer solution drag reduction data for over 30 investigators. It may be simplified to a power-law expression for Reynolds numbers in the range 4000 to 40000 (Figure 1.1(b)):

\[ f = 0.59 \text{Re}^{-0.58} \]

Equation 1.8

Lumley (5) has noted that if the value of \( R \times C \) (Equation 1.3) is calculated at a point on the maximum drag reduction asymptote to give/
FIGURE 1.1a  THE ONSET PHENOMENON

FIGURE 1.1b  THE ULTIMATE DRAG REDUCTION ASYMPTOTE
**FIGURE 1.2** DRAG REDUCTION (Prandl-von Karman co-ordinates)
asymptote to give \((R \times C)_{\text{max}}\) then a concentration can be defined by

\[ C_{\text{max}} = \frac{(R \times C)_{\text{max}}}{R_0} \]  

Equation 1.9

like \(R_0\), \(C_{\text{max}}\) varies with flow rate and polymer molecule chain length. Now, for any drag-reducing situation it is possible to define

\[ \xi = \frac{R}{R_0} \]  

Equation 1.10

\[ \gamma = \frac{C}{C_{\text{max}}} \]  

Equation 1.11

It has been found that, expressed in this way, drag reduction has a universal form

\[ \xi = \frac{1}{1 + \gamma} \]  

Equation 1.12

\(R_0\) and \(C_{\text{max}}\) can be expressed empirically as functions of the flow rate relative to that at onset and the polymer intrinsic viscosity.

Before any attempt is made to find an explanation for drag reduction on a molecular level, it is necessary to review the effects of the polymer molecules on the overall flow relationships of the fluid. Experimental investigations by Wells (17), Elata et al. (13), Patterson and Florez (18) and others, all indicated that the presence of the polymer molecules affected the turbulent velocity profile in pipe flow. Although great care has to be taken to ensure that flow-measuring devices are correctly calibrated for use in polymer solutions, close agreement was obtained between results using different methods, such as pitot tube (13, 18) and hot film anemometer (18).

The results obtained by Wells (17) for a 50 ppm solution of Guar gum in water are given in Figure 1.3. It can be seen that, for values/
Data of Wells (Ref. 17)
50 wppm. Guar Gum
0.65 in. i.d. pipe

○ Re=36000
□ Re=74000

Sublayer Law
$u^+ = y^+$

FIGURE 1.3 MEAN VELOCITY PROFILE IN DRAG-REDUCING SOLUTION
for values of $y^+$ in excess of 15, the velocity shows the same logarithmic dependence on $y^+$ that is observed in the turbulent flow of Newtonian liquids. A law-of-the-wall equation of the form

$$u^+ = A + \frac{1}{K} \log_e y^+ \quad \text{Equation 1.13}$$

where

$$u^+ = \frac{u}{u_t} \quad \text{and} \quad u = \text{point velocity}$$

$$u_t = \text{friction velocity}$$

$$A = \text{constant}$$

$$K = \text{von Kármán mixing constant}$$

$$y^+ = \frac{\rho y u_t}{\mu} \quad \text{and} \quad y = \text{distance from wall}$$

$$\rho = \text{fluid density}$$

$$\mu = \text{fluid viscosity}$$

can, therefore, be fitted to the data. In cases of moderate drag reduction (not approaching the asymptote of equation 1.7), the value of the mixing constant ($K$) has been found to be little different from that for water (0.4), although it may be slightly reduced. There is, however, a marked increase in the value of the constant $A$, which reflects the point of intersection of the logarithmic law (Equation 1.13) and the sublayer law ($u^+ = y^+$) valid near the wall. Physically, this represents a thickening of the viscous sublayer, and it has been shown that doubling the sublayer thickness results in an approximate halving of the wall friction.

Elata et al. (13) have expressed the increase in $A$ as an additional term in equation 1.13 incorporating the Deborah number (Equation 1.4) so that
\[ u^+ = A + \frac{1}{K} \log_{10} y^+ + \alpha \log_{10}(De) \] \text{Equation 1.14}

where A and K have values of 5.5 and 0.4, as for the Newtonian solvent (water). This equation was used to derive equation 1.5, which was found to predict well the relationship between Reynolds number and friction factor for drag-reducing solutions.

Virk et al. (19) have shown that in cases of drag reduction approaching the ultimate asymptote (equation 1.7) the buffer region extended virtually to the centre of the pipe. In these cases, the value of A was approximately 17, and the value of K was approximately 0.085.

It thus seems likely that the polymer molecules cause a thickening of the viscous sublayer. Further evidence that the effect producing drag reduction is concentrated in the wall region has been provided by the experiments of Wells and Spangler (20).

Comparisons of drag reduction caused by the wall injection of polymer solution and by an equivalent concentration in the bulk fluid have shown that it is the polymer in the wall region which is effective in drag reduction. It has also been reported by Davies and Ponter (21) that significant drag reduction may persist for some time after a polymer solution passing through a pipe has been replaced with water. This would appear to indicate that surface adsorption plays a part in the mechanism of drag reduction.

Hypothetical explanations for drag reduction have been sought in terms of both molecular and continuum approaches to the solution properties. In the molecular approach it is the length scales of the polymer molecules and fluid motions which are regarded as important.
The molecules will not affect the fluid properties unless their length is at least of the same order as the length of the smallest motions in the fluid. The continuum approach, however, regards the polymer solution as a homogeneous continuum, in which only time scales are important. Thus the polymer molecules will not affect the fluid motions unless some time characteristic of the polymer molecules in solution is at least of the same order as the smallest time scale which may be associated with the fluid motions.

As stated by Lumley (5), it is possible to construct a model of drag reduction which is in qualitative agreement with the experimental findings, but which is not dependent on any assumptions as to which of the above approaches is valid. However, a more detailed explanation requires a decision to be made as to whether it is a characteristic length or a characteristic time of the polymer molecules which is relevant.

Virk (14) has attempted to explain the onset of drag reduction in terms of a molecular (length-scaling) approach. The polymer scale chosen was a molecular diameter ($D_m$) equal to twice the root-mean-square radius of gyration of the unperturbed macromolecule, and $\nu/\mu_t$ (the ratio of kinematic viscosity to friction velocity) was a turbulence scale characteristic of the eddies at the peak of the dissipation spectrum. Typically, a value of $D_m$ might be 1600 Å (0.16 μm), which was about 100 times smaller than a typical value of $\nu/\mu_t$. It thus seems unlikely that the polymer molecules would affect the turbulent flow structure, and the use of a length-scaling approach must be questioned (14, 5, 22). Lumley (5) has stated that, at maximum/
at maximum drag reduction, the molecular concentration is very much less than that at which spheres (with a diameter as defined by Virk) would be in dense packing. This rules out an explanation of the maximum drag reduction asymptote in terms of a limiting degree of molecular packing, which would seem to indicate further that a length-scaling approach is not the correct one.

However, Gadd (2) and Fabula et al. (22) have suggested that this apparent disparity between molecular and turbulent length scales at the onset of drag reduction may be explained by an increase in the effective molecular diameter under the influence of shear, owing to either molecular elongation or the formation of clusters of molecules. Alternatively (22), it may be that the dynamically significant turbulence scale in the wall region is much smaller than $\sqrt{\nu/u^*}$.

Lumley (4) has stated that the "raggedness" observed in heat transfer measurements in drag-reducing fluids (random step changes in the mean signal level) may be due to the intermittent passage of molecular aggregates near the heat transfer surface. This, and other evidence reported by Fabula et al. (22), appears to indicate that the formation of molecular aggregates is an essential feature of drag reduction. However, it seems impossible to tell whether it is the aggregates or individual molecules (in a solution containing both) which are effective in drag reduction, since filtering to remove agglomerates seems to result in the production of more (Lumley 5).

Gadd (2) has proposed possible physical mechanisms for drag reduction/
reduction in terms of molecular approach. It may be that the thickening of the viscous sublayer (and consequent reduction in wall friction) is caused by the elongated polymer molecules aligning themselves near the wall in the direction of flow and inhibiting motions perpendicular to the wall. Alternatively, Lumley (14) has suggested that molecular entanglements may extend cross-stream, and so prevent the formation of energy-dissipating vortices (see section 1.3.1).

The continuum approach relies on the application of a suitable time-scaling analysis. The time scale most used to characterise the polymer molecule is its fundamental relaxation time \( t_1 \), given by (22):

\[
t_1 = a \frac{\eta_s}{\eta} \frac{100[\eta] M}{RT} \tag{1.15}
\]

where

\[
\begin{align*}
\eta_s &= \text{solvent viscosity} \\
[\eta] &= \text{intrinsic viscosity at zero shear in } 100 \text{ cm}^3/\text{gm.} \\
M &= \text{molecular weight (polymer assumed monodisperse)} \\
R &= \text{gas constant} \\
T &= \text{temperature (absolute)}
\end{align*}
\]

This may be related to a characteristic time scale of the turbulence, based on the reciprocal of a dominant frequency such as the peak of the dissipation spectrum. However, it has been found (15) that, although terminal relaxation times are of the same order as the shortest turbulence times, at onset they differ by three orders of magnitude.
It seems, therefore, that a continuum approach is as ineffective as a molecular approach in portraying the onset phenomenon in drag reduction.

The Deborah number (equation 1.4) is an alternative ratio based on a time-scaling approach. The comparison of relaxation time \( t_1 \) to the characteristic flow time \( \sqrt{u_t^2} \) yields a number which has been shown \( \text{(3, 13)} \) to correlate the experimental drag reduction data with reasonable accuracy (equations 1.5 and 1.14). The flow time \( \sqrt{u_t^2} \) is dependent on the bulk rather than microscopic (turbulent) properties of the fluid, and is, in fact, the characteristic length scale (used in the molecular approach) divided by the friction velocity. It can, therefore, be expected to be characteristic of the solution properties in the wall region.

Rodriguez et al. \( \text{(23)} \) found that a non-dimensionless Deborah number \( \text{(De}) \), defined by

\[
\text{De}^1 = \sqrt{t_1/d^{0.2}}
\]

\text{Equation 1.16}

correlated experimental data even more successfully. The weak dependence of drag reduction on diameter at constant flow velocity indicates that in commercial pipes the velocity should be at least as high as in small-scale equipment to achieve an equivalent drag reduction \( \text{(3)} \). This may well be outside the economic operating range for the larger pipes.

Although it seems that, like the molecular approach, the continuum approach fails to give an explanation of the phenomenon of onset, Lumley has stated \( \text{(5)} \) that attempts to reconcile the two hypotheses merely indicate the dominance of the continuum approach.
The answer to the problem of onset may lie in the choice of different time-scaling parameters, such as a molecular relaxation time derived by analogy to a "spring and dashpot" model, or a fluid characteristic time based on the deformation time of a fluid element (Gadd, 6).

However, there is certainly some factor missing, either in the experimental analysis of onset or in the structure of the hypothetical model of drag reduction. Lumley (5) and Gadd (6) have suggested experimental approaches which may assist in the building of a more consistent model of drag reduction than those described above. These include the measurement of onset data with mono-disperse polymers, determination of the extent of agglomeration and extension in drag-reducing flows, and the estimation of detailed turbulence spectra in the wall region.

Lumley (4) has stated that the main causes of disparity between the drag reduction results of different researchers are different methods of solution preparation, and differing degrees of polymer degradation. Because polymer degradation is such an important factor in all experimental situations, it will now be considered in more detail.

1.2.2. Polymer Degradation in Drag Reduction

Degradation of polymer molecules is one of the major causes of the disparities between the results of drag-reduction experiments by different research workers, as reported by Lumley (4). It may occur by either mechanical or chemical means, but the overall effect is the same: a reduction in drag-reducing effectiveness because /
ness because molecular scission lowers the mean molecular weight of the polymer molecules (Paterson and Abernathy, 24).

Brennen and Gadd (25) have found that molecular shear in turbulent flow or gentle mixing causes degradation of polymers (guar gum, polyethylene oxide and polyacrylamide). Initially the degradation only affects the secondary phenomena, such as normal stress differences and turbulence in a free jet, described by Gadd (2). This may be due to the breaking up of molecular aggregates. Further exposure to shear significantly reduces the effectiveness of solutions in drag reduction. Solutions left for several days have also exhibited degradation without undergoing shear. This suggests that there are two effects, one occurring in solutions at rest (possibly by biological or chemical action) and the other in turbulent flow (by shear scission).

The effect of shear degradation on various polymers has been investigated by several workers. However, their results are seldom fully consistent with each other, since the actual amount of degradation depends largely on the method of investigation. It seems generally true that natural polymers (such as guar gum) are more resistant to degradation than synthetic polymers, and that the initial rate of degradation is very rapid (particularly for polymers of very high molecular weight), with the average molecular weight approaching some asymptotic value (Patterson et al. 3). The highest molecular weight fractions of a polymer are thus the most susceptible to degradation, which will be accelerated by the presence of side chains or a "poor" solvent.

A comprehensive/
A comprehensive series of experiments on the effects of degradation on polyethylene oxides of various molecular weight grades was carried out by Paterson and Abernathy (24). It was found that significant degradation (decrease of drag reduction by as much as 50%) could occur in a comparatively short length of pipe (28 ft.). This effect was greatest at the highest Reynolds numbers, when the stresses in the fluid were greatest. The reduced friction factor was also found to be strongly dependent on the configuration of the pipe inlet (greater drag reduction was observed for a smooth inlet). Thermal and chemical degradation (of aqueous polyethylene oxide solutions) was negligible compared to shear degradation, which caused preferential scission of the larger molecules, with a consequent lowering of the mean molecular weight.

As mentioned above, Paterson and Abernathy (24) found that there was negligible chemical degradation of polyethylene oxide (Polyox) in aqueous solution. McGary (26) has found that various factors accelerate the chemical degradation of Polyox. These include the presence of strong acids, certain oxidising agents (including dissolved oxygen) and certain metallic ions (including ferrous and cuprous), and exposure to ultraviolet light. It seems that chemical degradation occurs by a process of autoxidation to form hydroperoxides followed by polymer chain cleavage. Certain compounds may be used to stabilise Polyox, one of the most effective being isopropyl alcohol. These may be used in very small quantities to lessen the degradation of Polyox in aqueous solution, presumably because they/
because they compete with the Polyox for the hydroperoxides formed by autoxidation.

In conclusion it may be stated that the mechanism of polymer degradation is highly complex. The effects of degradation may be minimised as far as possible by reducing the amount of shear (through valves, orifices etc.) and by removing substances known to cause chemical degradation (and possibly by using a stabilising agent). However, if results of drag reduction experiments are to be meaningful, some estimate of the amount of degradation which has occurred must be made. This is probably best achieved using an 'ideal' flow rig (in which shear degradation is known to be minimal) to investigate the effects of chemical degradation in a given application.

1.3 The Boundary Layer

1.3.1 Introduction

The present state of research into the nature of the boundary layer in turbulent flow has been summarised by Corino and Brodkey (27).

That fluid in turbulent flow forms a boundary layer adjacent to a wall has been known since the early part of this century (Prandtl, 1904). In this wall region, which may be regarded as a viscous sublayer and a buffer region, viscous effects are important enough to influence fluid motions. Flow in the sublayer is not laminar, but there is a relatively small amount of mixing compared to that in the turbulent core. Although the nature of the motions in the sublayer is not fully known, their extreme importance in the/
tance in the control of transport processes and turbulence generation has been realised.

Many research workers have assumed particular characteristics for the wall region and thence developed a model to predict rates of transport of mass, heat or momentum. The most important of these are listed in (27). As these predicted values are usually dependent on the value of one or more experimentally evaluated parameters, they can only be relied upon to give reasonable results over the range of validity of those parameters. However, as most of the models can be made to agree with experimental data, the insensitivity of the results to the assumptions means that it is not possible to decide which of the models accurately depicts the flow in the wall region. It is clearly necessary to find out more about the nature of the sublayer, so that a model can be developed which is not dependent on experimental constants of the bulk fluid, but only on parameters measured from sublayer motions (turbulence) directly.

Since 1950 the development of hot wire anemometry and other techniques has enabled measurements of turbulence characteristics within boundary layers to be made. Separate hot wire anemometer experiments in air by Klebanoff and by Laufer, correlated by Hinze (28), each showed that eddy size was smallest nearest the wall, and increased towards the buffer region (this was assumed in Prandtl's mixing-length theories). Laufer also found that turbulent energy distribution curves strongly illustrated the importance of the region $5 \leq y^+ \leq 20$. Production and dissipation of turbulent energy were greatest at $y^+ = 11.5$, and the whole region/
whole region both lost kinetic energy by diffusion towards the wall and gained pressure energy by diffusion from the core. There was also a viscous transfer of kinetic energy (mainly towards the wall) in the region $y^+ < 5$. At $y^+ \geq 20$ turbulence production and dissipation both decrease rapidly with increasing $y^+$, energy being lost by pressure diffusion to the wall region and gained by diffusion of kinetic energy from the wall region. Out in the core of the pipe the loss by dissipation is just balanced by the kinetic energy gain.

Visual investigation techniques have also been developed to give results which are quantitative, and can thus lead to the formulation of useful models of the sublayer. Early work by Fage and Townend (29), using an ultramicroscope to observe the motion of minute particles entrained in the fluid stream, indicated continual periodic departures from rectilinear flow in the region very close to the wall ($y^+ \ll 1$). Developments of this technique using entrained air bubbles (30), dye streaks and hydrogen bubbles (Kline and co-workers, 1959, 1963, 1965 and 1967 (31)), and colloidal magnesium oxide (27) have enabled a picture of the boundary layer to be formulated. This is summarised by Corino and Brodkey (27).

The fluid motions in the sublayer ($y^+ \leq 5$) exhibit small-scale, three-dimensional departures from rectilinear flow. These disturbances, which rarely leave the region, are produced and sustained by turbulence from the adjacent (generation) region. Their magnitude is thus influenced by the degree of turbulence in the generation region, and is, therefore, dependent on Reynolds number, there being more frequent disturbances at higher Reynolds numbers.
At high Reynolds numbers, fluid from the generation region often penetrates deeply into the sublayer, occasionally reaching the wall. This mixing between the two regions is of great importance in heat and mass transfer processes. It also ensures that the random periodicity within the generation region will be reflected within the sublayer, albeit in a considerably attenuated form.

The generation region \(5 \leq y^+ \leq 70\) contains an area \(5 \leq y^+ \leq 15\) in which ejections (spurts of fluid away from the wall) originate. These ejections have a frequency of occurrence and a velocity of ejection which are dependent on the mean flow, although the hydrodynamic reasons for this dependency are not apparent. Interaction between the ejections and the (higher velocity) mean flow occurs in localised areas of high shear within the region \(7 \leq y^+ \leq 30\), energy being extracted from the mean flow and converted to small-scale turbulence.

It has been postulated that the cause of the ejections is a hydrodynamic instability resulting in vortex formation. Ejections originate from areas of strong updraught between adjacent counter-rotating vortices. In the recent work of Corino and Brodkey \(^{(27)}\) no oscillatory instabilities or rotational vortices were observed using a camera mounted perpendicular to the mean flow and moving with it. However, it may be that these occur in a plane not aligned with the flow direction or are considerably larger than the field observed.

For example, Lumley \(^{(1)}\) and Gadd \(^{(6)}\) both cite evidence in support of the theory that the periodic ejections originate in the updraughts between pairs of counter-rotating vortices.
These vortices have their cores aligned with the stream direction (at \( y^+ \) around \( \frac{4}{0} \)) and their planes of circulation tipped normal to the direction of maximum strain rate. Their separation \( (z^+) \) is approximately 100.

Now,

\[
z^+ = \frac{\rho z u_z}{\mu} \quad \text{Equation 1.17}
\]

and

\[
y^+ = \frac{\rho y u_y}{\mu} \quad \text{Equation 1.18}
\]

so

\[
\frac{z^+}{y^+} = \frac{z}{y} \quad \text{Equation 1.19}
\]

The field of view observed in Corino and Brodkey's experiments is (for a magnification of 4.3) 0.069 in. (radial) x 0.095 in. (axial) x 0.027 in. (depth of focus in line of sight). The radial dimension corresponds, for a Reynolds number of 20000, to

\[
0 \leq y^+ \leq 45
\]

so that the depth of focus \( (z) \) corresponds to a range in \( z^+ \) of only 18 (using Equation 1.19). Since the separation of the vortices is at least five times this amount, the experimental observations can only be expected to show a small part of each vortex. No indication of vorticity will thus be apparent in the filmed record. The field of view may be seen, related to vortex size, in Figure 1.4.

The eddies in the core region \( (y^+ > 70) \) have been created in the generation region some distance upstream, since the turbulence requires a finite time to diffuse outwards, and the mean velocity in the core is greater than in the generation region. The size of the eddies increases as they move outwards, most change occurring within the region \( 50 \leq y^+ \leq 100 \), although the entire region to \( y^+ = 150 \) may be regarded as transitional.
FIGURE 1.4  THE RELATIONSHIP BETWEEN  
VORTEX SIZE AND FIELD OF VIEW FOR  
LIGHT-SCATTERING EXPERIMENTS (BRODKEY)
In addition to hot wire anemometer and visual techniques, turbulence within the boundary layer has been investigated using hot film anemometer, laser velocimeter, pressure fluctuation and electrochemical mass transfer measurements. These methods will now be examined to ascertain their suitability for use in drag-reducing liquid systems.

1.3.2 Methods for the Investigation of the Boundary Layer

As mentioned above, visual techniques have been used with considerable success to demonstrate the mechanisms of turbulence in the boundary layer, and quantitative results have been obtained from some of the measurements (27). However, it is doubtful whether these methods could be applied satisfactorily to the investigation of the boundary layer in drag-reducing solutions since the small solid particles introduced to produce light scattering are the same order of size as the polymer molecules. Colloidal magnesium oxide has a mean diameter of 0.6 μm (27), while the mean diameter of polyethylene oxide molecules (WSR-301) is 0.5 μm. (twice the radius of gyration quoted in (15)), and extended molecules will be much larger than this. The colloidal particles could well become entangled in the polymer molecules rather than follow the flow fluctuations.

Hot wire and hot film techniques have been used in drag-reducing solutions. They both suffer from the extreme disadvantage that the boundary layer thickness in liquid flows is of the same order of magnitude as the probe (in gases the boundary layer is much thicker), and they cannot therefore be used to measure the small-scale fluctuations within the boundary layer. The size of the /
of the probes in use is already a minimum compatible with structural strength for use in liquids. In addition, it has been reported (32, 33) that calibration difficulties arise with hot film anemometers, possibly because the heat transfer surface of the probe becomes intermittently coated with polymer.

Laser velocimeter measurements have also been made in drag-reducing solutions (34, 35). This technique appears to be entirely suitable for the measurement of turbulence levels in such solutions, as it in no way affects the flow, and can be finely adjusted to investigate small-scale fluctuations, with resolution down to 10 μm. The only problems appear to be the necessity for an optically exact square duct for the flow system, and the difficulty experienced in measuring the fluctuations in flow velocity perpendicular to the main flow. However, the laser and elaborate optical system required are relatively expensive.

Pressure fluctuation measurements may be made using piezo-electric transducers or pinhole microphones, which may be mounted either in a pressure probe (36) or flush with the wall (37). Pressure probes are unsuitable for boundary layer turbulence measurements, as they suffer from the same size limitations as hot wire and hot film anemometers in liquid applications. The relatively large size of transducer surfaces or microphone diaphragms makes it difficult to reduce the sensing area below, say, 1/32 in. (37). This is large compared to the small-scale fluctuations in the boundary layer (so that the high frequency response will be relatively poor), and the response of the instruments to the pressure fluctuations/
pressure fluctuations may well give rise to significant fluid motions in the boundary layer.

The remaining method, involving the measurement of fluctuating mass transport coefficients at a solid wall by an electrochemical technique, appears (despite certain difficulties in the direct interpretation of results) to be suitable for application to drag-reducing liquids. It does not appear to have previously been used in this context, and will be described in detail in the next section.

1.3.3 Boundary Layer Investigation by Electrochemical Techniques

The use of an electrochemical technique to measure fluctuating mass transport coefficients at a solid/liquid interface was first reported by Reiss and Hanratty in 1962 (38). Local rates of mass transfer were studied by measuring the mean and fluctuating components of the current flowing to a small nickel electrode mounted flush with the wall of a pipe through which was flowing a solution of potassium ferricyanide. The reaction at the electrode (reduction of the ferricyanide ion to ferrocyanide) is so fast that its rate is controlled, under conditions of electrode polarisation, by the mass transfer through the boundary layer to the pipe wall. The fluctuations in the current thus reflect fluctuations in the region from the wall to $y^+ = 0.5$ the approximate thickness of the concentration boundary layer (39) - very much closer to the wall than may be investigated using hot wire anemometry. Polarisation was achieved by the addition of a large excess of sodium hydroxide to an aqueous solution containing equimolar quantities of potassium ferricyanide and potassium ferrocyanide. A side reaction involving the reduction/
the reduction of dissolved oxygen \((\text{H}_2\text{O})\) may be prevented by saturating the solution with nitrogen \((\text{N}_2)\).

Under these conditions, the mean current flowing rises with applied voltage until a certain value of the applied potential is reached at which the ferricyanide concentration on the electrode surface is effectively zero. Beyond this point the rate of reaction is mass transfer controlled, and the mean current is constant over a fairly wide range of applied voltages (typically \(-0.3\) V. to \(-0.8\) V.). Within this range, the mean (limiting) current \((\bar{I})\) may be used to calculate the mean mass transfer coefficient \((\bar{k})\), since

\[
\bar{I} = \bar{FkAC_b}
\]

where

\(A = \) electrode area

\(C_b = \) bulk concentration of ferricyanide ion

and \(F = \) Faraday constant.

A derivation of this equation may be found in section 3.4.1.

Similarly, the fluctuations in current about the mean \((\bar{I})\) may be related to the fluctuations in mass transfer coefficient at the electrode surface, and thence to the turbulent structure of the fluid boundary layer adjacent to the pipe wall.

As expected, Reiss and Hanratty found \((38)\) that the value of the mean mass transfer coefficient increased with increasing Reynolds number (because of the greater turbulence levels, and hence transfer rates, within the boundary layer). In addition, they found \((39)\) that the value of \(\bar{k}\) increased with decreasing electrode size,
electrode size, indicating that the flow over each electrode surface was non-uniform. Uniformity of flow, implying that the electrode size is much smaller than the scales of the turbulence close to the wall, is essential if the current fluctuations are to reflect accurately the high-intensity velocity fluctuations in the boundary layer. If the electrode is too large, these small scale disturbances will tend to average out over its surface. The size of the smallest electrode used in the investigations of Reiss and Hanratty (39) had a diameter of 0.016 in. (0.0398 cm.), and clearly should be smaller if non-uniformity is to be minimised. If, however, non-uniformity is found to exist, a correction may be applied (Mitchell & Hanratty 41).

This apart, the main drawback of the method relates to the interpretation of the fluctuating mass transfer coefficient in terms of the turbulent structure at the wall. The concentration boundary layer exerts a capacitance effect (analogous to the thermal inertia effect in hot wire anemometry), and the mass transfer fluctuations are not, therefore, directly proportional to the velocity fluctuations. This effect may be minimised by reducing the electrode diameter or the Schmidt number of the fluid, and so reducing the thickness of the concentration boundary layer (39). Correction for this effect is also possible, using analytical techniques developed by Hanratty and co-workers (39, 41, 42).

However, in applications of the method to solutions displaying The Toms Effect, the main concern would be to show up differences in the/
differences in the boundary layer fluctuations between drag-reducing and Newtonian solutions. These differences, if they exist, will appear in mass transfer fluctuations as well as in velocity fluctuations. The problem of relating the mass transfer measurements to the velocity field is thus less critical, and can be ignored until such time as it is desired to create a physical model incorporating the differences in boundary layer behaviour.

A final limitation of the technique reported \(^{(38)}\) lies in the sensitivity of the circular electrodes to radial fluctuations moving in both axial and circumferential directions. The relative magnitudes of each of these types of fluctuation has been determined using rectangular electrodes, which are sensitive only to fluctuations perpendicular to their longest dimension \((l_1, l_3)\). It was found that the scale of the circumferential fluctuations was only about one thirtieth that of the axial fluctuations. A small circular electrode thus responds principally to radial fluctuations moving in an axial direction along the pipe wall.

In experiments using small electrodes inserted in a non-conducting wall \(^{(38, 39, l_1)}\), the concentration boundary layer will not be fully developed at the electrode, but will be continuously developing over the electrode surface. Experiments have also been reported \((l_4)\) in which the nickel test electrode was a small area embedded in a relatively large control electrode, also nickel. If the area of insulating material between test and control electrodes is small, and the same potential is applied to each, then the concentration boundary layer across the test electrode will be/
will be fully developed (providing it is situated far enough from
the upstream end of the control electrode). The average concen-
tration boundary layer thickness is, therefore, greater than that
over an unsurrounded electrode, and consequently the measured mass
transfer parameters differ from those reported in (38) and (39).
The concentration and velocity profiles for each case are shown in
Figures 1.5(a) and 1.5(b).

1.3.4 Results Obtained from Electrochemical Mass Transfer Measurements

The preliminary experiments reported by Reiss and Hanratty (38)
showed that the fluctuations in mass transfer coefficient increased
in frequency as Reynolds number rose. This was reflected in the
respective frequency spectra: the spectral power at a frequency
of 10 Hz was almost $10^4$ times greater at a Reynolds number of 34200
than at a Reynolds number of 3280, but at frequencies lower than
1 Hz, the power at the lower Reynolds number was greater.
Experiments with two electrodes at different spacings showed that
the correlation between the mass transfer signals at the two
electrodes decreased as the electrode spacing was increased.

In further experiments (39), average mass transfer coeffi-
cient measurements clearly showed the transition from laminar to
turbulent flow. The values were also dependent on the size of
the electrode, increasing as electrode diameter was decreased.
The intensity of the fluctuating signal was also found to increase
with decreasing electrode size, indicating non-uniform flow over
the electrode surface. A correction for non-uniform flow was
applied, but, although this produced a reasonable correlation,
it was later found to be invalid (44).
FIGURE 1.5a  BOUNDARY LAYER - UNSURROUNDED ELECTRODE

FIGURE 1.5b  BOUNDARY LAYER - SURROUNDED ELECTRODE
In all cases, the intensity (ratio of standard deviation to mean) of the fluctuations had a maximum value at a Reynolds number around 8000. This may be seen in Figure 1.6.

Longitudinal and circumferential correlations between pairs of electrodes at different spacings indicated that the integral scale of the longitudinal fluctuations was of the order of the pipe radius, while that of the circumferential fluctuations was an order of magnitude smaller. The mass transfer frequency spectra (non-dimensionalised, using pipe diameter and mean velocity) were found to give consistent values at high frequencies, although at frequencies less than 0.1 (non-dimensionalised by pipe diameter and mean velocity) some variation with Reynolds number was noted, possibly as a result of difficulties experienced in making accurate low-frequency measurements. The spectra were also compared to those obtained using other techniques (Figure 1.7). Values were well in agreement with those obtained by Harrison (45), using a pressure transducer mounted flush with the wall of a wind tunnel. The spectral densities were less (at high frequencies) than those obtained by Laufer and Klebanoff (reported in (27)), and by Sandborn, using hot wire anemometry techniques. However, the hot wire measurements were made some distance into the boundary layer, rather than actually at the wall, and this could well account for the differences.

The mass transfer measurements were also used (39) to calculate velocity data which could be compared directly to hot wire anemometry results. The average mass transfer coefficient was related/
FIGURE 1.6  MASS TRANSFER INTENSITIES
was related directly to the average velocity gradient (shear stress) at the wall, and velocity intensities were calculated from mass transfer intensities. In the latter case it was found that the local turbulent velocity intensities at the wall were around 10% (0.11). This was not entirely in agreement with the values obtained for the limiting velocity intensity at the wall by the extrapolation of the results of hot wire anemometer measurements in the boundary layer.

Shaw and Hanratty (45) carried out similar experiments with circular electrodes, this time in the surrounded configuration (Figure 1.5(b)). The mean mass transfer coefficients were found to agree well with those predicted theoretically, indicating that the discontinuity formed by the insulation between the test probe and the control electrode has a negligible effect on the concentration boundary layer. The intensity of the mass transfer fluctuations was found to decrease logarithmically with increasing Reynolds number, although the range of Reynolds numbers investigated was considerably smaller than in (28). The results of the two series of experiments (39 and 44) are compared in figure 1.6, and it is of interest to note that, in all cases, the mass transfer intensities recorded at the surrounded electrode were greater than those recorded at the unsurrounded electrode. A correction applied by Shaw and Hanratty (44) for effects of finite electrode size brought all the data points onto a horizontal line, indicating a limiting mass transfer intensity of around 50% (0.17). The fluctuations are thus of approximately the same magnitude as the mean mass/
mean mass transfer rate, indicating the chaotic nature of the mass transfer process. Longitudinal and circumferential correlations between pairs of electrodes indicated that the scale of the circumferential fluctuation was not one but two orders of magnitude smaller than that in the axial direction. The velocity of the axial disturbances, determined by correlation between pairs of electrodes, was approximately equal to the friction velocity, \( u_\tau \) (the local average velocity at \( y^+ = 1 \)). This value was very low compared to the disturbance velocity for pressure or shear stress fluctuations, which is approximately equal to the bulk average velocity of the fluid.

The frequency spectrum of the mass transfer fluctuations measured by Shaw and Hanratty may be compared, in Figure 1.7, with those mentioned earlier. It can be seen that the characteristic frequency was much lower in the case of the surrounded electrode than in the case of the unsurrounded electrode. This low characteristic frequency, together with the high intensity of the fluctuations, suggests that a surface renewal model, such as that proposed by Hanratty, might provide an approximation of the mass transfer process. Indeed, values of the mean transfer coefficient calculated by this method were found to agree reasonably well with those obtained experimentally.

Mitchell and Hanratty have obtained measurements using both circular and rectangular unsurrounded electrodes. At low Reynolds numbers the mean mass transfer coefficients for rectangular electrodes/
angular electrodes were found to be higher than predicted, possibly on account of the smaller ratio of (longitudinal) length to (circumferential) width. Longitudinal correlations gave an integral scale for the axial fluctuations that was slightly less than that obtained by Reiss and Hanratty (39). The circumferential scale was found to be only one thirtieth of the longitudinal scale, and, when normalised with respect to wall parameters ($u_\tau$ and $y$), was shown to be of the same order of magnitude as the thickness of the region ($\gamma = 11$) in which molecular viscosity affects the velocity profile.

The effect of non-uniformity of flow was shown using electrodes of different widths. As predicted, the intensity of the signal decreased as the width increased, and the correction for non-uniform flow used in this case was found to give good agreement between electrodes of different widths. Within the range observed, electrode length was not found to affect the intensity, and the limiting mass transfer intensity appears to be independent of Reynolds number, at around 10% (0.1). The corresponding velocity intensity was calculated and found to be 32% (0.32), considerably larger than the values obtained by Reiss and Hanratty (39).

The spectral density function, normalised with respect to the mean velocity and tube diameter, was found to be very close to that obtained by Reiss and Hanratty (39) - see Figure 1.7. Attempts were also made to calculate velocity spectra, although this was limited by experimental considerations to frequencies below 30 Hz. The velocity spectral densities were found to be somewhat lower (at similar frequencies) than those obtained using hot wire anemometry techniques.
FIGURE 1.7 REPORTED DIMENSIONLESS SPECTRA

**Velocity Spectra**

- Ref. 17: $Re$, $y^+$
  - $W_u \bar{u} / \bar{u}^2 a$
    - $\bigcirc$ 80000 3.13
    - $\square$ 25000 5.90
    - $\triangle$ 20300 2.72

**Pressure Spectra**

- Ref. 35: $\bar{u}$ (cm/s)
  - $W_p \bar{u} / \bar{p}^2 a$
    - $\bigcirc$ 6000
    - $\square$ 3000
    - $\triangle$ 1500

**Mass Transfer Spectra**

- Ref. 29: $Re$
  - $W_k \bar{u} / \bar{k}^2 a$
    - $\bigcirc$ 1640-17200

- Ref. 34: 13850
In addition to spectra and intensities, the amplitude distribution function and the amplitude density function of the mass transfer fluctuations were determined. It was noted that there were both positive and negative deviations from the mean, of the same magnitude as the mean.

Overall, the results \(^{(41)}\) indicated that only the velocity intensity, amplitude density function and circumferential integral scale were independent of Reynolds number when correlated with the wall parameters, \(u\) and \(\nu\). The spectral density function and longitudinal integral scale, on the other hand, could only be correlated using the bulk parameters, \(u\) and \(d\).

Son and Hanratty \(^{(47)}\) have shown that the results of Shaw and Hanratty \(^{(39)}\), corrected for an error in orifice plate calibration, may be used to predict a relationship for the eddy diffusivity \((\xi)\):

\[
\frac{\xi}{\nu} = 0.00032(y^+)\frac{1}{4}
\]

Equation 1.21

However, accurate measurements of the concentration profile close to the wall are needed to confirm this.

Hanratty \(^{(43)}\) reviews the work detailed in \(^{(39)}\), \(^{(41)}\), \(^{(44)}\) and \(^{(47)}\). No new experimental evidence is presented, but the data of Shaw and Hanratty \(^{(39)}\) are shown corrected for the manometer calibration error first mentioned in \(^{(47)}\).

Sirkar and Hanratty \(^{(48)}\) have measured limiting currents (and hence mean mass transfer coefficients) with rectangular electrodes at angles of \(12.5^\circ\), \(15^\circ\) and \(20^\circ\), as well as \(90^\circ\), to the mean flow. These electrodes were, therefore, sensitive to fluctuations moving in the circumferential, as well as longitudinal direction.
The effect of electrode orientation on mean mass transfer coefficient enabled the r.m.s. value of the transverse component of the fluctuations to be determined. This value was estimated to be 0.087 of the mean velocity gradient at the wall, a figure in agreement with that obtained by investigators using photographic techniques. Further work (49) showed that the frequency spectrum of the transverse fluctuations was similar to that for the fluctuations in the direction of mean flow. The amplitude distribution function of the transverse fluctuations was found to be approximately Gaussian.

Further considerations from a theoretical viewpoint are reported by Sirkar and Hanratty (42) in an attempt to relate the turbulent mass transfer to the velocity field. An order-of-magnitude analysis indicated that the turbulent exchange of mass was governed primarily by velocity fluctuations in the transverse direction and perpendicular to the wall. The transfer function used to relate the velocity spectrum to the mass transfer spectrum was such that high frequency velocity fluctuations were ineffective in causing mass transfer. It was found that only 1.0% of the energy of the velocity spectrum was in the same range of frequencies as 95% of the mass transfer spectrum. This enabled approximate relations between the mass transfer spectrum and the transverse velocity spectrum to be developed for high frequencies and for low frequencies using simplified models.

1.4 Turbulence Measurements in Drag-reducing Solutions

1.4.1 Grid and Core Turbulence

Little research on the/
Little research on the turbulent characteristics of drag-reducing polymer solutions was carried out prior to 1966, although by that time most of the basic features of drag reduction were known. Work of Fabula (10), reported by Friehe and Schwarz (50), on the measurement of the energy spectra of grid-generated turbulence in a solution of polyethylene oxide showed that great care was necessary in the interpretation of hot film anemometry results for polymer solutions. The spectra obtained using Fabula's conical-shaped heat transfer probe exhibited spurious high frequency signals which corresponded to a turbulent kinetic energy five times greater than that predicted theoretically. This "raggedness" was not found in aged polymer solutions, and was thought to be due to polymer aggregates striking the probe. Similar effects were observed by Smith et al. (51).

However, Friehe and Schwarz (33) have shown that the results obtained by hot film measurements in polymer solutions are dependent on the shape of the probe. It seems that conical-shaped probes give better results than probe shapes (such as cylinder) which involve a stagnation point. Unfortunately, it is not possible to construct a conical probe as small as some of the cylindrical probes which are available, so that measurements with conical films cannot be made so close to the solid boundary. A similar dependence on probe shape was observed by Serth and Kiser (32), who used mainly wedge-shaped probes in solutions of Separan and of Carbopol. Probes were sensitive to the intensity and probably to the scale of the turbulence as well as to local velocity. Again, variations up to/
variations up to 250% in heat transfer coefficient were observed.

Later grid turbulence measurements by Friese and Schwarz (50) in solutions of Dowell J-100 (a polyacrylamide) using a conical hot film probe, showed an increased intensity of velocity fluctuations compared to water. However, the precision of the results was poor, owing to polymer degradation. The intensity level was found to increase both with increasing mean velocity and with increasing polymer concentration. The grid pressure drop was lower for the polymer solution, but, away from the grid, the rate of decay of the grid-generated turbulence was greater in the drag-reducing solution. The energy spectrum of the polymer solution turbulence had the same shape as that for water, and had the same values when suitably normalised.

Greated (35) has used the more promising laser velocimeter technique to measure grid turbulence levels in an 80 ppm solution of Separan AP30. Measurements were only made at one flow rate (corresponding to a grid Reynolds number of 1000), but the presence of polymer was found to lower the intensity of the velocity fluctuations (cf. the results of Friese and Schwarz (50) reported above). Close to the grid there was a considerable decrease in the energy content at the high frequency end of the normalised spectra measured in the polymer solution, but further away (17 cm.) there was little difference from water.

Pressure measurements away from the wall have been made in polymer solutions by Smith et al. (51) and Friese and Schwarz (33). As in the case of hot film measurements, anomalous results were obtained.
It seemed that the discrepancy (in pitot-static reading) increased with flow velocity, polymer molecular weight and polymer concentration. However, the reading was also dependent on the diameter of the pitot orifice and on the ambient strain rate.

Thus it can be seen that few conclusive measurements of turbulence levels in drag-reducing solutions have been made. Perhaps those obtained using the laser velocimeter (Greated, 35) are least suspect, since there are less difficulties in applying the method to investigations in polymer solutions.

The measurements which have been made nearer to the wall in drag-reducing fluids will now be discussed.

1.4.2 Turbulence in the Vicinity of the Boundary Layer

As in the case of grid and core turbulence, several different methods have been used in attempts to characterise the turbulence in the wall region for flows of dilute polymer solutions. Johnson and Barchi (52) have used a conical hot film anemometer to measure velocity fluctuations in the boundary layer on a flat plate towed through a solution of polyethylene oxide. A reduction in the power of the fluctuations was observed throughout the range of the spectrum (20-4000 Hz.), but this reduction was greatest at high frequencies. This seems to indicate that the presence of the polymer causes a reduction in the amount of small-scale turbulence, although the measurements must be suspect on account of the relatively large scale of the probe compared to the thickness of the boundary layer, and because anomalous readings have been reported by other investigators (10, 33, 50, 51).
Although Johnson and Barchi (52) observed an increase in the intensity of the velocity fluctuations in the wall region, there was a reduction in the intensity of measured fluctuations in wall shear stress.

Wells et al. (36) and Kadykov and Lyamshev (53) have used pressure transducers to measure pressure fluctuations. Kadykov and Lyamshev observed a reduction in both low and high frequency pressure fluctuations at the boundary of a solid body in dilute polyethylene oxide solutions (0.1% and 0.01%). There was also a reduction in the spatial correlation between pressure signals measured at two transducers a small distance apart. However, Wells et al. (36), taking measurements in a 0.5% carboxymethyl-cellulose solution, observed a reduction only in the low-frequency energy of the frequency spectrum (normalised by the friction velocity), with an increase in the energies at higher frequencies. The exact transition point between the two kinds of behaviour was not well defined, but such a transition was observed at all Reynolds numbers and all distances from the wall. A similar, though less pronounced, effect was observed in the case of wave-number spectra (normalised by the intensity and diameter instead of by the friction velocity). The intensity of the velocity fluctuations as a fraction of the local velocity, calculated from pressure fluctuations by Wells (36) was found to be identical to that for water, and to be constant throughout the turbulent range of Reynolds numbers.

Rudd (34) made similar measurements both near to and away from the/
from the wall, using a laser velocimeter in a 0.01% solution of Separan AP30 at Reynolds numbers around 50000. He observed considerably higher axial velocity intensities, as fractions of the friction velocity, near the wall for the polymer solution, but in the core of the pipe there was a slight reduction (e.g. Friese and Schwarz, 50). In the sublayer, the velocity intensity increased in direct proportion to the distance from the wall, so that the intensity as a fraction of the local velocity remained constant, confirming the result of Wells et al. (36).

It would appear that, once again, the data obtained from laser velocimeter measurements are the most reliable; since the deficiencies of the pressure measurement and hot wire anemometry techniques render results obtained by these techniques highly suspect, particularly in the region close to the wall. Although Rudd (34) has produced useful results relating to the effect of polymer additives on the intensity of the velocity fluctuations in the wall region, the question as to what effect, if any, the additives have on the spectrum of the fluctuations remains open.

1.5 Summary

As has been shown, the experimental evidence relating to drag reduction is well documented, although a valid physical explanation of the phenomenon remains to be found. The bulk properties of drag-reducing solutions have been thoroughly investigated, but work remains to be done on their small-scale properties, and in particular on the effects of polymer additives on the structure of the turbulence in the boundary layer. Such experiments could lead directly/
lead directly to a closer physical insight into the phenomenon of drag reduction.

For reasons explained in the foregoing sections, many of the methods used to investigate the turbulent structure of Newtonian boundary layers are not suitable for use in polymer solutions. However, it seems that electrochemical mass-transfer measurements and laser velocimeter measurements could be made with equal facility in Newtonian and drag-reducing solutions.

The construction of an apparatus suitable for the measurement of fluctuating local mass-transfer coefficients at the wall of a pipe is described in Chapter 2. Particular attention is paid to the problem of polymer degradation, care being taken both to minimise the amount of degradation and to estimate how much has in fact taken place.

In Chapter 3 the techniques used to analyse the results obtained on the experimental apparatus as described, and in Chapter 4, the results themselves are presented. The results obtained in this series of experiments are also compared with those of other workers, and final conclusions and recommendations for further work may be found in Chapter 5.
CHAPTER TWO - APPARATUS DESIGN

2.1 General Description (See Figure 2.1)

The basic requirement was for a flow loop leading to a test section (T), in the wall of which the electrodes, at which the electrochemical reduction of the ferricyanide ions could take place, were to be inserted. As the electrolyte solution was relatively expensive, it was thought desirable to have a continuously recirculating flow system with a small storage tank. However, preliminary experiments with a loop using a centrifugal pump indicated that the mechanical degradation caused to the polymer molecules by the high shear rates encountered in pumping was too great to be tolerated: very little drag reduction could be obtained, even after only one pass through the pump. It was, therefore, decided to use a compressed gas to force the electrolyte through the flow loop. A pressure vessel (P) of approximately 275 gallons (1250 litres) capacity was purchased. This was large enough to hold sufficient electrolyte to give an experiment duration of at least 15 minutes at the highest flow rates to be used, and a holding tank (H) of similar size was constructed. This holding tank was situated at a higher level than the pressure vessel, so that when the experiment was complete, and the gas released from the pressure vessel, the electrolyte solution could be returned by gravity-feed for a further experiment. A dry cell was used to apply a voltage to the electrodes, and the electronic instrumentation for the circuits used was mounted beside the test section for ease of operation. Further details of the individual items of equipment may be found below.
FIGURE 2.1  GENERAL LAYOUT OF APPARATUS
2.2 Test Section and Calming Length

2.2.1 Electrodes

Ideally, each electrode should be smaller than the smallest eddy within the boundary layer, so that they may respond to the passing of these eddies. If the electrode were larger, there would be a tendency for the effects of two or more eddies arriving at the electrode at the same time to cancel each other out. This would result in a damping of the small-scale fluctuations in the current flowing to the electrode. However, the boundary layer itself is less than 0.003 in. (0.075 mm.) thick at a Reynolds Number of 20000 in a pipe of 1 in. (2.54 cm.) internal diameter, and the size of the smallest eddies will clearly be considerably less than this. It was impractical to manufacture an electrode of so small a size, and so a compromise between ease of fabrication and frequency response was necessary.

The material used for the electrodes was nickel, and, although fine nickel wire was available, it was decided to fabricate them from nickel rod for added strength. By careful turning, the diameter of the rod could be reduced to 0.012 in. (0.3 mm.) with considerable accuracy to form the electrode probe. Turning to a fine tolerance was only necessary for a short distance from the active tip of the electrode: 0.034 in. (0.86 mm.) from the tip of the probe the diameter could be increased to 0.025 in. (0.63 mm.) to lend strength to the assembly, and a further increase in diameter to 0.062 in. (1.57 mm.) allowed the electrode to seat on the outside surface of the test section of pipe with about 0.002 in. (0.051 mm.) protruding into the bore of the pipe. At this latter diameter the probe was substantial enough/
substantial enough to allow crocodile clips to be used to connect the electrical lead. A diagram of an electrode in its seating can be seen in Figure 2.2.

2.2.2 Test Section Pipe

The basic requirement was for a pipe of uniform bore and smooth interior surface, so that the boundary layer would not be disturbed in any way until well downstream of the electrodes. This precluded the use of a pipe of very small diameter, since the smaller the pipe the harder it is to machine, smooth and clean the inner surface effectively. Whilst convenient from a fabrication point of view, a larger pipe would require too great a volumetric flow rate, and hence a great amount of fluid and expensive storage tanks. It was thus decided to use a pipe of approximately 1 in. (2.54 cm.) bore, as this was readily available and was the smallest diameter which could be conveniently reamed internally to give a truly uniform bore.

Early experiments utilised a perspex pipe, into the wall of which the nickel electrodes were cemented with an Araldite resin. The pipe was then smoothed internally to ensure that the tips of the electrodes were flush with the interior wall, and the bore was finally polished with a perspex polish.

It was later decided that a test section should be prepared in which the nickel electrodes were to be mounted in, but insulated from, a nickel pipe wall. By applying a similar potential to wall and electrode, the concentration boundary layer across the electrodes could then be made fully developed if desired. The problem here was that the area/
FIGURE 2.2  ELECTRODE DIMENSIONS 1"±.02"
that the area of the insulation between electrode and wall should be small compared with the area of the electrode, so that the concentration boundary layer thickness would not fall appreciably between wall and electrode. The smaller the electrode, the greater would be this problem: here the area of the electrode was only 0.00011 in\(^2\) (0.073 mm\(^2\)), so that thickness of the insulation could only be of the order of 0.001 in. (0.025 mm).

A length of nickel pipe was acquired, and the test section was prepared by skimming the outside surface, fitting flanges, and reaming until the inner surface was smooth and concentric with the outer. A socket for an electrode was prepared in the pipe wall, this being bored 0.003 in. (0.08 mm.) oversize to accommodate the insulation. Thus a hole of 0.015 in. (0.38 mm.) diameter was bored right through the pipe wall, and a hole of 0.03 in. (0.76 mm.) diameter was bored to within 0.032 in. (0.81 mm.) of the inner surface to accommodate the electrode seating. With the pipe remaining exactly in position below the chuck of the drill, the electrode socket was carefully coated with an Araldite resin (Araldite HY11, with hardener HY11), which was left for 2 days to thoroughly harden. A hole of the exact dimensions of the electrode was then bored in the resin plug, and the electrode, firmly held in the drill chuck, was given a thin coating of the resin and lowered into place with extreme care. After checking for electrical insulation between pipe wall and electrode, the probe was left to set in place for a further two days.

The process was repeated for three additional electrodes, these being arranged/
being arranged co-linearly along the axis of the pipe. Their spacing was designed to give a wide range of possible separations for cross-correlation measurements, and the minimum separation was fixed by the closest distance at which two electrodes could be mounted by the above method - this was found to be 0.078 in. (0.198 cm.), and spacings of that distance, 0.122 in. (0.310 cm) and 0.237 in. (0.603 cm.) were used.

When all electrodes were finally in place, a block of the Araldite resin was built up around the exposed outer ends of the probes, to add rigidity to the assembly, and a small amount of resin was smeared around the protruding probe tips on the inside surface of the pipe (earlier trials had shown that if this were not done, polishing with emery cloth almost invariably broke off the delicate tips of the probes). When the resin had fully hardened, the bore of the pipe was carefully polished with fine emery cloth, so that the electrode tips were exactly flush with the curved interior metal surface and there was no excess resin intruding into the boundary layer.

Checks were then carried out to ensure that the electrodes themselves were fully conducting, but that they were still insulated from the pipe wall. After several attempts at fabrication by this method, a situation was achieved in which three of the four electrodes were satisfactorily located. In view of the difficulty which had been experienced in achieving even this amount of success, it was accepted that the need for the fourth electrode was less than the need to commence experimental work, and the test/
FIGURE 2.3 ELECTRODE CONFIGURATION 1" = .25"

DIRECTION OF FLOW

0.076 in. - 0.122 in. - 0.237 in.

0.062 in. - 0.025 in. - 0.012 in.
and the test section was deemed to be complete.

The external diameter of the test section was 1.301 in. (3.301 cm.), and its bore was 1.145 in. (2.908 cm.). Its overall length was 5.125 in. (13.02 cm.), and the first electrode (cathode) was situated 1.50 in. (3.81 cm.) from the upstream end - ample distance for the concentration boundary layer to become fully developed.

2.2.3 Reference Electrode

Immediately downstream of the test section was a 6 in. (15.25 cm.) perspex (insulator) section and a 7 in. (17.79 cm.) nickel reference electrode (anode), both machined to the same internal diameter as the test section itself (1.145 in.). The area of the anode had to be large compared to that of the cathode so that it would not limit the electrode circuit current. When only the small anodes were used, the above cathode was obviously suitable, but when the whole test section was used as the anode (surrounded electrode configuration), an additional downstream cathode had to be inserted. This took the form of a nickel foil sleeve which could be inserted in the flow loop downstream of the test section, and then connected in parallel with the permanently mounted cathode. It was 12 in. (30.5 cm.) long, so that the total cathode area was approximately three times that of the anode.

2.2.4 Calming Length

Upstream of the test section there must be a long, uniform length of pipe, along which the flow can settle into a constant configuration. In this length there must be no discontinuities in the pipe wall (these would disturb the boundary layer), and no bends,
no bends, valves or constrictions which would modify the flow pattern of the bulk fluid. It is generally accepted that such a calming length should be at least 80 pipe diameters long: the calming length prior to the test section was constructed from sections of perspex pipe to a total length of 9 ft. (2.74 m.), equivalent to 95 pipe diameters. It was tailored to a bore of exactly 1.145 in. (2.908 cm.) by the following procedure:

The downstream section of the calming length was skimmed externally to render the outside surface exactly circular, and at the downstream end a recess 0.155 in. (3.94 mm.) in length was bored to an internal diameter of 1.27 in. (3.22 cm.). At the upstream end a lap of identical diameter but 0.001 in. (0.025 mm.) greater in length was machined, and a similar lap was machined on the face of the flange at the upstream end of the test section. This latter lap was inserted in the recess at the downstream end of the perspex section, and the two were reamed together to the final bore of the test section (this was done before the electrodes had been inserted). Flanges (incorporating a rubber o-ring) were fitted at the joint, and marked so that the pipes could always be assembled in the same configuration. The final joint assembly was as shown in Figure 2.4. The perspex section was removed from the test section, and a further section of the calming length was machined and its recess fitted to the lap on the upstream end of the completed section. The two perspex sections were then reamed together to achieve uniformity of bore, and flanges were added.

This process/
FIGURE 2.4  TEST SECTION JOIN  1\textdegree.5"
This process was repeated, section by section, up the calming length. At the end nearest the test section, the length of the individual perspex sections of the calming length was around 4 in. (10.16 cm.), but further from the test section the length could be increased to 1 ft. (30.5 cm.), as the need for extreme accuracy in reaming was diminished. While the nominal bore of the perspex pipe was 1.125 in. (2.85 cm.), it was found that one purchased length of about 3 ft. (95.0 cm.) had a bore of exactly 1.145 in. (2.908 cm.), and so did not require reaming. The bore of the completed calming length was polished with perspex polish and assembled for final checking.

2.2.5 Pressure Drop Manometer

Connected to the test section and calming length, there had to be some means of measuring the pressure drop along the pipe. It was decided to use a manometer rather than a differential pressure transducer, since pressure transducers to deal with corrosive liquids were expensive and not readily available. The most suitable type of manometer was thought to be one of the inverted paraffin/water (solution) type, and one of these with a range of up to 14 in. (35 cm.) was fabricated. It was calculated that the pressure taps should be around 2 ft. (60 cm.) apart to give the widest useful range, and ideally they should be situated as close as possible to the test section, since polymer degradation in turbulent flow along the pipe made it desirable to determine the amount of drag reduction at the test section itself. Early experiments with simple pressure taps of aperture size 0.016 in. (0.406 mm.)/
size 0.016 in. (0.406 mm.) showed that the response time was too slow to be acceptable, and piezometer rings for insertion at flanged joints were fabricated from solid perspex, one to be inserted 4.5 in. (11.43 cm.) upstream of the test section, and the other a further 2.417 ft. (73.6 cm.) upstream. The rings were tapped and recessed in a similar manner to the sections of the calming length, and were carefully reamed in alignment with the bore of the flow pipe. They were connected to the manometer by lengths of flexible P.V.C. tubing of 0.118 in. (3.0 mm.) bore, incorporating screw clips which could be used to seal off the manometer if desired.

2.2.6 Mounting

The test section and calming length were rigidly mounted on a horizontal wooden board, 10 ft. (3.05 m.) long by 2 ft. (0.61 m.) wide, by means of formed wooden seats which held the flanges between the individual sections. The pipe was aligned with the electrodes rotated through about 120° clockwise from the vertical, so that any bubbles of gas collecting at the top of the bore (at low flow rates) would not interfere with the electrodes, and also to protect them from accidental damage. The configuration of the pipe was as shown in Figure 2.5.

The board was mounted on a "Handy Angle" frame, at a height of 3.33 ft. (1.02 m.) above the ground (for ease of operation). A vertical panel behind the test section was used as mounting for the manometer (eye-level) and the electronic instruments (described later - see section 2.5.2).
FIGURE 2.5 SCHEMATIC DIAGRAM OF FLOW PIPE 1" = 6"

inlet

---

reference electrode

test section

piezometer rings

insulating section

outlet

calming length

---

inlet
2.3 **Supply Tank**

2.3.1 **Tank Preparation**

As mentioned in section 2.1, a pressure vessel of 275 galls. (1250 l.) capacity was purchased. This allowed run durations in excess of 15 minutes, even at the maximum flow rate of 8000 lb./hr. (3640 kg./hr.), corresponding to a Reynolds Number of 45000.

The tank had to be chemically resistant to the caustic electrolyte solution, and had to withstand pressures of up to 50 lb./in² (350000 N./m²) above atmospheric. It was, therefore, shotblasted, and a coating of Solventless Epoxy Resin was applied to the internal surfaces to a thickness of approximately 0.007 in. (0.18 mm.). On delivery it was found that the shotblasting had made a small hole in one of the lower side-branches. This was plugged with a stainless-steel plug and rubber washer, and the tank was successfully pressure-tested to 100 lb./in² (700000 N./m²).

The general layout of the tank is shown in Figure 2.7, and the fittings attached to the various side-branches are described in section 2.3.2 below.

2.3.2 **Tank Fittings**

The number before each fitting refers to the number of the side-arm to which it is attached (see Figure 2.7).

1. A 1 in. (2.54 cm.) Saunders valve, type KB (straight through body, to minimize shear on the fluid), with cast iron body and general-purpose diaphragm, was bolted to this 9 in. (23 cm.) flange, and used to control the flow of solution down to the pressure vessel from the holding tank.
FIGURE 2.6  PRESSURE VESSEL  1in. = 2ft.
2. This 10 in. (25 cm.) flange was fitted with a Bailey Type 1640 angle pressure-relief valve rated at 41/70 lb./in² (280000/480000 N./m²), and with a 1/2 in. B.S. brass valve for release of gas to atmosphere. Both fittings were screwed into the flange.

3. Into this 8 in. (20 cm.) flange was screwed a 2 in. (5.1 cm.) diameter pressure gauge, of range 0-60 lb./in² (0-410000 N./m²).

4. This 6 in. (15 cm.) flange was fitted with a 3/16 in. B.S. brass valve, which was attached to the laboratory air supply.

5. This similar 6 in. (15 cm.) flange was also fitted with a 3/16 in. B.S. valve, connected via a 0.5 in. (1.27 cm.) flexible P.V.C. pipe to a cylinder of nitrogen gas. The cylinder itself was fitted with a 0-70 lb./in² (0-480000 N./m²) regulator.

6. Between these two 5 in. (13 cm.) flanges was fitted a 0.5 in. (1.27 cm.) sight-glass assembly, incorporating shut-off valves top and bottom and a blow-down valve. The length of the sight-glass was 28 in. (71 cm.), and a 70 cm. scale was built up behind the glass.

7. To this 11 in. (28 cm.) flange was bolted a 1 in. (2.54 cm.) glass-lined Saunders valve, leading to an elbow and screw-connector in 1.25 in. (3.2 cm.) "Polyorc" rigid P.V.C. tubing. A long length of 1.25 in. (3.2 cm.) flexible P.V.C. tubing could be attached to the screw-connector, for discharge of spent solution to the drain.
8. A 1 in. (2.54 cm.) type KB Saunders valve was bolted to this 7 in. (18 cm.) flange. The valve was connected, via a length of 1 in. (2.54 cm.) flexible P.V.C. tubing, to the upstream end of the calming length.

A schematic diagram of the tank fittings can be seen in Figure 2.1. The calibration of the tank will be described in section 2.6.

2.4 Miscellaneous Flow Equipment

2.4.1 Flow Loop

As mentioned above, the compressed gas in the pressure vessel forced the solution through the flow rig to the holding tank. The solution left the pressure vessel through the 1 in. (2.54 cm.) KB Saunders valve on the 7 in. (18 cm.) flange below the tank (fitting no. 8), and passed through flexible P.V.C. tubing to the calming length and test section. Immediately downstream of the test section was situated a flow control valve (see section 2.4.2), from which the solution flowed, through another length of 1 in. (2.54 cm.) flexible P.V.C. tubing, back along the length of the "Handy Angle" platform on which the test section was mounted, to a "Polyorc" rigid P.V.C. connector. This connector was bolted to the flange of a 1 in. (2.54 cm.) glass-lined Saunders valve, attached to the wall of the laboratory. "Polyorc" rigid P.V.C. tubing of 1 in. (2.54 cm.) bore led up from this valve through a tee-piece to the floor above, and a further 1 in. (2.54 cm.) Saunders valve on the side of the holding tank (see section 2.4.3). A plastic Saunders valve and screw-connector were attached to the other arm of the tee-piece, so that solution could be discharged directly from the holding tank.
From the holding tank solution could be returned to the pressure vessel through another 1 in. (2.54 cm.) glass-lined Saunders valve and a length of 1 in. (2.54 cm.) flexible P.V.C. tubing to the KB Saunders valve on the 9 in. (23 cm.) pressure vessel flange (fitting no. 1).

2.4.2 Control Valve

The requirement was for a control valve inert to the caustic electrolyte solution, which could be used to control with reasonable accuracy the amount of solution flowing through the loop, over a range from about 500 to 7000 lb./hr. (227 to 3180 kg./hr.). Preferably the valve should also compensate for any changes in upstream pressure, maintaining a constant flow rate under all conditions, and should cause a minimum amount of shear to the polymer molecules.

After extensive enquiries, it was found that a suitable control valve would be a 1½ in. (3.8 cm.) Type V "Flostat", manufactured by G.A. Platon Ltd. This instrument controls fluid flow rate at a selected value, despite changes in pressure, no outside power being needed as the control is derived from a small part of the pressure energy of the fluid. The pressure difference produced at an orifice incorporated in the valve body acts on a pressure-responsive element which positions the control valve. Thus, if the upstream pressure increases, the orifice differential increases, and moves the valve towards the closed position so that the original flow is restored.

One of these instruments, with a stainless-steel body and nitrile diaphragm,
nitrile diaphragm, was purchased and installed downstream of the test section (to minimise degradation effects prior to the test section). It was found to perform satisfactorily over the range 700 to 7500 lb./hr. (318 to 3410 kg./hr.), provided the upstream pressure was greater than about 30 lb./in$^2$ (210000 N./m$^2$). Any variations in flow rate would have been reflected in changes in the pressure-drop manometer reading.

2.4.3 Holding Tank

A holding tank of length 5 ft. (1.52 m.), width 3 ft. (0.91 m.) and height 4 ft. (1.22 m.) was constructed from $\frac{5}{8}$ in. (1.58 cm.) resin-bonded 3-ply. The edges were braced internally with $1\frac{1}{2}$ in. x $1\frac{1}{2}$ in. (3.8 cm. x 3.8 cm.) timber, to which the 3-ply was screwed and glued, and externally with 2 in. (5.1 cm.) angle-iron. The sides were diagonally braced externally with 2 in. x $1\frac{1}{2}$ in. (5.1 cm. x 3.8 cm.) timber. Its capacity was 290 galls. (1320 l.).

To the centre of one side, 4 in. (10.2 cm.) from the bottom and 9 in. (22.8 cm.) apart, were bolted two 1 in. (2.54 cm.) glass-lined Saunders valves for the inlet and outlet. The outlet incorporated a length of P.V.C. piping within the tank, bent and cut so that solution would be sucked through the outlet from the very base of the tank, which would thus be completely emptied. The tank was also fitted with a stainless-steel tap leading to a 0.236 in. (6.0 mm.) bore vertically-mounted glass tube, which acted as a level gauge.

The tank was coated internally with "Plascote 312", an epoxy-resin-based paint of considerable chemical resistance, the edges being/
edges being reinforced with glass-fibre matting (bonded with the paint). Finally, an angle-iron framework was erected to support a $\frac{1}{4}$ hp. (187 W.), 440 r.p.m. single-phase electric motor driving twin ¼ in. (10.2 cm.) diameter 3-blade stirrers within the tank.

2.5 Electrical Equipment

2.5.1 Electrode Circuit

The basic circuit required is shown in Figure 2.7. However, various factors dictated that the actual circuit used had to be considerably more complicated than this. Parallel circuits to the two cathodes, and a means of amplifying and recording the fluctuating component of each cathode current, were required. This necessitated the use of a constant bias signal, which, when fed with the cathode signal to a differential amplifier, gave a fluctuating output in the range 0 to -1 V. (for subsequent tape recording and computer analysis).

The final circuit, as shown in Figure 2.8, used an Ever-Ready 1.5 V. "Flag" battery (B) to power two "Helipot" 10-turn dial potentiometers (P1 and P2), one for the cathode supply and one for the bias to the amplifier. The cathode supply was split into two channels, one for each cathode (C1 and C2), and passed, through co-axial plug connectors, out of the main (screened) instrument cabinet. Each channel continued to its cathode (using low-loss co-axial cable) through a "Jay-Jay" 0 to 100000 Ohm variable resistance box (R1 and R2). The voltage drop across each resistance box (averaged using a digital voltmeter in position A1 or A2) gave the mean current flowing to each cathode. The voltage drop/
FIGURE 2.7  SIMPLE ELECTRODE CIRCUIT
FIGURE 2.8  CIRCUIT DIAGRAM
voltage drop across each electrolyte cell was measured, using the
digital voltmeter in position V1 or V2, between the cathode supply
and earth (as the anode was earthed in this system). This then
enabled the mean value of the resistance of each electrolyte cell
to be determined.

It was the fluctuating component of this second voltage, as
measured at V1 or V2, which had to be recorded. Accordingly, low-
loss cables were led from each cathode supply to the "+" input of
differential amplifiers X1 or X2. The bias supply from potenti-
meter P2 was split into two channels, each of which passed out of
the main cabinet (via co-axial connectors), and through low-loss
cable to the "-" inputs of the two amplifiers. Thus, by altering
the setting of potentiometer P2, the bias voltage could be adjusted
so that the output signal from each amplifier had a mean of roughly
-0.5 V. Any imbalance between the two channels (because of different
effective electrode areas) could be eradicated by adjusting either
resistance box (R1 or R2), and the amplitude of the output signals
could be brought within the range 0 to -1 V. by altering the
amplifier gains.

The outputs were passed to the input terminals of a twin-
channel A.M./F.M. tape-recorder (T), the output from which could
be used to drive a twin-channel cathode-ray oscilloscope (CRO),
a chart recorder (REC), or an analog-to-digital converter (A/D)
connected to a digital computer.

2.5.2 **Electronic Instruments**

1. **Amplifiers** (X1, X2)

   Rochar Electronique/
Roohar Electronique type A1338 differential amplifiers were used, mounted on the instrument panel above the test section. They had gain settings of 20, 50, 100, 200, 500 and 1000 (calibrated, with intermediate adjustment available), to give outputs in the range -10 V. to +10 V. The actual output was shown on a small voltmeter incorporated in the instrument. From D.C. to 25 kHz, there was excellent frequency response, but at higher frequencies there was considerable attenuation.

2. **Tape-Recorder (T)**

The tape-recorder used was an ElliottTandberg type 61/E2 twin-channel machine, which could be operated either directly or with Frequency Modulation. Three speeds were available: 7.5 in./sec. (19.05 cm./sec.), 3.75 in./sec. (9.53 cm./sec.) and 1.875 in./sec. (4.76 cm./sec.). To obtain frequency response below 40 Hz, it was necessary to use the Frequency Modulation system, which had upper frequency limits (to avoid attenuation) of 0.6 kHz (at 1.875 in./sec.), 1.2 kHz (at 3.75 in./sec.) or 2.4 kHz (at 7.5 in./sec.). It was thus necessary to achieve a compromise between slow tape speed (for records of longer duration on one reel of tape) and frequency response, and the speed usually used was 3.75 in./sec. (although some recordings were made at 7.5 in./sec.). Under these conditions the signal-to-noise ratio was 35 dB., and the amount of crosstalk (signal passed from one channel to another as noise) 15 dB.

Input signals must be in the range -1 V. to +1 V., and the overall gain of each channel (which could be adjusted) was around 2. The/
2. The output would thus be in the range -2V. to +2V., although in practice the signal was adjusted so that the output was within the range -2V. to 0V. (because this was then within the operating range of the analog-digital converter).

3. **Cathode-ray Oscilloscope** (CRO)

A Solartron CD1400 Oscilloscope system was used to monitor the output from the tape-recorder, being mounted, along with the tape-recorder, on a trolley adjacent to the test section. The instrument incorporated two type CX1441 wide-band Y-amplifiers, giving a twin-channel scan on a 1/2 in. (10.02 cm.) diameter screen. Frequency response was linear from D.C. to 15 MHz., and a wide range of gains and scan-speeds was available.

4. **Chart-recorder** (REC)

The chart-recorder used was a Servoscribe type RE511, with a range of chart speeds from 600 mm./min. to 30 mm./hr. (forwards or backwards). Full-scale deflections in the range from 2 mV. to 20 V. were available with coarse and fine zero-adjustment. Frequency response was poor, but some indication of general signal form could be obtained.

5. **Digital Voltmeter** (A1, A2, V1, V2)

A Solartron LM1420.2 digital voltmeter was used to measure the voltage drop across the resistances R1 and R2 (A1 and A2), and the applied voltage at each cathode (V1 and V2). The instrument had ranges from 20 mV. to 1000 V. (with automatic overload protection), and was equipped with "Hold" and "Sample" facilities - most useful when measuring the fluctuating voltages, as a series of samples can be averaged to obtain the mean.
2.6 Calibration

2.6.1 Pressure Vessel

The level scale on the pressure vessel was calibrated by running known volumes of water into the vessel from the holding-tank above. As the holding-tank was rectilinear, it was easy to relate depth of water to volume, and a large number of measurements of the relative depths in the two tanks could be taken with reasonable ease. Polynomials were fitted to the 95 data points obtained, and it was found that the best fit was given by a cubic curve, namely

\[ V = 84.01 + 11.67 x H + 0.2299 H^2 - 0.002092 H^3 \] (Equation 2.1)

where \( V \) = Volume of liquid in pressure vessel (litres)
and \( H \) = Height on scale of level gauge (cms.).

The agreement between polynomial and individual data points was excellent – hardly surprising, since the shape of the vessel (a cylinder with spherical ends) suggested that a cubic relationship could be exact.

The relationship between volume and height was not calculated empirically because it was difficult to determine the exact interior dimensions of the vessel and its numerous side connections.

2.6.2 Amplifiers

The amplifier for each channel was calibrated by applying a known input voltage to the electrode signal input terminal, and recording the output for various gains (x50, x100 and x 200). Care was taken to ensure that the bias input terminal was effectively earthed,
effectively earthed, and the procedure was repeated for further input voltages. Graphs of Input Voltage against Output Voltage were plotted (Figures 2.9 and 2.10), and it can be seen that in each case the actual gain was almost identical to the theoretical (set) gain.

2.6.3 Tape Recorder

Each channel of the tape-recorder was calibrated by applying known voltages to the input and recording the corresponding output voltages. Graphs plotted (Figure 2.11) give the gain for channel 1 ('upper') as 1.90, and for channel 2 as 1.74. Gain was much reduced if inputs exceeded ± 1 V., so great care had to be taken to keep inputs within this range.

Throughout the work EMI Professional Recording Tape was used, as this was recommended as being the best readily available tape at the present time.

2.7 Ideal Flow Rig

2.7.1 Introduction

Preliminary experiments with the continuously recirculating flow loop (using a centrifugal pump) indicated that if effective drag-reduction were to be obtained great care would have to be taken to eliminate degradation of the polymer molecules. In addition, the method by which the polymer was introduced into solution would have to be rigorously controlled. Rather than rely entirely on published data on drag-reduction, it was thought desirable to construct an 'ideal' flow rig, on which some measure of the drag reduction caused by a given amount of polymer could be obtained under/
FIGURE 2.9  AMPLIFIER CALIBRATION - CHANNEL 1
FIGURE 2.10  AMPLIFIER CALIBRATION - CHANNEL 2
FIGURE 2.11 CALIBRATION OF TAPE RECORDER AMPLIFIERS
obtained under conditions of minimal degradation, using either water or electrolyte solution.

2.7.2 Construction and Operation

The 'ideal' rig which was constructed is shown in Figure 2.12. A 1 in. (2.54 cm.) perspex tube, mounted vertically, acted as a reservoir for a horizontal 0.16 in. (4 mm.) bore capillary glass tube, of length about 5 ft. (1.52 m.) - various tubes were used, and their lengths differed slightly. Both tubes were held in place by metal spring clips screwed to 3-ply panelling mounted on a rigid "Handy Angle" framework. A removable stopper was available for the end of the glass tube, and the reservoir was fitted with a scale.

With the stopper in place, the reservoir was filled with polymer solution. The stopper was then removed, and the time taken for the reservoir level to fall between two given points on the scale was recorded using a stopwatch. The solution flowing from the open end of the glass tubing could either be discharged to waste or collected and returned to the reservoir for a further experiment. If water or electrolyte free of the polymer were used, the results could be compared with the theoretical time of fall, obtained by calculating the log-mean Reynolds number using Bernoulli's equation. The reduction in time of fall obtained by adding polymer could be used as a measure of the drag-reduction. Although this was only a mean value over the range of flow rates produced by the falling level in the reservoir, it could be related to the mean Reynolds Number and much useful/
FIGURE 2.12  IDEAL FLOW APPARATUS  1" ≈ 10"
and much useful information obtained. By repeatedly testing the same polymer solution, the effects of chemical (rather than mechanical) degradation could be determined, and the most effective time to leave a newly-prepared solution prior to carrying out an experiment could be estimated. Levels of drag-reduction obtained provided figures to aim for in the main flow rig.

2.8 Electrolyte Solution

2.8.1 Solution Make-up

The essential reaction at the cathode was

\[ \text{Fe(CN)}_6^{3-} + e^- \rightarrow \text{Fe(CN)}_6^{4-} \]  

(Ferricyanide \hspace{1cm} Ferrocyanide)

It was this reaction which took place so fast that its rate was determined simply by the rate of transfer of the ferricyanide ions to the cathode, and hence reflected the behaviour of the boundary layer. There was an equivalent reverse reaction at the downstream anode, but as the anode was relatively large this produced negligible transfer resistance. The electrolyte solution should therefore contain ferricyanide and ferrocyanide in roughly equimolar quantities, and must be polarised to prevent the migration of these ions under the influence of the electric field between the electrodes. This polarisation was achieved by adding a large excess of a further electrolyte - usually sodium hydroxide - to the solution.

Since the overall volume of solution required was very large (275 galls., 1250 l.), the concentration of the electrolytes had to be kept as low as possible to reduce the actual weight of each component needed,
component needed, and thus reduce the cost. Most other workers using this electrochemical method \(38,39,40,54,55\) have used ferricyanide and ferrocyanide concentrations in excess of 0.01 molar. However, it was found that this figure could be halved without significantly affecting the signal. The sodium hydroxide concentration was 0.5 molar; 100 times the ferricyanide concentration has been found to be a sufficient excess. Because of the large volume required it was impractical to use distilled water, and hence there was no real need to use particularly pure chemicals. "Technical" grade potassium ferricyanide and potassium ferrocyanide were used, with "I.C.I. Flake" sodium hydroxide as the bulk electrolyte. The actual amounts required for a typical solution make-up were as follows

\[
\begin{align*}
\text{NaOH} & \quad \text{Sodium hydroxide (0.5 M.)} \quad 25.1 \text{ kg.} \\
K_3\text{Fe(CN)}_6 & \quad \text{Potassium ferricyanide (0.005 M.)} \quad 2.06 \text{ kg.} \\
K_4\text{Fe(CN)}_6\cdot3\text{H}_2\text{O} & \quad \text{Potassium ferrocyanide (0.005 M.)} \quad 2.65 \text{ kg.}
\end{align*}
\]

The ferricyanide is quite readily oxidised by any dissolved air in the water, with the formation of ferric oxide gels in the flow rig. Nitrogen, rather than compressed air, is therefore used as the propellant gas, and care must be taken to saturate the solution as thoroughly as possible with nitrogen. To this end a perforated flexible pipe was attached to the nitrogen supply flange (within the pressure vessel), so that the gas would be forced to bubble through the solution. Even using nitrogen, the electrolyte began to oxidise significantly after three or four days, and had to be discharged.

2.8.2/
2.8.2 Properties

The density and viscosity of the electrolyte solution were measured and found, as expected, to be no different to those tabulated for aqueous sodium hydroxide solution. Density was thus assumed constant at 1.021 gm./cm$^3$ \( (56) \), and viscosity was assumed to be 1.109 times the viscosity of water at any given temperature \( (57) \). The viscosity of water was determined by linear interpolation on data from Perry \( (58) \).

The diffusivities of ferricyanide and ferrocyanide ions (for calculation of theoretical mean mass-transfer coefficient and Schmidt number) have been shown \( (59) \) to be well predicted from conductivity data when in aqueous solution. Actual values obtained \( (D_0) \) must be corrected for the presence of the large excess of sodium hydroxide by applying the Stokes-Einstein equation

\[
D = D_0 \left( \frac{\mu}{\mu_0} \right) \left( \frac{T}{T_0} \right),
\]

where \( \mu \) is the viscosity of water (1.00 cp.) at temperature \( T_0 = 293.15\,\text{K} \), and \( \mu_0 \) and \( T_0 \) are the viscosity and temperature of the electrolyte solution \( (60) \).

\[
D_0\text{ (ferricyanide)} = 0.89 \times 10^{-9} \,\text{m}^2/\text{sec.} \quad (59)
\]

\[
D_0\text{ (ferrocyanide)} = 0.74 \times 10^{-9} \,\text{m}^2/\text{sec.}
\]

Thus for a typical electrolyte solution \( \mu = 1.11, T = 20^\circ\text{C} \) the diffusivity of the ferricyanide ion is \( 0.801 \times 10^{-9} \,\text{m}^2/\text{sec.} \) and the Schmidt Number \( (Sc) \) is 1357.

2.8.3 Hazards

Although ferricyanides and ferrocyanides are not totally stable, they/
stable, they do not decompose to yield poisonous cyanides except under the most extreme conditions (boiling with dilute sulphuric acid). They are therefore quite safe to use freely (particularly in alkaline solution), but some care must be taken to prevent the inhalation of dust whilst a solution is being prepared, and a simple face mask was always worn at these times.

The main hazard lay in the caustic nature of the electrolyte solution, and in the difficulty experienced in dissolving some 25 kg. of sodium hydroxide in water. The heat of solution evolved was considerable, and the alkali could not just be added to water in the holding tank as it would cake in lumps and form local hot spots as it dissolved. Concentrated solutions were therefore prepared in plastic bins and later added to the water in the tank. The handling of these hot, concentrated caustic solutions required considerable care, and a face shield was worn as a protection against splashes.

The much more dilute prepared electrolyte was far less hazardous. On the completion of an experiment the solution was further diluted by adding a similar volume of water, and was discharged to the main drain outside the laboratory (because the internal drainage system led to a sump within the building).

2.8.3 Analysis

The exact concentration of each component of the electrolyte solution had to be determined, and a check established to ensure that the ferricyanide had not been significantly oxidised.

**Sodium hydroxide**

10 cm$^3$ samples/
10 cm$^3$. samples of the electrolyte solution were titrated against 0.1 M. hydrochloric acid solution (in a 100 cm$^2$. burette), using phenolphthalein indicator. The distinct colour change from pink to colourless marked the end-point, and the approximate titre was 50 cm$^3$. (for a 0.5 M. NaOH solution).

Potassium ferricyanide (51, 61, 62)

50 cm$^3$. samples of the electrolyte solution were acidified by the addition of 15 cm$^3$. of 2 N. sulphuric acid. 20 cm$^3$. of 10% potassium iodide and 15 cm$^3$. of $13\frac{1}{3}$% zinc sulphate solutions were then added, and the liberated iodine titrated against 0.01 N. sodium thiosulphate solution. Once the brown precipitate of potassium zinc ferrocyanide (formed on the addition of the zinc sulphate) had faded to a pale yellow, the end-point could be detected more readily by the addition of a few drops of starch, and observing the disappearance of the deep blue colour liberated. The approximate titre was 25 cm$^3$. (for 0.005 M. ferricyanide).

$$2K_3Fe(CN)_6 + 2KI \rightarrow 2K_4Fe(CN)_6 + I_2$$

Potassium ferrocyanide (51, 61)

A 50 cm$^3$. sample of the electrolyte solution was acidified by the addition of 50 cm$^3$. of 4N. sulphuric acid. 0.5 cm$^3$. of N-phenylanthranilic acid (solution in ethanol) was added as a redox indicator, with the formation of a white precipitate. This was titrated against 0.01 N. ceric sulphate (in a 50 cm$^3$. burette) to a sharp colour change from dark green to brown, the titre being around 25 cm$^3$. (for 0.005 M.).

All titrations were repeated to ensure consistent results and the methods/
and the methods were found to give reasonably correct concentrations when tested with a prepared standard electrolyte solution.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (Molarity)</th>
<th>Theoretical Titre</th>
<th>Actual Titre</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Hydroxide</td>
<td>0.50</td>
<td>50.0</td>
<td>48.62</td>
<td>3%</td>
</tr>
<tr>
<td>Potassium Ferricyanide</td>
<td>0.005</td>
<td>25.0</td>
<td>24.5</td>
<td>2%</td>
</tr>
<tr>
<td>Potassium Ferrocyanide</td>
<td>0.005</td>
<td>25.0</td>
<td>27.3</td>
<td>8%</td>
</tr>
<tr>
<td>Potassium Ferricyanide</td>
<td>0.0025</td>
<td>12.5</td>
<td>12.63</td>
<td>1%</td>
</tr>
<tr>
<td>Potassium Ferrocyanide</td>
<td>0.0025</td>
<td>12.5</td>
<td>13.13</td>
<td>5%</td>
</tr>
</tbody>
</table>

Errors in the potassium ferrocyanide titration were due to decay of the ceric sulphate solution, which is hard to keep for any length of time. This titration was of less importance than the other two.

2.9 Polymer

Numerous naturally-occurring and synthetic polymers have been found to cause drag reduction. A high molecular weight (at least 100000) and a high degree of linearity and flexibility are desirable ($\mu$). Synthetic materials are generally better than naturally-occurring ones, since they enable more control to be exercised over the molecular-weight distribution, which will generally be narrow for the synthetic polymers. Many polymers are subject to chemical or biological attack, and are readily degraded by mechanical shear. The result of either of these effects is a steady decrease in the drag-reducing effectiveness of the polymer as it ages.

It was/
It was felt that the most suitable water-soluble synthetic polymer was "Polyox" WSR-301, a polyethylene oxide with a mean molecular weight of around 8000000, manufactured by Union Carbide Corporation. Because of its high molecular weight, this polymer was a very effective drag-reducing agent, and has been used by many workers in this field. There is thus much data available on the drag-reducing effectiveness of solutions of different concentrations, and on the effects of degradation on the polymer.

The actual amount of drag-reduction obtained in a given situation is closely dependent on the method used to prepare the polymer solution, and on the chemical composition of the solution (as this will effect the rate of degradation). The means of dissolution of the polymer in the electrolyte solution was thus of great importance, and had to be carefully controlled.

Polyox is a white, powdery solid and, if added directly to water, forms agglomerates, which soon become encapsulated in a gel. This effectively seals the agglomerate from the water, drastically slowing the dissolution process. The best way to obtain a dispersion of (as far as possible) individual particles in water was to prepare a concentrated suspension of the polymer in alcohol (in which it is insoluble). This suspension could be rigorously agitated and slowly added to the stirred electrolyte solution to obtain a suitable dispersion. The amount of alcohol used was insignificant compared to the volume of the solution: indeed, it has been shown (63) that if a tertiary alcohol, such as iso-propanol, is used, the polymer will be partially stabilised against chemical degradation.
Since little was known of the effect of the electrolytes present in the flow solution on the rate of degradation of the polymer, experiments on the "ideal" flow rig were necessary to establish a suitable procedure for minimising the amount of degradation - these will be discussed later. It was, however, known that polyethylene oxide degradation is speeded by the presence of oxygen (40, 63) providing a further reason for the use of nitrogen as the propellant gas.

2.10 Experimental Procedure

The electrolyte solution was prepared in the holding tank by the addition of concentrated sodium hydroxide solution to about 150 galls. (650 l.) of water, with the stirrer continuously in operation. Concentrated potassium ferri- and ferro- cyanide solution was prepared by the addition of hot water to a mixture of the dry solids, and this was poured into the sodium hydroxide solution. Water was added (with further stirring) to bring the volume to 275 galls. (1250 l.), and the solution was run down to the pressure vessel, where a continuous bleed of nitrogen was passed through it to expel oxygen and assist mixing. When all the solution had descended, the inlet and air release valves were closed, and the tank was pressurised to 32 lb./in.\(^2\). (220000 N./m.\(^2\).) with nitrogen. A sample of solution for immediate test on the "ideal" flow rig, and for later chemical analysis, was taken from the level-gauge blow-down valve.

The electrode leads were connected to the two required cathodes, and the flow-control valve was set to the initial flow rate.
With all the valves in the main flow loop opened, the reading of the pressure vessel level-gauge was noted, and a stop-clock started. Variable resistance R1 was set to 10000 ohms., and potentiometer P1 adjusted to give a suitable applied voltage (around 0.3 V.). The bias potentiometer P2 and the gain of amplifier X1 were adjusted to bring the amplifier output signal into the range 0 to -1 V. Amplifier X2 gain was set to the same as that of amplifier X1, and resistance R2 was adjusted to bring the amplifier (X2) output into the same range (R2 may well be different from R1, to compensate for different effective electrode areas). With the tape-recorder recording, the output of each channel was monitored on the oscilloscope, and final adjustments to bias potentiometer P2 and resistance R2 were made to bring each output signal safely within acceptable limits (0 to -2V.).

Now that the signal level had been set up, the actual signal recording could be made, over a duration of at least 1½ minutes. While recording was in progress, the reading of the pressure-drop manometer was noted, and, on completion, the digital voltmeter was used to measure the applied voltage at each electrode (V1, V2), and the voltage drop across each resistance (A1, A2).

The final reading of the level-gauge and the elapsed time were noted (to calculate the exact flow rate), and the procedure was repeated at a further flow rate. With considerable practice, it proved possible to complete the above procedure (for one flow-rate) in three minutes, so that recordings could be obtained at eight different flow-rates/
eight different flow-rates (maximum, 7000, 6000, 5000, 4000, 2000, 1000 and 400 lb./hr.), even though at lower flow-rates longer durations had to be used to obtain a reasonable fall in level.

When the pressure vessel was nearly empty, the flow loop valves were shut, and the compressed nitrogen (about 2/3 of the contents of one cylinder) was released to atmosphere. A weighed amount of Polyox (in alcohol) was added to the electrolyte in the holding tank (with the stirrer in operation), and the solution was returned to the pressure vessel.

The solution from the previous run was analysed in this interval. When dissolution of the Polyox was complete, the entire experiment was repeated with the drag-reducing solution. The solution was then either discharged, or left to age until the Polyox had degraded completely away and a further experiment at a different concentration could be carried out.
3. ANALYSIS OF RESULTS

3.1 Introduction

The experiments described in the previous section produced data from two distinct sources: flow data from pressure-drop manometer and level gauge readings, and recorded data corresponding to the fluctuating mass-transfer coefficients at the electrodes. Flow data was to be processed to give information on the Reynolds Number and Friction Factor of the flowing solution. In addition, when solutions containing Polyox were used, the theoretical Friction Factor was to be estimated, so that the amount of Drag Reduction could be determined. The signal from the tape recorder was to be sampled at suitable intervals to give numerical data, which could be analysed to give simple statistical parameters for the signal (standard deviation, skewness, kurtosis, intensity). These could simply be related to the equivalent parameters for the actual fluctuations in mass-transfer coefficient. In addition, the autocorrelation function for the signal was to be determined, both because it yielded useful information on its own account and because it could be used to determine the frequency spectrum of the signal fluctuations.

It can readily be seen that this analysis could not be carried out without the use of computers. These enabled the recorded signal to be sampled at the high frequencies required, and could process the large amount of data so obtained (the calculation of one autocorrelation coefficient requires between $10^5$ and $10^6$ multiplications).
They could also be used to carry out more simple repeated calculations, such as those to determine the flow parameters of the solution.

3.2 Computers

3.2.1 I.B.M. 360/50

Most of the data processing was carried out on an I.B.M. 360/50 run by the Edinburgh Regional Computing Centre. This machine had a central processing unit with 512 k bytes of main storage coupled (through a common control unit) to line printer, card reader and card punch. Three 9-track magnetic tape units and three I.B.M. 2311 replaceable disk units were available, together with an I.B.M. 2314 multiple-spindle disk unit (with 7 drives) (64).

Although Fortran was available, the preferred language was Edinburgh IMP (65, 66) an automatic programming language of Algol type, developed from Atlas Autocode (67).

3.2.2 Digital PDP-8

A Digital PDP-8 computer was used, in conjunction with an Analog-to-digital Converter, to obtain a paper tape of binary digits sampled from the recorded signal. High-speed paper-tape reading and punching facilities were available. The limited capacity of the machine (4096 locations to take both program code and data) prevented its use for any serious statistical analysis of the data, but towards the end of the project (July 1971), a PDP-8/E computer became available. The increased capacity obtained using this machine (8192 locations) enabled fairly sophisticated data processing programs to be accommodated along with large blocks of/
blocks of data, and several of the statistical programs from the 360/50 were translated for use on the PDP-8/E.

The language used on both the PDP-8 and the PDP-8/E was PAL III (Progam Assembly Language, version 3). This is a two-pass assembler which defines user symbols on the first pass, and on the second pass produces a binary program tape which can be fed to the computer for execution (68,69). While very much more difficult than the 360/50 to program, the PDP-8 computers had the advantage that they could be used conversationally (the user could change parameters at will during the execution of programs), and they could be linked to the tape recorder through the Analog-to-digital converter.

In descriptions of PAL III programs, use is made of octal representation of numbers. Octal digits (corresponding to multiples of powers of 8) are formed by groups of three binary digits (bits), so that octal notation may be used as a convenient shorthand for binary notation. An octal number is thus formed by dividing a binary number into groups of three bits (from the right), and converting each group to its octal equivalent. Thus 101₂ becomes 5₈ and 1100101₀₂ becomes 31₂₈, binary numbers being indicated by the subscript₂ and octal numbers by the subscript₈.

3.3 Analysis of Flow Data
3.3.1 Flow Theory

For a given flow situation the Reynolds Number, the Friction Factor and, if polymer is present, the amount of Drag Reduction must be calculated.

Reynolds Number (Re) is given by
Re = \frac{\rho \bar{u} d}{\mu} \quad ............\text{Equation 3.1}

where

\rho = \text{fluid density (kg./m}^3)\\
\bar{u} = \text{mean fluid velocity (m./sec.)}\\
d = \text{pipe internal diameter (m.)}\\
\mu = \text{fluid viscosity (kg./m.sec.)}

The density (assumed constant since it varies by less than 0.5% over the temperature range 0-25\degree C) was taken as 1000 kg./m$^3$ for water and 1021 kg./m$^3$ for the electrolyte solution (see section 2.8.2). The volumetric flow rate of the solution, and hence the mean fluid velocity, were calculated, using Equation 2.1, from the fall of level in the pressure vessel. The pipe internal diameter was 0.02908 m., and the viscosity of the solution was calculated by using data from Perry (70) to obtain the viscosity of water at the solution temperature and multiplying that value by 1.109 (see section 2.8.2)

Friction Factor ($f$) is given by

\[ f = \frac{d}{2 \rho \bar{u}^2} \frac{dP}{dx} \quad ............\text{Equation 3.2} \]

where

\[ \frac{dP}{dx} = \text{pressure gradient along pipe (N/m}^2\text{m.}). \]

\[ \frac{dP}{dx} \] was measured by the pressure drop $\Delta P$ (N/m$^2$.) along the length $\Delta x$ (0.736 m.) between the manometer pressure taps.

The specific gravity of the paraffin used in the manometer was 0.773, and the pressure drop $\Delta P$ was obtained from P&G, the pressure manometer reading (cm.).

The amount/
The amount of Drag Reduction (DR) was expressed as the percentage reduction in friction factor \( f \) at a constant Reynolds number.

\[
DR = \frac{f_t - f}{f_t} \times 100 \quad \% \quad \text{Equation 3.3}
\]

where

\( f = \) friction factor (experimentally determined using Equation 3.2)

\( f_t = \) theoretical friction factor

The theoretical friction factor, \( f_t \), was determined at the Reynolds number of the flow in the pipe (Equation 3.1) by the Blasius equation for turbulent flow in a smooth pipe (valid since drag reduction took place only in turbulent flow, and the inside surface of the pipe was smooth):

\[
f_t = 0.079 \ Re^{-0.25} \quad \text{Equation 3.4}
\]

3.3.2 Errors

Since drag reduction occurred (in the present investigation) at Reynolds numbers in excess of 20000, it was not necessary to determine the flow parameters with great accuracy at lower flow rates than this. Thus, although experiments were carried out at Reynolds numbers as low as 3000, error bounds are only presented for Reynolds numbers of 40000 and 20000. At the lowest flow rates, errors were considerably larger than those indicated below, mainly on account of the much greater relative errors in level gauge and pressure-drop manometer readings.

Reynolds number:
Reynolds number:

Error in level measurement: \( \pm 0.1 \) cm. each reading, \( \pm 0.2 \) cm. overall.

Error in flow velocity (\( u \)): \( Re = 40000 \) \( \pm 2\% \)
\( Re = 20000 \) \( \pm 3\% \)

Error in temperature measurement: \( \pm 1^\circ C \)

Error in viscosity (\( \mu \)): \( Re = 40000 \) or \( 20000 \) \( \pm 2\% \)

Error in density (\( \rho \)): \( Re = 40000 \) or \( 20000 \) \( \pm 0.5\% \)

Overall error in Reynolds number: \( Re = 40000 \pm 1800 \) (\( \pm 4\% \))
\( Re = 20000 \pm 1000 \) (\( \pm 5\% \))

Friction Factor:

Error in flow velocity (\( u \)): \( Re = 40000 \) \( \pm 2\% \)
\( Re = 20000 \) \( \pm 3\% \)

Error in density (\( \rho \)): \( Re = 40000 \) or \( 20000 \) \( \pm 0.5\% \)

Error in pressure-drop manometer reading: \( \pm 0.2 \) cm.

Error in pressure drop (\( \Delta P \)): \( Re = 40000 \) \( \pm 1\% \)
\( Re = 20000 \) \( \pm 3\% \)

Overall error in friction factor: \( Re = 40000 \)
\( Re = 40000 \) \( f = 0.0056 \pm 0.0003 \) (\( \pm 5\% \))
\( Re = 20000 \) \( f = 0.0068 \pm 0.0006 \) (\( \pm 9\% \))

Drag Reduction:

Error in theoretical friction factor (\( f_r \)):

\( Re = 40000 \) \( \pm 1\% \)
\( Re = 20000 \) \( \pm 2\% \)
Error in actual friction factor (f): 
\[ \text{Re} = 40000 \pm 5\% \]
\[ \text{Re} = 20000 \pm 9\% \]

Overall error in percentage drag reduction:
\[ \text{Re} = 40000 \pm 6\% \]
\[ \text{Re} = 20000 \pm 11\% \]

3.3.3 **Flow Analysis Program**

An IMP program for the 360/50 was written to perform the calculations described in sections 3.3.1 above. A block diagram is shown in Figure 3.1, and a listing is given in Appendix A.1.

3.4 **Analysis of Recorded Signal**

3.4.1 **Origin of Signal**

In general, for mass transfer occurring at a solid surface

\[ N_a = KA (C_b - C_s) \]  
Equation 3.5

where

\[ N_a = \text{No. of kg. equiv of reacting species transferred per unit time (kg.equiv/sec.)} \]
\[ K = \text{Instantaneous mass transfer coefficient (m/sec.)} \]
\[ A = \text{Area of transfer (m^2.)} \]
\[ C_b = \text{Concentration of reacting species in bulk fluid (kg.equiv/m^3.)} \]
\[ C_s = \text{Concentration of reacting species at the solid surface (kg.equiv/m^3.)} \]

In the technique used, the reacting species was the ferricyanide ion, and the reaction involved was that given in Equation 2.2. The reaction was carried out in such a manner that concentration polarisation existed at the cathode. Thus the actual mean (limiting) current/
FIGURE 3.1 BLOCK DIAGRAM OF FLOW ANALYSIS PROGRAM
(limiting) current flowing to the cathode was (over a fairly wide range of applied voltages) constant, irrespective of the actual voltage applied. Under these conditions there were fluctuations in the cathode current which reflected similar fluctuations in mass-transfer coefficient at the cathode surface, since

\[ I = F N_a \]  

Equation 3.6

where

- \( I \) = current flowing (A.)
- \( F \) = Faraday constant, 96500000 coulombs/kg. equivalent.

The reaction takes place so fast that its overall rate is controlled by the rate of transfer of the ferricyanide ion to the cathode. The fluctuations in mass transfer coefficient must thus reflect physical flow fluctuations in the body of fluid between the bulk fluid (in which the ferricyanide ion concentration is constant) and the wall, i.e. in the boundary layer. In addition, the speed of the reaction is so fast compared with the rate of transfer of the ferricyanide to the electrode that the concentration at the solid surface (\( C_s \)) is effectively zero.

Equations 3.5 and 3.6 may therefore be combined:

\[ I = F K A C_b \]  

Equation 3.7

Now

\[ I = \bar{I} + i \]  

Equation 3.8

and

\[ K = \bar{K} + k \]  

Equation 3.9

where

- \( \bar{I} \) = mean current flowing (limiting current) (A.)
- \( i \) = instantaneous deviation from mean current (A.)
- \( \bar{K} \) = mean (time averaged) mass transfer coefficient (m./sec.)
- \( k \) = instantaneous deviation from mean mass transfer coefficient (m./sec.)
Thus \( \bar{I} = F \bar{K} A C_b \) ............ Equation 3.10

and measurements of the limiting current flowing to a polarised cathode \( (\bar{I}) \) enabled the mean mass transfer coefficient \( (\bar{K}) \) to be determined. There were two reasons why the experimentally determined values of \( \bar{K} \) should not agree exactly with values obtained using techniques designed specifically to evaluate the mean mass transfer coefficient.

i) There was always difficulty in determining the actual ('active') area of the electrode, since this could be greater (because of surface roughnesses) or less (because of oxidised inactive areas) than the calculated area.

ii) In the case of the unsurrounded electrode, the concentration boundary layer was developing over the electrode surface, and hence the mass transfer coefficient varied over that surface: the limiting current indicated its mean value.

Mean mass transfer coefficient \( (\bar{K}) \) was one of the parameters which might be affected by the addition of polymer to the electrolyte solution. To obtain a more detailed knowledge of the effects of the polymer, it was necessary to analyse the fluctuating component of the mass transfer coefficient:

\[ i = F k A C_b \]  ............ Equation 3.11

It was the fluctuating current \( (i) \), or rather the fluctuating voltage drop \( (v) \) across a resistance \( (R) \), which was recorded on the tape-recorder (with an arbitrary bias introduced for convenience).

3.4.2 Simple Parameters of Fluctuating Signal \((54, 71, 72)\)

The simple parameters/
The simple parameters of the signal which yield information about the turbulent structure of the boundary layer include the various moments (mean, standard deviation, skewness and kurtosis), the intensity, and the autocorrelation function. A more complex parameter, considered in section 3.4.3, is the power spectral density (spectrum) of the signal.

Since analysis equipment required to derive these signal parameters electronically was not available, the signal had to be sampled and digitised using the PDP-8 computer and analog-to-digital converter. The sample interval (Δ) and number of samples (N) required were dependent on the range of spectrum required; this will be discussed in the next section. Sample intervals varied from 0.03333 sec. to 0.0001 sec., and the number of samples was usually 1024 (2^10) or 3072 (3 x 2^10). Frequently used values, which gave good statistical results (close agreement between different samples of the same signal), were 0.003333 sec. and 1024 samples.

The various parameters obtained from this sampled signal were

1) Mean

Because of the arbitrary bias, introduced to bring the fluctuating voltage into the best range for recording, the actual mean value of the recorded signal was not relevant to a description of the boundary layer flow. However, it had to be determined, so that the sampled signal could be normalised by subtracting the mean.

\[
\overline{x} = \frac{1}{N} \sum_{i=1}^{N} x_i
\]

\[\text{Equation 3.12}\]
where
\[ x_i = \text{the } i\text{th. of } N \text{ signal values} \]
\[ \bar{x} = \text{the signal mean.} \]

ii) **Standard Deviation**

The standard deviation of the sampled signal \((\sigma_x)\) is defined by
\[ \sigma_x = \frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N} \]

\[ \cdots \cdots \text{Equation 3.13} \]

It is an indication of the degree of spread of the sampled signal about its mean.

Because the standard deviation, as defined above, is dependent on the units in which \(x\) is measured (i.e. it is not dimensionless), it had to be converted to a standard deviation of the fluctuations in mass transfer coefficient \((\sigma_k)\). This was achieved by the following procedure:

1) Divide \(\sigma_x\) by A- to -D conversion constant (see section 3.4.4) to obtain \(\sigma_v\) (based on recorder output voltage fluctuations).

2) Divide by combined amplification factor of amplifier and tape recorder.

3) Divide by resistance of electrolyte cell \((R_c)\) to obtain \(\sigma_i\) (based on cell current fluctuations).

4) Convert to \(\sigma_k\), using Equation 3.11 to obtain
\[ \sigma_k = \frac{\sigma_i}{FA C_b} \]

\[ \cdots \cdots \text{Equation 3.14} \]

iii) **Skewness**

The skewness of the sampled signal \((S_x)\) is the dimensionless form
less form of the third central moment, and is defined by:

$$S_x = \frac{\sum_{i=1}^{N} (x_i - \bar{x})^3}{N \sigma_x^3}$$  \hspace{1cm} \text{Equation 3.15}

It is the first measure of asymmetry of the signal, and indicates the relative sizes of the positive and negative 'tails' of the probability distribution. As skewness is dimensionless, no scaling was necessary as $S_x$ (based on the fluctuations in mass transfer coefficient) equals $S_x$. Brangwin (54) has shown that values of skewness less than ±0.25 are probably not significant of a departure from an even (Gaussian) distribution, while values in excess of ±0.50 indicate a significant amount of skewness.

iv) Kurtosis

The kurtosis of the sampled signal ($K_x$) is the non-dimensional form of the fourth central moment, and is defined by:

$$K_x = \frac{\sum_{i=1}^{N} (x_i - \bar{x})^4}{N \sigma_x^4}$$  \hspace{1cm} \text{Equation 3.16}

Kurtosis, or flatness factor, is the second measure of asymmetry, and will be larger for broader (flatter) 'tails'. Again no scaling was necessary as $K_x$ equaled $K_x$. A kurtosis of around 3.00 is to be expected for a Gaussian distribution, with values in excess of 4 or less than 2 being highly significant of a departure from Gaussian distribution (54).

v) Intensity

The intensity of the fluctuations in mass transfer coefficient ($I_k$) is $\alpha$. 
is a measure of the spread of the individual results about the mean. It was obtained by dividing the standard deviation of the mass transfer coefficient fluctuations \( \sigma_k \), by the mean value of the coefficient \( \mu_k \) and is really a dimensionless form of the standard deviation.

\[
I_k = \frac{\sigma_k}{\mu_k}
\]

\[ \text{Equation 3.16} \]

vi) **Autocorrelation Function**

The autocorrelation function is formed by a series of autocorrelation coefficients \( R(j) \) \((j = 0, 1, M)\), each of which represents the degree of correlation between the signal \( x_r \) (starting at time \( T \)) and the same signal delayed by a time \( t \), namely \( x_{r+t} \). The time delay \( t \) (secs.) is expressed as a number of lags, \( j \), each of duration \( \Delta \) (the sample interval), up to a maximum of \( M \) lags (\( M \) is usually about \( 1/10 \) of the number of samples, \( N \)). Dividing by the variance \( \sigma_x^2 \) renders the autocorrelation coefficients dimensionless, so that the autocorrelation function is applicable to both recorded signal and mass transfer coefficient fluctuations.

\[
R(j) = \frac{\sum_{i=1}^{N-j} (x_i - \overline{x})(x_{i+j} - \overline{x})}{\sigma_x^2 / (N-j)} ; j = 0, 1, M
\]

\[ \text{Equation 3.18} \]

Clearly, when \( j = 0 \), \( R(j) = 1 \), and in general \( R(j) \) always lies within the range +1 to -1, +1 indicating perfect correlation (identical signals) and -1 indicating perfect negative correlation (e.g. identical size waves out of phase by \( 180^\circ \)).

For a typical/
For a typical random signal, the autocorrelation coefficient will decrease from unity with increasing lag, and will eventually become negative. The delay \( t_0 \) (secs.) needed for the correlation coefficient to fall to zero may be used to characterise the signal, and Brangwin has shown (by dimensional analysis) that

\[
\frac{t_0 u}{d} = f(Re)(So)
\]

\[\text{......... Equation 3.19}\]

where

\[\begin{align*}
u &= \text{mean flow velocity (m/sec.)} \\
d &= \text{pipe diameter (m.)} \\
Re &= \text{Reynolds number (} \rho ud/\mu) \\
So &= \text{Schmidt number (} \rho/\mu D)\end{align*}\]

Since the Schmidt number is effectively constant, the dimensionless group \( \frac{t_0 u}{d} \) may be plotted simply as a function of Reynolds number.

Other quantities, such as the microscale of the turbulence \( (\bar{M}_t, \text{the smallest time over which fluctuations take place}) \) and the macroscale of the turbulence \( (\bar{M}_t, \text{the largest time over which the flow pattern at a point in a fluid is autocorrelated}) \), may be calculated from the autocorrelation function, but it is doubtful whether any real significance can be attached to these:

\[
\bar{M}_i = \sqrt{\frac{2}{\int \frac{R(t)}{dt^2} \bigg|_{t=0}^t}}
\]

\[\text{......... Equation 3.20}\]

\[
\bar{M}_a = \int_0^\infty R(t)dt
\]

\[\text{......... Equation 3.21}\]

However, the most important use of the autocorrelation function is as/
function is as a step in the calculation of the spectral density function of the signal. This will be discussed in detail in section 3.4.3.

vii) Crosscorrelation Function

The crosscorrelation function \( R(j) \) is analogous to the autocorrelation function, but differs in that it is two different signals, \( x \) and \( y \), which are correlated. Thus

\[
R(j) = \frac{\sum_{i=1}^{N-j} (x_i - \bar{x})(y_i + j - \bar{y}) \big( N - j \big)}{\sigma_x \sigma_y}; \quad j = 0, 1, M
\]

\[
\text{Equation 3.22}
\]

where \( \bar{x} \) and \( \bar{y} \) are the means of the two signals, and \( \sigma_x \) and \( \sigma_y \) their respective standard deviations. In this case the two functions \( x \) and \( y \) are the simultaneously recorded signals from two different electrodes, the delayed signal \( y \) being that from the downstream electrode. The initial crosscorrelation coefficient is less than 1, and increases with increasing lag to reach a maximum (still less than 1) at a delay \( t_0 \). It then decreases to zero at a time \( t_0 \). At the maximum of the crosscorrelation function the point has been reached at which fluctuations recorded at the upstream electrode are reflected (with minimum distortion) in the signal from the downstream electrode at a time \( t_0 \) later. \( t_0 \) thus reflects the convective velocity \( v_c \) in the boundary layer, which may be expressed as a percentage of the mean flow velocity:

\[
v_c = \frac{S}{t_0 u} \times 100 \quad (\%) \quad \text{Equation 3.23}
\]

where \( S = \text{separation of electrodes (m.)} \).
The actual correlation coefficient at delay \( t_0 \) gives an indication of the amount of distortion (or decay), \( E \), of the mass transfer fluctuations in passing between the two electrodes:

\[
E = (1 - C(t_0)) \times 100 \quad (\%) \quad \cdots \text{Equation 3.24}
\]

The calculation of the crosscorrelation coefficients \( C(j) \) required simultaneous sampling of the two recorded signals by the analog-to-digital converter. This could be accomplished using a multiplexer, but (although on order) one was not available. Attempts at sampling the two channels at separate times (using an artificially generated starting pulse to align the two signals) met with very limited success, and crosscorrelation analysis was abandoned until such time as a multiplexer became available.

3.4.3 Spectral Density Function \((71,72)\)

The recorded signal (and hence fluctuating mass transfer coefficient) is simply described by its autocorrelation function, \( R(t) \). An equivalent description, in the frequency rather than time domain, is provided by the spectral density function (spectrum), \( S(f) \). The spectral density function is the Fourier transform of the autocorrelation function, and shows how the variance of the signal is distributed with frequency.

\[
S(f) = \int_{-\infty}^{\infty} R(t)e^{-2\pi ft} \, dt \quad \cdots \text{Equation 3.25}
\]

Classical Fourier analysis is not possible, as the recorded signal is not continuous, but merely a relatively short series of discrete samples of an infinitely long and continuously varying record.
It can be seen that the variance of the spectrum (i.e. the mean error associated with it) will decrease as the length of the sample increases, a phenomenon which does not occur if classical Fourier analysis is used. The technique must, therefore, be modified for the analysis of time series such as this, the general objective being to obtain a spectral estimate as close as possible to the actual (theoretical) spectrum of the signal from a sample of finite length.

In particular, the spectral estimate should have high fidelity (it should faithfully reproduce the detail in the actual spectrum) and high stability (it should have a low variance). However, in practical cases these two criteria tend to have conflicting requirements, as will be shown below, and a compromise must be sought. This involves choosing a suitable spectral 'window' and finding optimum parameters for the case in hand. The relevant parameters are the sample interval, \( \Delta \), the truncation point, \( M \) (the point beyond which no information is taken from the autocorrelation function, expressed as a number of lags), and the length of record, \( T \).

The spectral window \( W(f) \), is a smoothing correction which is used to minimise errors due to the length of the sampled signal being finite. In general, the estimate of the spectrum \( S(f) \) obtained from the sampled signal has an expected value which corresponds to that obtained by looking at the theoretical spectrum through a spectral window, \( W(f) \), which has a distorting effect due to the finite length of the sample. The inverse transform of the spectral window, \( w(t) \) (the lag window), may be used to obtain a better estimate of the theoretical spectrum (i.e. one with less variance) from the autocorrelation/
from the autocorrelation function of the sampled signal. Thus

\[ w(t) = \int_{-\infty}^{\infty} W(f)e^{j2\pi ft} df \quad \text{......... Equation 3.26} \]

and \( S(f) = W(f)S(f) = \int_{-\infty}^{\infty} w(t)R(t)e^{-2\pi ft} dt \quad \text{......... Equation 3.27} \)
gives a spectral estimate with less variance than \( S(f) \) (Equation 3.25).

Several shapes of spectral window may be used, and either the Tukey window \( W_t(f) \) or the Parzen window \( W_p(f) \) may be used to obtain a good spectrum of the recorded signal. The Tukey window was chosen because the width of the Parzen window requires the calculation of considerably more autocorrelations - and hence larger computing time.

\[ W_t(f) = M\left(\frac{\sin \frac{2\pi fM}{2\pi fM}}{\left(1 - \left(2fM\right)^2\right)}\right) \quad \text{......... Equation 3.28} \]

The corresponding lag window is

\[ \frac{1}{2}(1 + \cos \frac{\pi t}{M}), \quad |t| \leq M \]

\[ W_p(t) = \begin{cases} 1 & |t| \leq M \\ 0 & |t| > M \end{cases} \quad \text{......... Equation 3.29} \]

and this is used to calculate weights for each autocorrelation coefficient up to the truncation point \( M \).

For the design of a spectral analysis calculation, four basic requirements must be met:

1) The sample interval, \( \Delta \), must be chosen so that

\[ \Delta < \frac{1}{2f_0} \quad \text{(sec.)} \quad \text{......... Equation 3.30} \]
for the analysis of frequencies in the range \(0 \leq f \leq f_c\).

ii) Aliasing must be avoided, either by choosing \(\Delta\) so that the value of the spectral density function (spectrum) is effectively zero for all \(f > f_c\), or by filtering electronically before sampling.

iii) A truncation point, \(M\), must be chosen so that the bandwidth (B) is less than the width of the narrowest peak or detail in the spectrum (a), where (for the Tukey spectral window)

\[
B = \frac{1.33}{M \Delta} \quad \text{(Hz.)} \quad \text{Equation 3.31}
\]

iv) The estimate must be tied to a given stability by choosing a number of degrees of freedom, \(v\) (say 15 to 30), which enables us to determine the length of record, \(T\), required, where

\[
T = \frac{v}{2a} \quad \text{Equation 3.32}
\]

The width of the 80\% or 95\% confidence limits on the spectrum may then be determined from statistical tables for the chosen number of degrees of freedom. These limits indicate the points between which there is an 80\% (or 95\%) probability that the spectrum lies, the possible error being due to the restricted length of the sample.

Thus it can be seen that to reproduce fine detail (i.e. if \(a\) is small) the bandwidth (B) must be small, and so the truncation point (M) must be high (Equation 3.31). In addition, the sample length (T) must be large to obtain sufficient degrees of freedom (\(v\)) to give reasonable stability (Equation 3.32). Thus to obtain high fidelity and high stability, both \(M\) and \(T\) must be large, and, as the time taken to compute the autocorrelation function is proportional to both \(M\) and \(T\), this will result in the use of considerable amounts of computer time.
The above theory was applied to the analysis of the recorded cathode signal, in which the highest frequency present was 1500 Hz (the limit of the frequency response of the tape recorder). The sample interval, $\Delta$, should therefore be less than 0.0003333 sec. (Equation 3.30), and as long as this interval was not exceeded aliasing would be avoided without recourse to electronic filtering.

The capacity of the PDP-8 computer restricted the number of samples ($N$) to 3072, so that, since

$$T = N \Delta \quad \text{(sec.)} \quad \ldots \ldots \quad \text{Equation 3.33}$$

the sample length could not exceed 1 second at the above sample interval. For 30 degrees of freedom (which give a 30% proportional error at the 80% confidence level), the width of the smallest detail which could be defined was therefore 15 Hz (Equation 3.32). The bandwidth, $B$, should be less than this, so that the truncation point had to be at least 267 (Equation 3.31). This was the number of lags for which the autocorrelation function had to be computed.

This is as far as it is possible to go by the application of theory alone. It may be that the bandwidth is too large for the particular spectrum that is under investigation, so that important fine detail is missed: the bandwidth can be reduced only at the expense of stability, but this may be acceptable in some circumstances. Conversely, the bandwidth may be smaller than necessary if there is little fine detail in the spectrum, and a useful increase in stability may be obtained by increasing the bandwidth. This process of determining the best bandwidth for a given spectral analysis/
spectral analysis is known as "window closing", and is an important step in obtaining the best spectral estimate. It is, of course, very much a case of trial and error, as different spectra will require different parameters.

Preliminary analysis of the recorded signal was carried out using the computer programs described in sections 3.4.4, 3.4.5 and 3.4.6. The spectrum program (3.4.6) calculated the weights (for the Tukey lag window) by a discrete version of Equation 3.29, namely

\[ w(I) = 0.5(1 + \cos(\pi I/M)), \quad I = 1, 1, M - 1 \]

Equation 3.34

The spectrum was then calculated for \( F \) frequency points, where \( F \) was up to three times the truncation point \( (M) \). To determine the spectrum an algorithm was used for the transform

\[ \overline{S}(I) = 2 \Delta \left[ R(0) + 2 \sum_{J=1}^{M-1} w(J)R(J)\cos(\pi J/F) \right]; \quad I = 0, 1, F \]

Equation 3.35

to minimise computing time (only one cosine had to be calculated for each frequency point if the algorithm were used - see Figure 3.7 for details).

It was found that the spectra of the recorded signals were fairly smooth (i.e. there was little fine detail), and the truncation point could be reduced considerably below the value of 267 determined above. A value of 160 was generally suitable, and this could in some instances be halved to 80. A corresponding reduction in the/
Reduction in the number of samples needed could be made without any loss of stability, since substitution for $T$ and $\alpha$ in Equation 3.32 ($\alpha$ is equal to $\beta$, the bandwidth) yields

$$\gamma = \frac{3N}{2M} \quad \text{---------- Equation 3.35}$$

In addition, it was found that the general shape of the spectra included a steep fall in spectral density at higher frequencies. The sampling interval could thus be increased from 0.0003333 sec. without introducing aliasing, enabling information to be obtained on spectral densities at frequencies below those within the range of the original analysis. Spectra from samples with differing sampling intervals were found to agree well over their common frequency range.

The relationship between the various parameters of the spectral analysis is given in Figure 3.2. It may be seen that two suitable analysis procedures involves 3072 samples at a sample interval of 0.0001 sec. with a truncation point of 160 (frequency range 1500+ to 100 Hz), and 1024 samples at a sample interval of 0.003333 sec. with a truncation point of 80 (frequency range 150+ to 5 Hz).

Spectra were usually plotted as logarithm of spectral density versus logarithm of frequency, as this enabled a large frequency range to be included in one graph. However, it is not possible to represent bandwidth (a fixed frequency interval) readily on such plots, and if it is desired to show fine fluctuations in the spectral density a plot of logarithm of spectral density against actual frequency may be more suitable. In either case the confidence limits on the actual spectrum may easily be represented.
<table>
<thead>
<tr>
<th>Sample Interval $\Delta$</th>
<th>0.0001</th>
<th>0.0003333</th>
<th>0.003333</th>
<th>0.03333</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Freq. Limit</td>
<td>5000</td>
<td>1670</td>
<td>167</td>
<td>16.7</td>
</tr>
<tr>
<td>No. of Samples $= 1024$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trunc. Point</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deg. of Freedom</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Approx. 80% Level of Signif.</td>
<td>$\pm$ 40%</td>
<td>$\pm$ 35%</td>
<td>$\pm$ 25%</td>
<td>$\pm$ 20%</td>
</tr>
<tr>
<td>Bandwidth $B$ Hz.</td>
<td>50</td>
<td>15</td>
<td>1.5</td>
<td>0.15</td>
</tr>
<tr>
<td>No. of Samples $= 3072$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Approx. 80% Level of Signif.</td>
<td>$\pm$ 30%</td>
<td>$\pm$ 20%</td>
<td>$\pm$ 15%</td>
<td>$\pm$ 15%</td>
</tr>
<tr>
<td>Degree of Freedom</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trunc. Point</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>267</td>
<td>160</td>
<td>80</td>
<td>40</td>
</tr>
<tr>
<td>L</td>
<td>10</td>
<td>17</td>
<td>33</td>
<td>67</td>
</tr>
<tr>
<td>L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.2: Spectrum Parameters and Associated Fidelity and Stability.

1. Choose a number of samples (1024 left, 3072 right).
2. Choose a truncation point ($M$).
3. Are associated degrees of freedom ($\nu$) and level of 80% significance (L) suitable? If not, try a lower $M$.
4. Choose a sample interval ($\Delta$) to give the desired upper frequency limit.
5. Look down to obtain the Bandwidth ($B$) for the selected truncation point.
6. Is this acceptable? If not, try a higher $M$ or higher $\Delta$. 
3.4.4 Sampling Program

A sampling program was developed for use on the Digital PDP-8 computer with its associated type 139E analog-to-digital converter. This converts an analog input in the range 0 to -10 V. to a signed 6- to 12-bit binary number. Thus a 0 V. input yields a digital output of \(4096\), -5 V. produces \(0000\) and -10 V. gives an output of \(3777\). The accuracy selected for the output determines the conversion time, and hence the maximum conversion rate. In this case 12-bit accuracy was always used, and the time of execution for the sampling loop was 63.5 \(\mu\)sec. The program also incorporated a delay loop of 13.5 \(\mu\)sec. duration, which could be cycled any number of times between \(0001\) and \(7777\) between conversions.

Available sample intervals were thus between 0.0001 sec. and 0.05 sec. A table giving the number of delay loop cycles (D) for each sample interval used follows:

<table>
<thead>
<tr>
<th>Theoretical Sample Interval (sec.)</th>
<th>Number of Delay Loops</th>
<th>Actual Sample Interval (\Delta) (sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(D_{10})</td>
<td>(D_{8})</td>
</tr>
<tr>
<td>0.03333</td>
<td>2462</td>
<td>4636(_8)</td>
</tr>
<tr>
<td>0.003333</td>
<td>242</td>
<td>0362(_8)</td>
</tr>
<tr>
<td>0.0003333</td>
<td>20</td>
<td>0024(_8)</td>
</tr>
<tr>
<td>0.0001</td>
<td>3</td>
<td>0003(_8)</td>
</tr>
</tbody>
</table>

Figure 3.3: Sample Intervals and Delay Loop Timings
The number of samples which could be taken was limited by the
capacity of the computer, since the sample interval was usually
too short to allow each number to be punched out before the sub-
sequent conversion. 3968 memory locations were available, the
remaining 128 being taken up by the conversion program itself.
The number of samples actually taken was usually either 1024 \( (2000_8) \)
or 3072 \( (6000_8) \).

Because the accuracy of conversion (12 binary digits) was
greater than the accuracy available on punching (8 binary digits
on 8-hole paper tape), a check was incorporated to test the four
most significant bits of each number. If one or more of these bits
were constant for all numbers, the constant code could be punched
separately, and the next 8 bits punched as the output number, with
a significant increase in accuracy. Thus, if all numbers were of
the form

\[
\begin{array}{cccccccccccc}
\end{array}
\]

Bit No. 11 10 9 8 7 6 5 4 3 2 1 0

a code corresponding to a '1' in bit 11 and a '0' in bit 10 could
be punched separately, and the next eight bits (9 to 2 inclusive)
punched for each number. The effective accuracy was thus increased
from 8 bits to 10 bits. The value of the constant code was not itself
important, since it was only indicative of the arbitrary (biased)
mean signal value. However, the total number of significant bits
determined the conversion factor required to change the sample
standard deviation \( (\sigma_x) \) to a voltage standard deviation \( (\sigma_y) \).

Since the/
Since the total range from \texttt{0000} to \texttt{7777} (4096) represented 10 V, the conversion factor ($F_c$) for a 12-bit number was 409.6 V$^{-1}$.

($\sigma_X = \sigma_X / F_c$). For an 11-bit overall accuracy the factor was half this, and for a 10-bit number the factor had to be divided by four. The factors used are shown in Figure 3.4.

<table>
<thead>
<tr>
<th>Constant Code (Binary Digits)</th>
<th>Overall Accuracy (Binary Digits)</th>
<th>Conversion Factor (V$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>12</td>
<td>409.6</td>
</tr>
<tr>
<td>3</td>
<td>11</td>
<td>204.8</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>102.4</td>
</tr>
<tr>
<td>1</td>
<td>9</td>
<td>51.2</td>
</tr>
<tr>
<td>0</td>
<td>8</td>
<td>25.6</td>
</tr>
</tbody>
</table>

Figure 3.4: Analog-to-digital Conversion Factors (139 E). A block diagram for the sampling program follows (Figure 3.5), and a listing is given in Appendix A.2.

3.4.5 Autocorrelation Program

A program was written in IMP to calculate the standard deviation, skewness and kurtosis of the sampled signal, and to compute autocorrelation coefficients for the required number of lags. Prior to execution of the program, the binary data on paper tape was transferred to a temporary magnetic tape file BINDATA on the 360/50. During execution of the program this data was transferred to a labelled permanent magnetic tape file, so that it could readily be recovered at a later date without re-reading the/
FIGURE 3.5

BLOCK DIAGRAM OF SAMPLING PROGRAM
reading the paper tape. On completion of the calculations, the autocorrelation coefficients were stored on a direct-access data file (disk), for later processing by the spectrum program. A block diagram is shown in Figure 3.6, and a program listing may be found in Appendix A.3.

A program was written to perform similar operations on the Digital PDP-8/E when this machine became available during the later stages of the project.

3.4.6 Spectrum Program

Calculation of the spectral density function from the autocorrelation function was carried out by a further IMP program. The method used was described in section 3.4.3, and a block diagram of the program follows (Figure 3.7). A program listing is given in Appendix A.4.

Again, a PAL III program for the PDP-8/E was developed in the later stages of the project.

3.5 Sample Calculation

A sample calculation for a \#H (030501) at a flow rate of approximately 8000 lb./hr., with no Polyox, is presented.

**Flow Analysis**: Temperature = 22.0°C
Flow time = 3.0 mins
Initial level reading = 64.9 cm.
Therefore volume in vessel = 1238 l. (Equation 2.1)
Final level reading = 54.5 cm.
Therefore volume in vessel = 1064 l.

**Flow rate (V)** = \((1238 - 1064)/3 = 58.0\ l./min = 0.000967\ m^3/sec.\)
FIGURE 3.6 BLOCK DIAGRAM FOR AUTOCORRELATION PROGRAM
\textbf{SPEC ALGORITHM (Ref. 72)}

- \( M \): truncation point
- \( NF \): no. of freq. pts.
- \( \Delta \): sampling interval
- \( R(I) \): autocorrelation fn.
- \( \text{SPEC}(I) \): spectrum

\begin{align*}
\text{for} \quad \text{SPEC}(I), \quad I = 0, 1, NF \\
\text{set} \quad C = \cos \left( \frac{\pi I}{NF} \right); \quad V_0 = 0; V_1 = 0 \\
\text{then for} \quad K = M - 1, -1, 1 \\
\text{do} \quad V_2 = 2 \times C \times V_1 - V_0 + W(K) \times R(K) \\
\quad V_0 = V_1 \\
\quad V_1 = V_2 \\
\quad \text{SPEC}(I) = 2 \times \Delta \times R(0) + 2 \times (V_1 \times C - V_0)
\end{align*}

\textbf{FIGURE 3.7} \quad \text{BLOCK DIAGRAM FOR SPECTRUM PROGRAM}
Diameter of pipe \( (d) \) = 1.145 in. = 0.02908 m. 

Cross sectional area \( (A) \) = \( \pi \times 0.02908^2/4 \) = 0.000665 m\(^2\). 

Therefore flow velocity \( (u) \) = \( \frac{V}{A} \) = \( \frac{0.000967}{0.000665} \) = 1.455 m/sec. 

Specific gravity of electrolyte solution = 1.021 
Therefore density of solution \( (\rho) \) = 1021 kg./m\(^3\). 

Solution viscosity = viscosity of water \( \times 1.109 \) 
Viscosity of water \( @ 22.0^\circ C \) = 0.9579 \( \mu_p \) = 0.0009579 kg./m.sec. 
Therefore solution viscosity \( (\mu) \) = 1.109 x 0.0009579 
\[ = 0.001061 \text{ kg./m.sec.} \]

Reynolds number \( (Re) \) = \( \rho \mu d/\mu \) = 1021 x 1.455 x 0.02908/0.001061 
\[ Re = 40700 \]

Pressure-drop manometer reading = 28.50 cm. in paraffin/solution manometer. 

Specific gravity of paraffin = 0.773. 
Specific gravity of solution = 1.021. 
Differential specific gravity = 1.021 - 0.773 = 0.248 
Therefore pressure-drop \( (\Delta P) \) = 28.5 x 0.248/1.000 = 7.06 cm. H\(_2\)O 
\[ = 7.06 \times 98.1 = 694 \text{ N/m}^2 \text{ (kg./m.sec}^2 \text{.)} \]

Distance between pressure taps \( (\Delta x) \) = 2.417 ft. = 0.736 m. 
Friction factor \( (f) \) = \( \frac{d}{2 \rho u^2} \times \frac{\Delta P}{\Delta x} \) = \( \frac{0.02908}{2 \times 1021 \times 1.455^2} \times \frac{694}{0.736} \) 
\[ f = 0.00634 \] 

Theoretical Friction factor \( (f_t) \) = 0.079 \( Re^{\frac{1}{4}} \) (Equation 3.4) 
Re = 40700, \( Re^{\frac{1}{4}} = 14.2 \), \( Re^{\frac{1}{4}} = 0.0704 \) 
\[ f_t = 0.079 \times 0.0704 = 0.00556 \]
Signal Analysis:

A recording was made, on tape number 8 between counter readings 5 and 40, of the signal from electrodes 1 and 3. The following characteristics were measured:

Ferricyanide concentration = 0.00514 M = 0.07532 kg. equivalents/m³.

Electrode 1: Applied voltage = 0.270 V;

Electrode area = 7.31 x 10⁻⁸ m².

Voltage drop across 1000 Ohm resistance = 0.050 V.

Amplifier gain = x 100; Recorder (track 4) gain = x 1.90

Mean current (I) = 0.050 / 10000 = 0.0000050 = 5.0 μA.

Therefore mean mass transfer coefficient k = \( \frac{I}{\nabla C_0} \) (Equation 3.10)

\[
= \frac{5.0 \times 10^{-6}}{96.5 \times 10^6 \times 7.31 \times 10^{-8} \times 16.32 \times 10^{-3}} = 31.7 \times 10^{-6} \text{ m}/\text{sec.}
\]

Resistance of electrolytic cell (R_c) = \( \frac{0.271}{5.0 \times 10^{-6}} \)

= 54200 Ohms.

The recorded signal was sampled 1024 times at a sample interval of 0.003333 sec. The parameters for the sampling program were therefore 03620 (delay loops for timer) and 20000 (number of samples).

The tape was punched out with constant code 2000, 1000, 0020, signifying 2 constant bits (third number), the first of which is a '1' (first number) and the second a '0' (second number). The code was followed by a space and 1024 characters, which were analysed by the computer.

The results/
The results of the autocorrelation program were as follows:

Mean 1114.21 (this incorporated the constant code).

Standard deviation $\sigma_x$ 35.40
Skewness $S_x$ 0.0073
Kurtosis $K_x$ 0.0025
Intensity $I_x$ 0.0318

There was no significance in the mean (or intensity, as this incorporated the signal mean). The standard deviation was analysed as follows:

Because there is 10-bit accuracy

$$\sigma_v = \frac{\sigma_x \times 102.4}{102.4} = \frac{35.40}{102.4} = 0.346 \text{ V},$$

Dividing by the amplification factors for tape recorder and amplifier,

$$\sigma_v = \frac{0.346}{(100 \times 1.90)} = 0.00182 \text{ V}.$$

Thus $\sigma_i = \sigma_v / R_c = 0.00182 / 54200 = 0.0000000336 \text{ A} = 0.0336 \mu \text{A}$

and $\sigma_k = \frac{\sigma_i \times 10^{-3}}{16.32 \times 10^{-8}}$

$$= \frac{3.36 \times 10^{-8}}{96.5 \times 10^{-6} \times 7.31 \times 10^{-8} \times 16.32 \times 10^{-3}}$$

$$= 0.292 \times 10^{-6} \text{ m/sec. (Equation 3.14)}$$

$S_k = S_x = 0.0073; K_k = K_x = 0.0025$

$I_k = \frac{\sigma_k}{K} = \frac{0.292 \times 10^{-6}}{3.17 \times 10^{-6}}$

$$= 0.0921$$

The autocorrelation function was calculated for 200 lags, the first few autocorrelation coefficients being 1.0000, 0.9337, 0.7847, 0.6169, 0.4642 etc. As the function first reached zero after 10.24 lags

$$t_o = 10.24 \times 0.003333 = 0.0341 \text{ sec.}$$
and \( \frac{t_o u}{d} = \frac{0.0341 \times 1.458}{0.0291} = 1.708 \)

Curve fitting and differentiation gave

\[ \left( \frac{\partial^2 R}{\partial t^2} \right)_{t=0} = -744.3 \quad \text{so} \quad M_i = \sqrt{-\frac{2}{-744.3}} = 0.0164 \text{ sec.} \]

The turbulence macroscale was given by:

\[ M_a = \int_{0}^{\infty} R(t) \, dt = \frac{1}{2} t_o = 0.017 \text{ sec,} \]

The autocorrelation coefficients were used as data for the spectrum program, and spectra were calculated for 160, 80, 40 and 20 truncation points. The spectrum for 80 truncation points, with 5 Hz bandwidth and 34 degrees of freedom, was most useful, and a suitable graph was plotted.
CHAPTER FOUR

4. RESULTS

4.1 Ideal Flow Rig

4.1.1 Water

The reservoir of the ideal test rig (Figure 2.12) was filled with water. On removing the stopper from the end of the capillary tube, water flowed from the apparatus, and the time taken for the reservoir level to fall through certain scale intervals (between readings of 0 and of 60) was measured. From the time of fall the mean Reynolds number of the flow was determined, and the experiment was repeated several times to check the consistency of the results. The time of fall and mean Reynolds number over each level interval is given in Table 4.1.

<table>
<thead>
<tr>
<th>Scale Reading 10 = 6&quot;</th>
<th>Time of Fall (secs.)</th>
<th>Mean Reynolds Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial 10 Final 20</td>
<td>7.0</td>
<td>3649</td>
</tr>
<tr>
<td>Initial 10 Final 30</td>
<td>14.5</td>
<td>3523</td>
</tr>
<tr>
<td>Initial 10 Final 40</td>
<td>23.0</td>
<td>3331</td>
</tr>
<tr>
<td>Initial 10 Final 50</td>
<td>34.0</td>
<td>3005</td>
</tr>
<tr>
<td>Initial 10 Final 60</td>
<td>47.0</td>
<td>2717</td>
</tr>
</tbody>
</table>

Table 4.1: Times of Fall and Reynolds Number for water (Ideal Flow Rig)

It can be seen that the mean Reynolds number was only around 3500. However, as will now be shown, this was still sufficient for polyethylene oxide to exhibit a considerable degree of drag reduction.
4.1.2 Aqueous Polymer Solution

Similar experiments to those described above (4.1.1) were carried out using dilute aqueous solutions of the polyethylene oxide "Polyox WSR-301" (Section 2.9). These solutions were carefully prepared, using small amounts of iso-propand to ensure thorough dispersion of the polymer. The results are presented in Figure 4.1, and it can be seen that even very small quantities of polymer (10 ppm, by weight) produced reductions in drag (as measured by time of fall) of around 25%. However, larger quantities of polymer were not very much more effective in producing drag reduction. This was in agreement with the predictions of Virk et al. (16), since, as can be seen from Figure 1.1b, at such low Reynolds numbers (around 2500) the maximum drag reduction asymptote (Equation 1.8) may be reached with reductions in drag of less than 50%.

4.1.3 Mechanical Degradation of Polymer Solution

The extent to which the polymer molecules in aqueous solution degraded under the influence of mechanical shear was investigated. Polymer solutions were passed repeatedly through the apparatus, being collected on leaving the capillary and returned to the reservoir for further runs. It can be seen (Figure 4.2) that when the solution was collected in a beaker and gently poured back into the reservoir (passes 1-11) there was very little mechanical degradation of the polymer, the time of fall remaining almost constant. Indeed, there was some tendency for the amount of drag reduction actually to increase slightly over the first few passes, possibly as a result of initially incomplete mixing and dissolution of the polymer. In the later part of the experiment (passes 12 to 16) the solution was returned to the reservoir through a small/
FIGURE 4.1  DRAG REDUCTION IN IDEAL FLOW 
RIG USING 'POLYOX' WSR-301
FIGURE 4.2  MECHANICAL DEGRADATION OF 50 ppm POLYOX SOLUTION
a small peristaltic pump. This produced a considerable increase in the rate of polymer degradation, reflected in a tendency for the time of fall to revert to that obtained using water alone.

4.1.4 Chemical Degradation of Polymer Solution

A large quantity of the electrolyte solution described in section 2.8 was prepared. On testing by the method outlined above (4.1.1), it was found to produce results identical to those for water, as summarised in Table 4.1. Sufficient Polyox was added to the remainder of the electrolyte to make a 50 ppm solution, and samples of this stock solution were tested in the ideal flow rig at fixed intervals. The samples were not returned to stock after each run, but were discarded, so eliminating mechanical degradation from the considerations. With the polymer dissolved in water it was several days before any significant change was observed. However, as may be seen from Figure 4.3, chemical degradation took place very rapidly in the electrolyte solution, drag reduction being reduced to negligible proportions after only three hours.

4.1.5 Conclusions from Experiments with Ideal Test Rig

The over-riding conclusion to be drawn from the above experiments was that the limiting factor for polymer drag reduction in the electrolyte solution to be used is chemical degradation. If chemical degradation is to be minimised, the drag reduction experiments must be carried out as soon as possible after mixing the polymer into the electrolyte - preferably within one hour.

Compared to chemical degradation, the effect of mechanical degradation (in the ideal flow rig, at any rate) is minimal. Further tests with/
FIGURE 4.3  CHEMICAL DEGRADATION OF 50 ppm POLYOX IN ELECTROLYTE SOLUTION
tests with the larger experimental apparatus were needed to reveal whether or not mechanical degradation was also negligible at the much greater shear rates developed under the more severe conditions which were to be used.

The Reynolds number of the flow developed in the ideal test rig is too small to allow any valid prediction of drag reduction levels to be expected in the larger rig. However, unless unexpectedly high levels of mechanical degradation are encountered, the percentage drag reduction at the higher Reynolds numbers should, at the very least, be of the same order as that obtained in the ideal flow rig, namely 25%.

4.2 Drag Reduction in the Full-scale Apparatus

4.2.1 Aqueous Polymer Solution

Prior to any work with the electrolyte solution, measurements of Reynolds number and friction factor were made with water, and with a solution of Polyox in water. The object of the water experiments was to check that close agreement with the theoretical relationship (Equation 3.4) could be obtained. As can be seen from Figure 4.4, the results obtained were very close to the predicted values.

Further experiments were carried out with a 30 ppm (by weight) solution of Polyox, and significant drag reduction was obtained at Reynolds numbers in excess of 12000 (Figure 4.5). The greatest amount of drag reduction obtained was 50% (at a Reynolds number of 45000).

Repeated passes of the same (30 ppm) polymer solution through the flow loop resulted in a considerable decrease in the amount of drag reduction (Figure 4.6), although the Reynolds number at onset (and hence the onset shear stress) remained approximately constant.

Mechanical degradation/
**FIGURE 4.4** FLOW OF WATER

**FIGURE 4.5** DRAG REDUCTION WITH 30 ppm POLYOX
Mechanical degradation was thus a significant factor in the main flow rig, although it was still of less importance than chemical degradation when electrolyte solution was used.

The effect of polymer concentration on drag reduction was also investigated. It was found (Figure 4.7) that at a concentration below 30 ppm, the amount of drag reduction (at comparable Reynolds numbers) was decreased. However, increasing the concentration to 50 ppm did not greatly increase the amount of drag reduction. It also seemed that at the lowest concentration (10 ppm) the onset Reynolds number was increased somewhat (from 12000 to 15000).

Comparison of Figure 4.6 and Figure 4.7 shows a distinct similarity between the behaviour of a 10 ppm Polyox solution on its first pass through the apparatus and that of a 30 ppm solution on its second or third pass. It therefore seemed that, in the apparatus used, at any rate, mechanical degradation could simply be regarded as a reduction in the effective polymer concentration.

4.2.2 Polyox in Electrolyte Solution

Several experiments were carried out, the Polyox concentrations used being 25, 50, 75, 100 and 200 ppm (by weight). After each experiment the apparatus was flushed out, and new electrolyte solution was made up. Since it could not be guaranteed that conditions would be identical from one experiment to the next, each Polyox run was immediately preceded by a Reference run using the electrolyte solution without Polyox. There were also several Additional calibration runs, which were carried out during calibration of the electronic apparatus. The reference number and type (Polyox, Reference or Additional calibration) of each run carried/
**FIGURE 4.6** MECHANICAL DEGRADATION OF 30 ppm. POLYOX IN WATER

**FIGURE 4.7** EFFECT OF POLYMER CONCENTRATION ON DRAG REDUCTION (IN WATER)
run carried out during the project is given in Appendix B.1.

In Figure 4.8, friction factor was plotted as a function of Reynolds number for the Reference runs and the Additional runs. With the exception of runs 1/4, 1/5, and 1/6, the data at each set flow rate was very closely grouped, and the mean values of Reynolds number and friction factor over all the other Reference runs and Additional runs were therefore used to plot the graph. It can be seen that the experimentally-determined friction factors were greater than those obtained using the Blasius equation (Equation 3.4) - possibly owing to roughness effects. However, the close agreement between results obtained on widely differing dates indicated that the discrepancy was at least consistent, and the friction factors obtained in the Reference runs could be used with confidence as standards for comparison with the corresponding Polyox runs.

Figures 4.9 to 4.13 show the amount of drag reduction obtained with differing quantities of Polyox added to the electrolyte solution. For clarity, the figures obtained at Reynolds numbers of around 4000 and 2000 are not included. In these cases (as stated in section 3.3.2) the magnitude of possible errors was considerable, and there was no significant difference between friction factors with and without polymer. The respective values of the Reynolds number at onset and the percentage drag reduction at a Reynolds number of 40000 are given in Table 4.2.

Table 4.2/
FIGURE 4.8  FLOW OF ELECTROLYTE SOLUTION

- Friction limits of error
- Reference runs
- Calibration runs

Equation 3.4: $f = 0.079 \times Re^{-0.25}$
FIGURE 4.9  POLYMER DRAG REDUCTION

**Friction Factor vs. Reynolds Number**

- **Eqn. 1.8**
- **Limits of error**

- **Points:**
  - ○ 7/1 0 ppm.
  - ● 7/3 25 ppm.
FIGURE 4.10 POLYMER DRAG REDUCTION
FRICTION FACTOR

REYNOLDS NUMBER

limits of error

Eqn. 1.8

○ 3/2 0 ppm. ; ▲ 3/4 75 ppm. (pass 2)
○ 3/3 75 ppm. (pass 1); ● 3/5 75 ppm. (pass 3)

FIGURE 4.11 POLYMER DRAG REDUCTION
FIGURE 4.12  POLYMER DRAG REDUCTION

---

**FIGURE 4.12** POLYMER DRAG REDUCTION

---

**FRICCTION FACTOR**

- Eqn. 1.8

---

**REYNOLDS NUMBER**

- ○ 2/4 0 ppm.
- ▲ 2/6 100 ppm. (pass 2)
- ○ 2/5 100 ppm. (pass 1)
- □ 2/7 100 ppm. (pass 3)

---

**Limits of error**
FIGURE 4.13 POLYMER DRAG REDUCTION

FRICCTION FACTOR

REYNOLDS NUMBER

limits of error

Eqn. 1.8

○ 6/1 0 ppm.
○ 6/2 200 ppm.
Table 4.2: Drag Reduction - Main Parameters

It can be seen that increasing the polymer concentration caused an increase in the amount of drag reduction. However, the increase did not appear to be related to the actual polymer concentration, and was nowhere as great as might be expected from the theory of Virk et al. (16). In no case did the friction factor approach his "Maximum drag reduction asymptote" (Equation 1.8, shown in the bottom left-hand corner of each figure), although the highest polymer concentration (200 ppm, by weight), was high compared to that used in most drag reduction experiments. The reason for this probably lay in the critical balance between dissolution and degradation of the polymer in electrolyte solution. Chemical degradation took place so rapidly that it was likely that the effective polymer concentration had been reduced even before dissolution was complete. The effective concentration was not, therefore, as great as that calculated from the weight of polymer added.
Further insight into the problem of degradation was provided by Figures 4.11 and 4.12. It can be seen that (at a Reynolds number of 14000) the drag-reducing effectiveness of a 75 ppm Polyoxy solution was reduced from 31% on the first pass through the apparatus to 8% on the second pass, and on the third pass the friction factor was indistinguishable from that of the pure electrolyte solution (Figure 4.11). Similarly (Figure 4.12), the effectiveness of a 100 ppm solution was reduced from 43% on the first pass to 16% on the second pass and to zero on the third pass. The actual time between subsequent passes was at most two hours, so it may be concluded that degradation effects were immediate and severe.

4.2.3 Wall Parameters

The pressure drop data already obtained enabled wall shear stress ($\tau_w = \frac{d \Delta P}{L \Delta x}$, Equation 1.2) and friction velocity ($u_t = \sqrt{\frac{T}{\rho}}$) to be calculated. These were useful as scaling parameters in the analysis of the fluctuations in mass-transfer coefficient. Since any change in wall shear stress or friction velocity on the addition of polymer merely reflects the corresponding change in friction factor, there is no need to tabulate this data.

However, it has also been shown (13, 14, 15) that wall shear stress provides a more useful indication of the onset point of drag reduction than does the Reynolds number. It may be seen from Table 4.2 that the Reynolds number at the onset of drag reduction was approximately 15000 and the friction factor 0.0082. This corresponded to an onset wall shear stress of 0.126 kg/ms² and an onset friction velocity of 0.0352 m/s. It is interesting to note that in the ideal flow rig (4.1), while the mean/
the mean Reynolds number was only around 3000, the wall shear stress was approximately 2.4 kg/m². This was greater than the onset wall shear stress given above (1.264 kg/m²), and it was, in fact, found that drag reduction did take place in the ideal flow rig, despite the extremely low Reynolds number.

4.3 Electrode Calibration and General Parameters

4.3.1 Calibration - Unsurrounded Electrode

Calibration curves for the electrodes in an unsurrounded configuration were plotted (Figures 4.14, 4.15 and 4.16). In general shape, these agreed well with those obtained by Reiss and Hanratty\(^{38,39}\), in that, as the applied voltage was increased, a region of constant (limiting) electrode current was reached. In this region, the fluctuations in the electrode current about its mean value could clearly be observed. If the voltage was further increased, there was a sudden rise in electrode current as electrolysis began to take place: bubbles of gas were observed to be forming on the electrodes. As the Reynolds number was raised, so the limiting electrode current for each electrode rose, but it could be seen that at each Reynolds number the limiting current was not the same for all electrodes. It seems likely that the reason for this was a considerable difference between the effective (active) areas of the electrodes, since Hanratty has found the limiting current density (limiting current divided by electrode area) to be constant for electrodes of differing sizes. Electrode 3 would appear to have had a smaller effective area than electrode 1, while that of electrode 2 was very much smaller still (around half that of electrode 1). As stated in Chapter 2, the fourth electrode did not function satisfactorily.
Figure 4.14

Unsurrounded Electrode Calibration at $Re = 3939$
ELECTRODE CURRENT

- ELECTRODE 1
  Limiting Current 4.1 μA.
  Voltage Range -0.25 to -0.55 V.

- ELECTRODE 2
  Limiting Current 2.0 μA.
  Voltage Range -0.2 to -0.45 V.

- ELECTRODE 3
  Limiting Current 3.4 μA.
  Voltage Range -0.25 to -0.5 V.

FIGURE 4.15 UNSURROUNDED ELECTRODE
CALIBRATION AT Re = 20756
### ELECTRODE 1
- **Limiting Current**: $5.0 \mu A$
- **Voltage Range**: -0.25 to -0.5 V

### ELECTRODE 3
- **Limiting Current**: $4.2 \mu A$
- **Voltage Range**: -0.25 to -0.5 V

---

**Figure 4.16**

**Unsurrounded Electrode Calibration at $Re = 39635$**
The most important deduction from the calibration graphs was that an applied voltage in the range $-0.3$ to $-0.4$ V. yielded an electrode current which was limiting at each electrode and at all Reynolds numbers. This was also found to be a suitable range in the Hanratty experiments $^{38}$.  

4.3.2 Calibration - Surrounded Electrode  

The procedure for calibration of the electrodes in the surrounded configuration was to apply a potential of around $-0.3$ V. to the point electrode, so as to induce a limiting electrode current. A background potential was then applied to the surrounding nickel pipe, and this negative potential was increased until it was of the same magnitude as that applied to the point electrode. However, as may be seen from Figure 4.17, when the background potential approached the point electrode voltage ($-0.336$ V.) the electrode current decreased markedly, falling to zero when the two potentials were equal. In this situation, no fluctuations in electrode current were visible. If the background potential was further decreased, the current actually began to flow in the opposite direction.

This would seem to indicate some level of electrical contact between point electrode and surround, but thorough investigation failed to reveal any such contact. A satisfactory signal could not, therefore, be obtained in the surrounded-electrode configuration, and it was decided to concentrate on the much more promising unsurrounded case.  

4.3.3 Cell Resistance  

The resistance of the electrolytic cell was the first of the overall (time-averaged) properties to be determined. It was of interest in that the electrical resistance of the cell was composed mainly of the/
FIGURE 4.17  SUROUNDED ELECTRODE CALIBRATION
mainly of the resistance in the boundary layer at the point electrode, and was thus analogous to the resistance to mass, momentum or heat transfer at that point. The cell resistance was plotted as a function of friction factor (Figure 4.18), being theoretically proportional to the friction factor raised to the power 3.2 (Chilton-Colburn analogy and Blasius equation). It can be seen that, both in the case of the cell resistance averaged over all Reference runs and in one individual case (3/2), the relationship between the two parameters was almost linear, since the slope of the logarithmic plot was about 45°. The discrepancy was probably due to the developing nature of the concentration boundary layer.

It was noted that there were considerable differences between the cell resistances at similar Reynolds numbers, but on different days. This was probably due to changes in the effective electrode area caused by oxidation of the electrode surface, since in the short term (if an experiment were repeated on the same day) the resistance remained reasonably constant. Slight short-term variation was to be expected, since the resistance was dependent on the ferricyanide concentration, which fell slightly during the course of an experiment.

It might be expected that, since cell resistance could be related to friction factor, the addition of a drag-reducing polymer would have some effect on the cell resistance. This was, in fact, found to be the case. However, this effect will be reflected in a change in mean mass transfer coefficient (4.3.14), which, at a constant applied voltage, is inversely proportional to the cell resistance (Equation 3.10).

4.3.14
FIGURE 4.18  CELL RESISTANCE (REFERENCE RUNS)
4.3.4 Mean Mass Transfer Coefficient and Sherwood Number

Mean mass transfer coefficients (Equation 1.20) and Sherwood numbers \((Sh = \frac{\bar{m}d}{D})\) were calculated for each Reference and Polyox run and mass transfer coefficient was plotted as a function of Reynolds number for each pair of runs (Figures 4.19 and 4.20). It may be seen that, in each case, the mean mass transfer coefficient seemed to be reduced by the addition of polymer. However, the reduction was not as great as the reduction in friction factor which had been observed (a maximum of 16%, compared to a maximum of 48%), and it did not appear to be confined to the higher Reynolds numbers (above the 'onset' at 15000).

In an attempt to confirm whether or not the observed reduction in mass transfer coefficient was a consequence of the addition of polymer, the same data was calculated for runs 2/4, 2/5, 2/6 and 2/7 - the second and third passes of the electrolyte solution with 75 and 100 ppm of polymer. The results for runs 2/4, 2/5, 2/6 and 2/7 (Electrode 1) are presented in Table 4.3, and it can be seen that the reduction in mean mass transfer coefficient was greatest on the first pass of the polymer solution. On the second and third passes the effect was less, in just the same way that the friction factor decrease had been found

<table>
<thead>
<tr>
<th>Reynolds Number</th>
<th>37092</th>
<th>34968</th>
<th>29952</th>
<th>25712</th>
<th>19651</th>
<th>9856</th>
<th>4452</th>
<th>2036</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 2/4 (0 ppm.)</td>
<td>46.8</td>
<td>45.9</td>
<td>44.1</td>
<td>38.7</td>
<td>35.1</td>
<td>26.1</td>
<td>18.0</td>
<td>12.6</td>
</tr>
<tr>
<td>Theoretical</td>
<td>31.0</td>
<td>29.5</td>
<td>26.2</td>
<td>23.8</td>
<td>18.6</td>
<td>10.8</td>
<td>5.6</td>
<td>3.0</td>
</tr>
<tr>
<td>Run 2/5 (100 ppm., pass 1)</td>
<td>39.9</td>
<td>39.6</td>
<td>37.8</td>
<td>34.2</td>
<td>32.4</td>
<td>24.3</td>
<td>18.0</td>
<td>11.7</td>
</tr>
<tr>
<td>% Reduction</td>
<td>15%</td>
<td>13%</td>
<td>14%</td>
<td>12%</td>
<td>8%</td>
<td>7%</td>
<td>-</td>
<td>7%</td>
</tr>
<tr>
<td>Run 2/6 (100 ppm., pass 2)</td>
<td>43.2</td>
<td>41.4</td>
<td>39.6</td>
<td>36.0</td>
<td>34.2</td>
<td>25.2</td>
<td>17.1</td>
<td>11.7</td>
</tr>
<tr>
<td>% Reduction</td>
<td>8%</td>
<td>10%</td>
<td>10%</td>
<td>7%</td>
<td>3%</td>
<td>3%</td>
<td>5%</td>
<td>7%</td>
</tr>
<tr>
<td>Run 2/7 (100 ppm., pass 3)</td>
<td>44.1</td>
<td>44.1</td>
<td>42.3</td>
<td>38.7</td>
<td>35.1</td>
<td>25.2</td>
<td>18.0</td>
<td>11.7</td>
</tr>
<tr>
<td>% Reduction</td>
<td>6%</td>
<td>4%</td>
<td>3%</td>
<td>-</td>
<td>-</td>
<td>3%</td>
<td>-</td>
<td>7%</td>
</tr>
</tbody>
</table>
**FIGURE 4.19** MEAN MASS TRANSFER COEFFICIENTS

(25 & 50 ppm)
FIGURE 4.20  MEAN MASS TRANSFER COEFFICIENT

(75, 100 & 200 ppm)
to be reduced after the first pass. Whilst there was no definite 'onset' point for the reduction in mass transfer coefficient, the effect was found to diminish as the Reynolds number was reduced.

The experimentally determined mass transfer coefficients were compared with those calculated using the Chilton-Colburn analogy ($\text{Sh} = 0.023 \text{Re}^{0.8} \text{Sc}^{0.33}$). Although the experimental figures (Table 4.3) were somewhat greater than those calculated empirically, they exhibited a similar dependence on Reynolds number. It can be seen from Figure 4.20 that the coefficients obtained from run 2/4 were greater than those of any other Reference run. The data from other runs would thus approach the predicted values more closely, the discrepancies probably being due to the developing (rather than fully-developed) concentration boundary layer.

The Sherwood number is dependent only on the mean mass transfer coefficient and on the diffusion of the ferricyanide ion. Since the diffusion varied only between $0.786 \times 10^{-9} \text{m}^2\text{s}^{-1}$ and $0.796 \times 10^{-9} \text{m}^2\text{s}^{-1}$, the Sherwood number was effectively proportional to the mean mass transfer coefficient. There was, therefore, an equivalent drop in Sherwood number corresponding to each observed fall in mass transfer coefficient.

4.4 Simple Parameters of Mass Transfer Fluctuations

4.4.1 The Recorded Signal and Its Sampling

The recorded signals, representing the fluctuations in mass transfer coefficient at an electrode, were observed on the oscilloscope and chart recorder. Although the highest frequency which could readily be observed using these instruments was only of the order of 10 Hz, there was/
10 Hz, there was a very noticeable reduction in the number of sharp peaks as the flow rate was reduced. At a Reynolds number of around 40000 the signal fluctuated rapidly, but in the transition region (at a Reynolds number just over 2000) it was virtually constant. However, the addition of polymer caused no visible change to the observed signal, and it was necessary to carry out a thorough analysis of the recordings to ascertain what effect, if any, the polymer had had.

As explained in Chapter 3, the selection of a suitable sampling interval is a question of compromise between length of record (for response to low frequency fluctuations) and brevity of sampling interval (for investigation of high frequencies). If the sampling interval is very short (1/3000 sec.), the response to high frequencies will be good (up to 1500 Hz), but, since the number of samples is limited to 1024 (or, at most, 3072), the total record length is only 1/3 sec. (1 sec. at most). The low frequency response (below 3 Hz) will thus be poor, and there will also be comparatively large variations between parameters estimated using different records from the same signal (i.e. the parameters will have a high variance). Conversely, a long sampling interval (1/30 sec.) allows a total record length of 30 sec., which will be sufficient to yield information on fluctuations of only 1/30 Hz. There will also be a low variance associated with each parameter calculated from the samples, but there will be no response to fluctuations at frequencies in excess of 15 Hz.

With this in mind, an analysis of the standard deviation, intensity skewness and kurtosis of the fluctuations in mass transfer coefficient was carried out. Initially, each recording (one for each of eight flow rates/
flow rates during each of the Reference and Polyox runs in Appendix B.1) was sampled once at each of three sampling intervals: 1/30, 1/300 and 1/30000 sec. This data was analysed on the IBM 360/50, and provided much useful information, but the arrival of the PDP-8E (October 1971) enabled the sampling and data analysis to be speeded up tenfold. In the next three months many of the recordings were analysed several times, so that some level of statistical significance could be applied to the results.

4.4.2 Standard Deviation

An initial analysis of the standard deviations of the recorded signals confirmed many of the predictions noted above (4.4.1). Typical results are shown in Figure 4.21, data at three different sampling rates being included. Results from other runs at differing polymer concentrations showed a similar pattern, although, as in the case of the mean value of the mass transfer coefficient, there was considerable variation in the actual standard deviation values from experiments on different dates.

It can be seen (Figure 4.21) that there was considerable scatter in the values obtained at a sampling interval of 1/30000 sec. (represented by circles). This scatter seemed to be greater in the case of the Polymer run (3/3) than in the case of the Reference run (3/2). However, a reasonable pattern emerged from the data at sample intervals of 1/300 sec. (triangles) and 1/30 sec. (squares). It would appear that, since comparable standard deviations at these two sampling rates were very close together, there was little to be gained (in terms of response to low frequency fluctuations) by reducing the sample interval below 1/300 sec.

The actual results obtained at differing polymer concentrations can be seen/
FIGURE 4.21 VARIATION OF STANDARD DEVIATION WITH SAMPLING INTERVAL
can be seen in Figures 4.22 and 4.23, all standard deviations being obtained over 1024 samples at a sampling interval of 1/300 sec.

There were considerable differences both in actual standard deviation values and in the general shape of the curves. In the case of run 6/1 (Reference), the standard deviation values were smaller, by a factor of ten, than any others determined in the course of the experiment. There seemed to be some gross experimental error in this run (possibly as the result of a partial short-circuit of the electrode), and the results from runs 6/1 and 6/2 (200 ppm) have, therefore, been omitted.

The differences between the individual pairs of runs notwithstanding, it seems that there was a definite reduction in the standard deviation on the addition of polymer. This reduction was most pronounced at the higher Reynolds numbers (20000 and above), and the estimated percentage reductions in standard deviation were compared with the percentage reduction in friction factor (Table 4.14).

<table>
<thead>
<tr>
<th>Runs</th>
<th>7/1, 7/3</th>
<th>4/1, 4/2</th>
<th>5/1, 5/2</th>
<th>3/2, 3/3</th>
<th>2/4, 2/5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Conc.</td>
<td>25 ppm.</td>
<td>50 ppm.</td>
<td>50 ppm.</td>
<td>75 ppm.</td>
<td>100 ppm.</td>
</tr>
<tr>
<td>% Reduction in Standard Deviation</td>
<td>12%</td>
<td>13%</td>
<td>11%</td>
<td>18%</td>
<td>31%</td>
</tr>
<tr>
<td>% Reduction in Friction Factor</td>
<td>24%</td>
<td>29%</td>
<td>29%</td>
<td>31%</td>
<td>43%</td>
</tr>
</tbody>
</table>

Table 4.14: Estimated Reduction in Standard Deviation at Reynolds Number 40000.

There seemed to be a promising general trend, but, as the figures in Table 4.14 were obtained from only one set of samples, the statistical significance of the results could not be assessed. When the PDP8-E became/
Figure 4.22: Estimated Standard Deviation

(25 & 50 ppm.)
FIGURE 4.23  ESTIMATED STANDARD DEVIATION

(75 & 100 ppm)
PDF8-E became available, further analyses at 1/300 sec. Sampling interval were carried out for selected runs. Four standard deviation values were calculated for each of the runs 2/4 to 2/7 and 3/2 to 3/5, both for electrode 1 and electrode 3. The mean of each set of four values was determined, and the statistical significance of any departure, in the Polymer runs, from the values obtained in the Reference runs (2/4 and 3/2) was assessed.

The results obtained by analysis of the signal from each electrode for all the runs were plotted (Figures 4.24 and 4.25), and approximate levels of significance (probability that the difference between the Reference and Polyox runs was due to chance alone) were added. In the case of runs 2/4 to 2/7 (Figure 4.24), the difference was significant at the 5% level for Reynolds numbers of 20000 and above, but not at Reynolds numbers below 10000. This indicated an 'onset' Reynolds number of around 15000 for significant reduction in standard deviation, as well as for actual drag reduction.

Similar results were obtained from runs 3/2 to 3/5 (75 ppm Polyox - Figure 4.25), when the signal from electrode 1 was used. However, the standard deviation values obtained from the current fluctuations at electrode 3 were somewhat anomalous, in that the initial reduction on the first pass of the polymer solution (3/3) did not take place. Increases, compared to run 3/3, were observed in runs 3/4 and 3/5, so it seems that it was the data from the Reference run which was in error.

The reduction in standard deviation at electrode 1, for a Reynolds number of 40000, was estimated from Figures 4.24 and 4.25 (Table 4.5).
FIGURE 4.24  MEAN STANDARD DEVIATION (100 ppm)
FIGURE 4.25 MEAN STANDARD DEVIATION (75 ppm)
It can be seen that, just as the amount of drag reduction decreased on successive passes of the polymer solution, so the reduction in mean standard deviation also decreased. In addition, there was little real difference between the reduction in standard deviation estimated from only one set of samples at each Reynolds number (Table 4.4) and that obtained by averaging four such values (Table 4.5). The respective figures were 18% and 22% (for a 75 ppm. solution), and 31% and 30% (100 ppm.). The figures in Table 4.4, and the corresponding graphs (Figures 4.22 and 4.23) may, therefore, be taken as a true indication of the amount of reduction in standard deviation.

4.4.3 Intensity

It has been shown that both the mean values and standard deviations of the mass transfer coefficients at the electrodes were reduced by the addition of polymer. Since the reduction in standard deviation (Figures 4.22 and 4.23) was, in general, greater than the reduction in mean value (Figures 4.19 and 4.20), it was expected that the result of the addition of polymer would be a slight reduction in the/
tion in the intensity (ratio of standard deviation to mean) of the fluctuating signal. However, since the intensity is dimensionless, the effect of differences between electrode conditions in different experiments should be minimised. The data from different runs should thus be closer together, as should the results from the different electrodes.

Intensities calculated from mean standard deviation values for runs 2/4, 2/5, 3/2 and 3/3 (Figures 4.24 and 4.25) were plotted as a function of Reynolds number (Figures 4.26 and 4.27). In the case of electrode 1, the intensities (Figure 4.26) were much more consistent between experiments than the standard deviations had been (0.58% and 0.80% compared to 0.71 m/s. and 1.18 m/s. for runs 3/2 and 2/4 at a Reynolds number of 40000). The agreement between intensities at the different electrodes was also closer (run 2/4, Figures 4.26 and 4.27 - 0.80% and 0.66%) than that between the standard deviations (Figure 4.24 - 1.18 m/s. and 0.53 m/s. at a Reynolds number of 40000). However, the results from electrode 3 for runs 3/2 and 3/3 continued to show marked abnormality.

The point of greatest interest was that the intensity levels were approximately constant at Reynolds numbers of 20000 and above. The reduction in intensity on the addition of polymer was thus also constant over this range of flow rates, and at Reynolds numbers of 10000 and below there was no significant difference between data for the Reference and the Polyox runs. Once again, there appeared to be an 'onset' Reynolds number of around 15000. The actual reductions in intensity (at electrode 1) were 14% (for a 75 ppm solution)
FIGURE 4.26  MASS TRANSFER INTENSITY (Electrode 1)
**FIGURE 4.27** MASS TRANSFER INTENSITY (Electrode 3)
solution) and 20% (100 ppm.) - considerably less than the reductions
in standard deviation recorded in Table 4.5.

Compared to the data of Hanratty\(^{(29)}\), plotted in Figure 1.6, the observed intensities were considerably reduced (Hanratty's data is presented as fractions, rather than percentage). The rapid fall-off in intensity at Reynolds numbers below 10000 was confirmed, but there was little evidence to support a gradual decline at Reynolds numbers in excess of this value.

4.4.4 Skewness

For each set of data samples taken for the standard deviation analysis (4.4.2), skewness and kurtosis were calculated. The skewness indicated the degree of positive or negative bias for the fluctuations in standard deviation about their mean value. There appeared to be no general trends in the calculated skewness values which could be related to differences in Reynolds number, electrode number, Polymer concentration, or even to changes in sampling interval or number of samples. Typical values (run 3/2, electrode 1, 1024 samples at 1/300 sec.) were, at the Reynolds number shown: -0.0038 at 40205, 0.014 at 39996, 0.0017 at 33647, 0.0089 at 27738, -0.0045 at 20929, -0.0038 at 10362, -0.0128 at 4545 and -0.0075 at 2343.

However, the skewness never exceeded \(\pm 0.015\). Fisher\(^{(73)}\) has shown how the standard error of the skewness may be related to the number of samples. In this case (the maximum number of samples being 3072), the skewness had to exceed \(\pm 0.0884\) to be indicative of any departure from normality. It was therefore concluded that the skewness of the sample distribution was indistinguishable from that of a normal distribution; there was no bias to either the positive or the negative side of the mean.
4.4.5 **Kurtosis**

Observation of the calculated values of the kurtosis (the fourth moment of the distribution) showed that they were to a great extent independent of Reynolds number, polymer concentration or electrode number. However, the kurtosis was almost inversely proportional to the number of samples taken. For 1024 samples the kurtosis was almost invariably in the range 0.002 to 0.003, while for 3072 samples it was around 0.0008. These values are not indicative of any departure from normality - they would have to exceed 0.1766 to do so.

4.5 **The Autocorrelation Function**

4.5.1 **The Function**

The series of autocorrelation coefficients which form the autocorrelation function were calculated from the sampled signal values. In general, the function must have an initial value (at zero lags) of +1. As the number of lags was increased, the function value fell to zero, and continued to oscillate in the region 0 to +0.15 until calculation was terminated.

However, as in the case of the estimates of standard deviation, the precise form of the autocorrelation function was highly dependent on the sampling interval. At very short sampling intervals (1/3000 sec.) there was considerable variance between individual sets of samples from the signal, and at the lower Reynolds numbers the number of lags for which the function had to be computed became unmanageable. The longest interval (1/30 sec.) resulted in a function which fell to zero after only one lag. Once again, a sampling interval of 1/300 sec. provided a satisfactory compromise: consistency between different sets of/
sets of samples was good, and the function fell to zero after at least 8 lags (for the highest Reynolds numbers) and not more than 100 or so (for the lowest). Examples may be seen in Figure 4.28.

Since the data used to calculate the autocorrelation function had been normalised, it was expected that the effects of differing effective electrode area which have already been commented on would be minimised. There should be good agreement between data from runs in different experiments under similar conditions of flow and polymer concentration.

4.5.2 A Turbulence Macroscale

As described in section 3.4.2, a turbulence macroscale (a measure of the longest time over which the flow pattern at the electrode is autocorrelated) may be obtained by integration of the autocorrelation function to infinite time. In practice, since the latter part of the function often consists of positive and negative fluctuations which largely cancel each other out, this may usually be approximated to by integration to $t_0$, the time at which zero level of autocorrelation is first reached.

In this case it was found that the shape of the initial part of the function could be considered to be a right-angled triangle of height 1 and base $t_0$. The turbulence macroscale was, therefore, the area of this triangle, or $\frac{1}{2} t_0$. This procedure is illustrated in Figure 4.29.

Problems were encountered in obtaining a reliable and consistent estimate of $t_0$, since small scale fluctuations often caused the function to be asymptotic to a zero value, so artificially delaying $t_0$. After trials/
FIGURE 4.28  SAMPLE AUTOCORRELATION FUNCTIONS — RUN 3/2
FIGURE 4.29 AUTOCORRELATION FUNCTION AND TURBULENCE MACROSCALE

MACROSCALE = AREA OF TRIANGLE ABC

= $\frac{1}{2} t_o$
After trials in which the earlier (and more consistent) part of the
function was extrapolated to the point at which it crossed the line
representing a zero value, it was decided that the 'best' estimate
of $t_o$ was obtained by doubling the time taken for the function to
fall from a value of 1 to a value of 0.5. This estimate was in good
agreement with that obtained by graphical extrapolation, and gave
consistent values for different sets of data from the same run.

Initially, the macroscale values were estimated from auto-
correlation functions calculated using 1024 data points obtained at
a sampling interval of 1/300 sec. The results were plotted as a
function of Reynolds number (Figures 4.30 and 4.31).

It can be seen that the results from different runs were more
closely grouped than those obtained earlier for parameters (such as
standard deviation) calculated using non-normalised data. There
was a definite increase in the turbulence macroscale, particularly
at high Reynolds numbers, when polymer was added. The approximate
increase in macroscale, at a Reynolds number of 40000, was compared
with the reduction in friction factor at the same flow rate and
polymer concentration (Table 4.6). It can be seen that the increase
was considerable.
FIGURE 4.30 ESTIMATED TURBULENCE MACROSCALE
FIGURE 4.31 ESTIMATED TURBULENCE MACROSCALE
<table>
<thead>
<tr>
<th>Runs</th>
<th>7/1,7/3</th>
<th>4/1,4/2</th>
<th>5/1,5/2</th>
<th>3/1,3/2</th>
<th>2/4,2/5</th>
<th>6/1,6/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Conc.</td>
<td>25 ppm.</td>
<td>50 ppm.</td>
<td>50 ppm.</td>
<td>75 ppm.</td>
<td>100 ppm.</td>
<td>200 ppm.</td>
</tr>
<tr>
<td>% Increase in Macroscale</td>
<td>22%</td>
<td>40%</td>
<td>42%</td>
<td>48%</td>
<td>82%</td>
<td>100%</td>
</tr>
<tr>
<td>% Reduction in Friction Factor</td>
<td>24%</td>
<td>29%</td>
<td>29%</td>
<td>31%</td>
<td>43%</td>
<td>48%</td>
</tr>
</tbody>
</table>

Table 4.6: Estimated Increase in Turbulence Macroscale at a Reynolds Number of 40000.

Further analyses of data from runs 3/2 to 3/5 and 2/4 to 2/7 were therefore carried out. A mean value of $t_o$ was obtained from four estimations, so reducing the considerable variance of the earlier results. Plots of the macroscale as a function of Reynolds number (Figure 4.32 and 4.33) yielded the data for Table 4.7.

<table>
<thead>
<tr>
<th>Polymer Conc.</th>
<th>75 ppm.</th>
<th>100 ppm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run</td>
<td>3/3</td>
<td>2/5</td>
</tr>
<tr>
<td>Pass</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>% Increase in Macroscale</td>
<td>33%</td>
<td>53%</td>
</tr>
<tr>
<td>% Reduction in Friction Factor</td>
<td>31%</td>
<td>43%</td>
</tr>
</tbody>
</table>

Table 4.7: Mean Increase in Turbulence Macroscale at a Reynolds number of 40000.

It can be seen that the increase in macroscale corresponded to the reduction in friction factor to a very marked extent. In addition, there was little evidence of any significant increase in macroscale at Reynolds number of 10000 and below.

For all/
TURBULENCE MACROSCALE

\[ t_0/2 \] (sec.)

REYNOLDS NUMBER

**FIGURE 4.32** MEAN TURBULENCE MACROSCALE
**Figure 4.33** Mean Turbulence Macroscale

- **Turbulence Macroscale**
- **$t_o/2$** (sec.)
- **Reynolds Number**

Legend:
- ♦ 2/4 0 ppm.
- □ 2/5 100 ppm. pass 1
- ▲ 2/6 100 ppm. pass 2
- □ 2/7 100 ppm. pass 3
For all the Reference runs, the logarithmic plot of macroscale was a straight line of slope approximately $45^\circ$, indicating an inverse proportionality between macroscale and Reynolds number. Reiss and Hanretty (38, 39) and Brangwine (54) have suggested that the dimensionless group $t_o u/d$ might be independent of Reynolds number, and this would seem to be a consequence of such an inverse proportionality. To confirm this, the group $t_o u/d$ was plotted against Reynolds number for the data of Figures 4.32 and 4.33. It can be seen (Figure 4.34 and 4.35) that the value of the dimensionless group was, indeed, approximately constant, at about 1.3, for the data both of Run 2/4 and Run 3/2. The addition of polymer to the solution caused the value to rise, corresponding to the increase in $t_o$ already reported.

4.5.3 A Turbulence Microscale

A turbulence microscale (the smallest time over which fluctuations take place) may be defined in terms of the second derivative of the autocorrelation function, evaluated at zero time (Equation 3.21). This derivative was evaluated, by differentiation of a quadratic equation fitted to the first three points of each autocorrelation function, for each Polymer and Reference run.

The results for Runs 3/2 to 3/5 and 2/4 to 2/7 were plotted as a function of Reynolds number (Figures 4.36 and 4.37). There was a marked similarity, both qualitative and quantitative, between these microscale values and the macroscale levels plotted earlier (Figures 4.32 and 4.33), suggesting that the two time scales involved are not truly independent. However, this is not, strictly speaking, a paradoxical situation, since, by definition (see above), the two quantities are...
FIGURE 4.34 DIMENSIONLESS GROUP $\frac{t_u}{d}$ (75ppm.)
FIGURE 4.35 DIMENSIONLESS GROUP $\frac{t_u}{d}$ (100ppm)
FIGURE 4.36  MEAN TURBULENCE MICROSCALE
Figure 4.37  Mean Turbulence Microscale
quantities are not exactly comparable. Indeed, judging by the similarity between the method of performing the two calculations, it was expected that the two parameters would be of the same order of magnitude, and this has also been observed by Ponton (55).

The actual values of microscale obtained were in good agreement with those of Brangwein (54) - approximately 0.02 sec. at a Reynolds number of 40000. He does not quote values for turbulence macroscale, so no comparison is possible here. It is hard to see how the values obtained for macroscale, even by the $\frac{1}{2}t_0$ estimate, could be an order of magnitude too small, both in the present experiments and those of Ponton (55).

Increases in microscale, comparable with the increases in macroscale already reported, were obtained on the addition of polymer to the solution. Once again, there was some evidence of an 'onset' effect, and the changes due to polymer degradation after more than one pass were readily observed (Figure 4.36 and 4.37).

4.6 The Crosscorrelation Function

4.6.1 The Function

The object of the crosscorrelation function was to provide a measure of the degree of similarity between signals from neighbouring electrodes, and hence give a measure of the length of the turbulent fluctuations passing along the pipe wall. With the arrival of the PDP-8E, it became possible to carry out crosscorrelation analyses, although considerable difficulties were encountered in doing this.

As the separation between the electrodes was very short (0.20 in., or 0.51 cm., for electrodes 1 and 3 - the pair usually used), there was only/
was only a very short time lag before the peak of the crosscorrelation function. It was, therefore, necessary to sample at very short intervals to obtain sufficient lags (a minimum of five or six) before the peak to give a good estimate of its actual position. However, the fast sampling rate used (1/3000 sec.) reduced the overall record length to such an extent that the variance of the individual results was quite considerable. The only way of reducing the variance was to take as many samples as possible - but this was limited (for crosscorrelations) to \(1024\) by the capacity of the computer. It was, therefore, necessary to do several estimations from each recording to obtain a reasonably consistent mean value for the delay to the peak and the peak height. A sample crosscorrelation is shown in Figure 4.38.

From the delay to the peak \((t_c)\) and the peak height \((h_c)\) the convection velocity \((v_c)\) and degree of distortion \((E)\) of the eddies passing between the two electrodes could be estimated (section 3.4.2).

4.6.2 Delay to Peak and Convection Velocity

The delay to the peak of the crosscorrelation function was determined from eight independent records at each flow rate, \(1024\) samples being taken at intervals of \(1/3000\) sec. in each case. As stated above, the number of lags before the peak was reached varied considerably, as can be seen from the results presented in Table 4.8.
FIGURE 4.38: SAMPLE CROSSCORRELATION FUNCTIONS - RUN 3/2
Table 4.8: Variation of Convection Velocity with Flow Rate, for Electrodes 1 and 3, Run 3/2, 1024 Samples at 1/3000 sec. interval.

The mean value was used to calculate the delay time to the peak \( t_c \), and hence the convection velocity \( v_c \) (Equation 3.23). The convection velocity was found to be approximately equal to the mean flow rate \( \bar{u} \). This result was rather surprising, since the velocity of the fluid actually adjacent to the pipe wall (the friction velocity, \( u_t \)) was less than 10% of the mean flow rate. However, similar results have been obtained by Ponton. It seems, then, that the fluctuations in the boundary layer originate in the bulk of the fluid, rather than in the high-shear region close to the wall.

There was no evidence for any significant difference in convection velocity in the presence of polymer. Once again, the convection velocity was approximately the same as the main-stream velocity.

4.6.3/
4.6.3 Peak Height and Degree of Distortion

As in the case of \( N_0 \) (4.6.2 above), the height \( (h_e) \) of the peak of the crosscorrelation function was subject to considerable variance. However, when the average of eight values was taken it was found that the mean peak height was significantly increased in the presence of polymer. From the data for Runs 3/2 and 3/3 (Table 4.9) it can be seen that, once again, the difference ceased to be significant at Reynolds numbers below 20000. In this case, the lower levels of significance at the highest Reynolds numbers were indicative of the particularly high variance of these rapidly fluctuating signals.

<table>
<thead>
<tr>
<th>Mean Reynolds Number</th>
<th>Run 3/2, 0 ppm.</th>
<th>Run 3/3, 75 ppm.</th>
<th>Increase in Peak Height (%)</th>
<th>Significance Level (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean Peak Height</td>
<td>Distortion (%)</td>
<td>Mean Peak Height</td>
<td>Distortion (%)</td>
</tr>
<tr>
<td>40020</td>
<td>.706</td>
<td>29.4</td>
<td>.836</td>
<td>16.4</td>
</tr>
<tr>
<td>39182</td>
<td>.720</td>
<td>28.0</td>
<td>.853</td>
<td>14.7</td>
</tr>
<tr>
<td>33112</td>
<td>.661</td>
<td>33.9</td>
<td>.879</td>
<td>12.1</td>
</tr>
<tr>
<td>27308</td>
<td>.779</td>
<td>22.1</td>
<td>.887</td>
<td>11.3</td>
</tr>
<tr>
<td>21164</td>
<td>.752</td>
<td>24.8</td>
<td>.846</td>
<td>15.4</td>
</tr>
<tr>
<td>10466</td>
<td>.830</td>
<td>17.0</td>
<td>.904</td>
<td>9.6</td>
</tr>
</tbody>
</table>

Table 4.9: Crosscorrelation Peak Height - Runs 3/2 and 3/3.

Since an increase in peak height is indicative of a higher level of correlation between the signals from the two electrodes, it seemed that the boundary layer eddies in the solution with polymer were/
polymer were more stable than those in the pure electrolyte. They therefore existed for longer (in the time domain), and the distortion between the two electrodes (owing to decay of the eddies) was reduced.

4.7 The Power Spectral Density Function

4.7.1 Raw Spectra

The spectrum program (3.4.6 and Appendix A.4) calculated spectral data for a specified sampled signal, stored as its autocorrelation. A truncation point was selected, and this, for a given number of samples and sampling interval, determined the frequency interval, bandwidth and number of degrees of freedom. The printout consisted of a tabulation of frequency, spectral density, and logarithm of spectral density for the full frequency range of the spectrum. In addition, logarithm of spectral density was plotted as a function of frequency. This form of spectrum was useful in that, as the frequency scale was linear, the bandwidth corresponded to a constant interval on the plot. The significance or otherwise, of a peak in the spectrum could thus be readily assessed.

However, admirable though this technique was when it was desired to examine fine details in the spectrum, the physical length of the table or graph (the interval from 1005 Hz. to 1006 Hz. occupied the same space as that from 5 Hz. to 6Hz.) meant that broad trends in the form of the spectrum were difficult to discern.

Examination of the raw spectral data showed no significant difference between the spectra obtained for solutions with and without polymer. Typical spectra are shown (in logarithmic form) in Figure/
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However, admirable though this technique was when it was desired to examine fine details in the spectrum, the physical length of the table or graph (the interval from 1005 Hz. to 1006 Hz. occupied the same space as that from 5 Hz. to 6Hz.) meant that broad trends in the form of the spectrum were difficult to discern.

Examination of the raw spectral data showed no significant difference between the spectra obtained for solutions with and without polymer. Typical spectra are shown (in logarithmic form) in Figure/
It was noted that there was, as might be expected, a tendency for the relative power at higher frequencies to be reduced as the flow rate was reduced. To compensate for this, and to present the data in a form which would show up general trends in the spectra, the spectral density and frequency values were normalised as well as being plotted on logarithmic scales (4.7.2).

4.7.2 Normalised Spectra

Frequency was normalised by multiplying by $d/u$, the ratio of pipe diameter to mean flow velocity, and spectral density was normalised by multiplying by $u/d$. The spectra were plotted, typical results being those for runs 2/4 (0 ppm.) and 2/5 (100 ppm.), shown in Figures 4.40 and 4.41. These spectra are in fact composites, consisting of data from two spectrum calculations covering the ranges 0.1 Hz. to 14 Hz. (sampling interval 1/30 sec.) and 15 Hz. to 1500 Hz. (sampling interval 1/10000 sec.). It can be seen that there was no appreciable discontinuity between the spectra (at 15 Hz., or $fd/u = 0.5$) and that the data from runs at differing flow rates were brought together somewhat by the process of normalisation.

The main features of the spectra were the level plateau at a dimensionless spectral density of around 5, and the rapid fall in power at normalised frequencies in excess of 0.5. There was reasonably good agreement between these mass transfer spectra and those obtained by other workers (Reiss and Hanratty, 38, 39, and Branguin, 54; see Figure 1.7).

It seemed, from plots such as those of Figures 4.40 and 4.41, that there was little, if any, difference between spectra obtained from Polymer/
**Figure 4.39**  
POWER SPECTRA - RUN 2/4
FIGURE 4.40  NORMALISED POWER SPECTRA  RUN 2/4 (0 ppm.)
Figure 4.41 Normalised Power Spectra Run 2/5 (100 ppm.)
from Polymer runs and those from Reference runs. In an attempt to confirm this, some spectra obtained at individual, similar flow rates were compared. One such pair (2/4 and 2/5 at a Reynolds number of 40000) is shown in Figure 1.42. The only point at which there was a significant difference between these two spectra was in the high frequency range, and it seemed (from reference to Figure 1.40) that it was an anomaly in the data from the Reference run (2/4) which caused this, rather than some real difference in the two spectra.

Overall, there was no evidence of a change in the spectral density function which might have resulted from the addition of polymer to the solution. However, it may be that some other means of presentation of the spectra could show up such a difference. Limitations of time, both actual and computer prevented further investigations.
Figure 4.42: Normalised Power Spectra Runs 2/4 & 2/5 (Re = 40000)
CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

5.1 Introduction

During the course of the series of experiments described above, several differences in behaviour between pure electrolyte solutions and those containing polymer have been observed. These differences have been found to be greatest when the polymer concentration (and hence the amount of drag reduction) was greatest, and were much diminished at Reynolds numbers below 15000; the onset Reynolds number for drag reduction in the apparatus used. It therefore seems that the observed phenomena were related to drag reduction in some way. However, a distinction must be drawn between effects which are consequential on the existence of drag reduction, and phenomena which may reveal a contributory cause of drag reduction. It is these more fundamental phenomena which may give rise to a better understanding of the mechanisms of drag reduction. In these cases, the implications of the experimental findings will be discussed (5.3).

5.2 Experimental Conclusions

5.2.1 Friction Factor (Figures 4.9-4.13)

A considerable reduction in friction factor is caused by the presence of small quantities of polymer. This basic phenomenon of drag reduction is greatest at high flow rates, and does not occur below a critical 'onset' wall shear stress of around 1 kg/ms². Chemical, and (to a lesser extent) mechanical, degradation of the polymer in solution causes a marked decrease in the degree of drag reduction.
5.2.2 Cell Resistance (Figure 4.18)

The resistance at a point electrode is increased by the presence of polymer in the electrolyte solution. This inhibition of electron transfer reflects the inhibition of momentum transfer which manifests itself as a reduction in friction factor. The increased electrical resistance must thus be regarded as consequential on the presence of drag reduction, rather than contributing to its cause.

5.2.3 Mean Mass Transfer Coefficient and Sherwood Number (Figures 4.19 and 4.20)

The mean mass transfer coefficient and hence Sherwood number at a small electrode in the wall of a pipe is reduced by the presence of polymer in the electrolyte solution. This is a direct consequence of the increase in cell resistance noted above (2), rather than a contributory cause of drag reduction.

5.2.4 Standard Deviation of Mass Transfer Fluctuations (Figures 4.22-4.25)

The standard deviation of the fluctuations in mass transfer coefficient is reduced when the electrolyte contains polymer. These fluctuations reflect the flow fluctuations in the wall region, and so this phenomenon would appear to indicate one of the causes of drag reduction. Further discussion follows (5.3).

5.2.5 Intensity of Mass Transfer Fluctuations (Figures 4.26 and 4.27)

The intensity of the fluctuations in mass transfer coefficient is reduced when polymer is present in the electrolyte solution. This simply reflects the reductions in mean and standard deviation already noted. Since/
noted. Since the relative reduction in standard deviation is the greater, the intensity (standard deviation divided by mean) is reduced.

5.2.6 **Macroscale of Turbulent Fluctuations** (Figure 4.29-4.33)

The macroscale of the fluctuations in mass transfer coefficient is increased in the presence of polymer. This indicates an increase in the largest time scale of the turbulent fluctuations in the boundary layer, and this phenomenon would, therefore, seem to play a part in the mechanism of polymer drag reduction (see 5.3 below).

5.2.7 **Microscale of Turbulent Fluctuations** (Figures 4.36 and 4.37)

The microscale of the mass transfer coefficient fluctuations is of the same order of magnitude as the macroscale described above, and is increased by a similar amount on the addition of polymer. This parameter reflects the smallest time over which the boundary layer turbulent fluctuations take place, and its increase would thus appear to be part of the mechanism of drag reduction (5.3).

5.2.8 **Convection Velocity** (4.6.2)

The convection velocity of the turbulent eddies along the pipe wall is approximately equal to the mean flow velocity. It is not affected by the addition of polymer to the electrolyte solution.

5.2.9 **Degree of Distortion** (4.6.3)

The amount of distortion of the mass transfer fluctuations in passing between two fixed points on the pipe wall is reduced when polymer is added to the electrolyte solution. Since it implies an increase in the stability of the fluctuations, this phenomenon would seem to be an important factor in the mechanism of drag reduction (5.3).
5.2.10 **Turbulent Spectrum** (Figures 4.39-4.42)

The form of the spectral density function for the fluctuations in mass transfer coefficient does not seem to be altered by the addition of polymer to the electrolyte solution.

5.3 **Discussion**

Whilst no detailed quantitative analysis of drag reduction is possible in the light of the present results, the implications of the above conclusions are considerable. It seems that the presence of polymer molecules causes considerable changes in the flow structure adjacent to the pipe wall. These changes are both spatial and temporal - possibly the reason why purely time-scaling or length-scaling approaches have thus far failed to produce an adequate explanation for drag reduction. Consideration of the implications of each of these changes enables a qualitative picture of the mechanism of drag reduction to be built up.

The reduction in the standard deviation of the mass transfer fluctuations (5.2.4) implies a reduction in the size (amplitude) of the turbulent eddies in the boundary layer. This damping is not selective, but applies equally over the whole range of frequencies of the eddies (5.2.13). How the polymer molecules cause the damping is not clear, but further quantitative analysis of the phenomenon may yield insight here.

The other experimental conclusions lead to implications involving time-scale effects. Turbulence macroscales (5.2.6) and micro-scales (5.2.7) are both increased in the presence of polymer. This would seem to indicate an enhanced stability of the boundary layer fluctuations.
layer fluctuations. Further, more direct, evidence for this is provided by the reduced amount of crosscorrelation distortion in the presence of polymer (5.2.9).

With these conclusions in mind, a tentative and, of necessity, incomplete model of boundary layer turbulence in a drag reducing solution is proposed. It appears that the turbulent eddies originate in the bulk (turbulent core) of the fluid. They penetrate the boundary layer and continue, with unabated velocity (5.2.8), losing energy to the slower-moving fluid around them. This process of decay is three-dimensional, in that energy is lost radially and circumferentially, as well as axially. Eventually, the eddies may return to the turbulent core. Alternatively, it may be that they eventually dissipate all their energy and merge with the slower-moving boundary layer fluid, although no evidence for the existence of slower-moving (decelerating) eddies has been found.

The overall picture (Figure 5.1) is not changed by the presence of polymer in the fluid. However, the size of the eddies is reduced, and their stability is increased (Figure 5.2). This reduced rate of decay causes a reduction in the rate of transfer of mass, heat or momentum to the solid wall, and hence the reduction in friction factor which is known as drag reduction.

5.4 Recommendations for Further Work

5.4.1 Present Results

There is further scope for the analysis of the data obtained from the present series of experiments. In particular, it may be possible to obtain spectral density functions in some form which shows up/
**Figure 5.1** Proposed Turbulence Model: No Polymer Present

**Figure 5.2** Proposed Turbulence Model: Polymer Added

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Amplitude</td>
</tr>
<tr>
<td>t</td>
<td>Time scale (stability)</td>
</tr>
<tr>
<td>f</td>
<td>Frequency distribution</td>
</tr>
<tr>
<td>u</td>
<td>Forward speed</td>
</tr>
</tbody>
</table>
shows up a difference between the spectra from solutions with and without polymer. Analysis for frequencies below 0.1 Hz. (the minimum investigated during the project) may prove fruitful. However, it is unlikely that increasing the upper frequency limit above 1500 Hz. (the limitation of the tape recorder) would produce useful results, since it has been shown (4.7) that the relative power is greatly diminished in this region.

5.4.2 Quantitative Analysis of Flow Field

Mathematical treatments for relating the mass transfer fluctuations to velocity field fluctuations in the boundary layer have been developed (39, 41, 42, 43). Although these techniques are still in the course of development, their use in the analysis of the present results would enable the conclusions described above to be extended on a more quantitative basis.

One particular aspect of the problem which could well repay investigation is consideration of the energy levels associated with the process of turbulent decay in the boundary layer. Once the size, time scale and frequency distribution of the turbulent fluctuations are known, it should be possible to determine the energy which will be given up by a particular eddy on decaying. Hence the difference in this decay energy when polymer is added could be calculated, and attempts made to relate this to the energy levels associated with the polymer molecules.

5.4.3 Additional Experiments

Additional experiments using the "surrounded" electrode configuration would undoubtedly yield useful information, since this creates a/
creates a concentration boundary layer which corresponds more closely to the normal turbulent boundary layer. Further crosscorrelation measurements between pairs of electrodes at increasing separations would enable information to be obtained on the lateral decay of the turbulent fluctuations. Alternative polymers to "Polyox" could be used, since this would assist the 'energy level' calculations mentioned above (5.4.2).
APPENDIX A.1

%COMMENT A.1 FLOW ANALYSIS PROGRAM

%COMMENT COMPUTES REYNOLDS NUMBERS AND FRICTION FACTORS.

%REAL SLONG
%BEGIN

%COMMENT DECLARATIONS
%REAL DATE, TEMP, G, RE, DP, FF, TFF, DR, PPM, U, D, RHO
%REAL V
%REAL PMR, CORRECTION, TOTAL
%INTEGER I, N
%ROUTINE %SPEC HEADING
%ROUTINE %SPEC FLOWDATA
%ROUTINE %SPEC PDDATA
%ROUTINE %SPEC THEORY
%REAL %SPEC REYNOLDSNO
%REAL %SPEC FRICFACT

%COMMENT READ INITIAL DATA
1: READ (DATE) ; !SIX DIGIT NUMBER E.G. 040370
%IF DATE=0 %THEN -> 3
READ (TEMP) ; !DEG. CENTIGRADE
READ (PPM) ; !POLYMER CONCENTRATION
READ (N) ; !NUMBER OF EXPTS. IN SET
READ (CORRECTION) ; !MANOMETER CORRECTION (CM.)

%COMMENT CONTROL PROGRAM
HEADING ; !PRINT HEADINGS
TOTAL=0
%CYCLE I=1, 1, N ; !FOR EACH EXPT.
FLOWDATA ; !READ IN DATA, CALCULATE RE.
RE=REYNOLDSNO ; PRINT (RE, 5, 0)
PDDATA ; !CALCULATE PRESSURE DROP, FF
FF=FRICFACT ; PRINT (FF, 1, 4)
TFF=0.079*EXP(-0.25*LOG (RE)); DR=100*(TFF-FF)/TFF
SPACE ; PRINT (TFF, 1, 4)
%IF DR>=0 %AND PPM>0 %THEN PRINT (DR, 2, 1)
%IF CORRECTION=0 %THEN THEORY
NEWLINE
%REPEAT
%IF CORRECTION=0 %THEN %START
TOTAL=TOTAL/N
NEWLINES (2) ; %PRINTTEXT 'CORRECTION FACTOR SHOULD BE'
PRINT (TOTAL, 1, 2)
%FINISH
NEWPAGE
-> 1 ; !NEXT DATE OF RUN

3: NEWPAGE ; %STOP
%COMMENT HEADING SUBROUTINE
%ROUTINE HEADING
NEWLINES(5)
%PRINTTEXT ' EXPERIMENT DATE : ' ; NEWLINES(2)
DATE=DATE/10**4 ; WRITE(INTPT(DATE),2)
DATE=FRACPT(DATE)*10**2
%PRINTTEXT '/' ; WRITE(INTPT(DATE),2)
DATE=FRACPT(DATE)*10**2
%PRINTTEXT ' / ' ; WRITE(INTPT(DATE),2) ; NEWLINES(2)
%PRINTTEXT ' EXPERIMENT REF. NO. : ' ; NEWLINES(4)
%PRINTTEXT ' P.D. MANOMETER CORRECTION : '
PRINT(CORRECTION,1,2)
%PRINTTEXT ' CMS. ' ; NEWLINES
%PRINTTEXT ' WATER TEMPERATURE = ' ; PRINT(TMP,1)
%PRINTTEXT ' DEG.C ' ; NEWLINES
%PRINTTEXT ' POLYOX CONCENTRATION = ' ; PRINT(PPM,1,2)
%PRINTTEXT ' W.P.P.M. ' ; NEWLINES
%PRINTTEXT ' VALVE SET. ABSOLUTE FLOW
%PRINTTEXT ' MEASUREMENT REYNOLDS
%PRINTTEXT ' P.D. MANOMETER FRICTION THEOR. ' 
NEWLINES
%PRINTTEXT ' LB/HR. TIME H1 V1 H2
%PRINTTEXT ' V2 M/SEC LB/HR NUMBER CMS. ' 
%PRINTTEXT ' TYPE DP FACTOR F.F. %DR' 
NEWLINES(3)
%END

%COMMENT THEORETICAL FRICTION FACTOR SUBROUTINE
%ROUTINE THEORY
%REAL TPMR
NEWLINES ; SPACES(56)
TPMR=PMR*TFF/FF
PRINT(TPMR,2,2)
%PRINTTEXT ' PARA ' ; SPACES(8)
PRINT(TFF,1,4)
%PRINTTEXT '('
PRINT(TPMR-PMR,1,2)
%PRINTTEXT ')'
TOTAL=TOTAL+TPMR-PMR
%END
%COMMENT FLOW PARAMETER SUBROUTINE
%ROUTINE FLOWDATA
%REAL VALVE,MR,FR,TIME,H1,H2,V1,V2,A
2: READ(VALVE) ;!VALVE SETTING (LB./HR.)
%IF VALVE=-1 %THEN %START
READ(TEMP)
%PRINTTEXT 'WATER TEMP. CHANGES TO'
PRINT(TEMP,2,1)
%PRINTTEXT ' DEG.C.' ; NEWLINE
->2
%FINISH
%IF VALVE=-2 %THEN %START
READ(PPM)
%PRINTTEXT 'POLYOX CONCENTRATION CHANGES TO'
PRINT(PPM,3,0)
%PRINTTEXT ' P.P.M.' ; NEWLINE
->2
%FINISH
%IF VALVE=-3 %THEN %START
READ(CORRECTION)
%PRINTTEXT 'MANOMETER CORRECTION CHANGES TO'
PRINT(CORRECTION,1,2) ; NEWLINE
->2
%FINISH
SPACE ; PRINT(VALVE,4,0)
SPACES(3)
READ(TIME) ;!FLOW MEASURING TIME (MINS.)
SPACES(2) ; PRINT(TIME,2,1)
READ(H1) ;!INITIAL HEIGHT IN TANK (CM.)
SPACES(2) ; PRINT(H1,2,1)
V1=((-0.002092*H1+0.2299)*H1+11.67)*H1+84.01
SPACE ; PRINT(V1,4,0)
READ(H2) ;!FINAL HEIGHT IN TANK (CM.)
SPACE ; PRINT(H2,2,1)
V2=((-0.002092*H2+0.2299)*H2+11.67)*H2+84.01
SPACE ; PRINT(V2,4,0)
V=(V1-V2)/TIME ;!FLOW RATE (L/MIN)
G=135.0*V ;!FLOW RATE(LB./HR)
V=V/60 ;!L/SEC
V=V/1000 ;!M/SEC
D=0.02908 ;!M
A=π*D**2/4 ;!M2
U=V/A ; SPACES(2) ; PRINT(U,1,4) ;!VELOCITY (M/SEC)
SPACE ; PRINT(G,4,0) ; SPACES(2)
%END
%COMMENT PRESSURE DROP SUBROUTINE
%ROUTINE PDDATA
READ(PMR) ;!P.D. MANOMETER READING (CM.)
ZIF PMR+CORRECTION<=0 ZTHEN %START SPACE ; %PRINTTEXT 'NC'; PRINT(PMR,1,2) ; ->4
%FINISH
PMR=PMR+CORRECTION
SPACES(2) ; PRINT(PMR,2,2)
4: %PRINTTEXT 'PARA'
%COMMENT DP = PRESSURE DROP (N/M2)
DP=PMR*0.248*249.089/2.54 ;!PARA DENS.=0.773, RD=0.248
PRINT(DP,4,1)
SPACE
%END

%COMMENT FUNCTION = REYNOLDS NUMBER
%REALFN REYNOLDSNO ;!RE = RHO*U*D/MU
%REAL MU,TC
RHO=1021 ;!DENSITY(KG/M3)
TC=TEMP-8.435
MU=2.1482*(TC+SORT(8078.4+TC**2))-120
MU=1/MU ;!WATER VISCOSITY (CP.)
MU=MU/10
MU=MU*1.109 ;!SOLN. VISCOSITY
%RESULT=RHO*U*D/MU
%END

%COMMENT FUNCTION = FRICTION FACTOR
%REALFN FRICTFACT ;!FF = D*DP/2*RHO*U**2*DX
%REAL DX
DX=0.736
%RESULT=D*DP/(2*RHO*DX*U**2)
%END

%END OF %PROGRAM
APPENDIX A.2

/A.2  SAMPLER PROGRAM
/
/ANALOG-DIGITAL CONVERSION : SINGLE CHANNEL
/INCORPORATING ACCURACY CHECK
/
*

0001 0000  TIMER, 0
0002 4001  K 4001, 4001
0003 0377  K 377, 377
   *10
0010 0000  P1, 0
0011 0177  PNT1, STK
0012 0000  NSAMP, 0
0013 0000  CNTR, 0
0014 7773  BITS, -5
0015 7777  CHK1, 7777
0016 7777  CHKO, 7777
0017 0000  TEMP, 0
   *20

0020 7200  BEGIN CLA
0021 6026  PLS
0022 1125  TAD K 7777
0023 3015  DCA CHK1
0024 1125  TAD K 7777
0025 3016  DCA CHK0
0026 7402  HLT
0027 7404  DSR
0030 7041  CIA
0031 3001  DCA TIMER
0032 7402  HLT
0033 7404  DSR
0034 7041  CIA
0035 3012  DCA NSAMP
0036 4127  JMS SET
   /SET STACK AND COUNTER

0037 4136  GO,  JMS CLOCK
0040 6532  ADCV
0041 6531  ADSF
0042 5041  JMP -1
0043 6534  ADRB
0044 3410  DCA I P1
0045 2013  ISZ CNTR
0046 5037  JMP GO
0047 4127  JMS SET
   /RESET STACK AND COUNTER
0050 4147  JMS RUNOUT
0051 7402  HLT
   /SAMPLE

0054 6532  ADCV
0055 6531  ADSF
0056 5041  JMP -1
0057 6534  ADRB
0058 3411  DCA I P1
0059 2013  ISZ CNTR
0060 5037  JMP GO
0061 4127  JMS SET
   /RESET STACK AND COUNTER
0064 7402  HLT
   /SAMPLE
0052  1410  CHECK, TAD I P1  ; GET SAMPLE
0053   3017  DCA TEMP  ; COMPARE WITH CHECKS
0054  1017  TAD TEMP
0055  0015  AND CHK1
0056  3015  DCA CHK1
0057  1017  TAD TEMP
0060  7040  CMA
0061  0016  AND CHKO
0062  3016  DCA CHKO
0063  2013  ISZ CNTR
0064  5052  JMP CHECK
0065  1015  TAD CHK1
0066  4165  JMS FIXOUT
0067  1016  TAD CHKO
0070  4165  JMS FIXOUT
0071  3017  DCA TEMP
0072  1015  TAD CHK1
0073  1016  TAD CHKO
0074  7104  CLL RAL
0075  7420  SNL
0076   5101  JMP *.+3
0077  2017  ISZ TEMP
0100  5074  JMP *.4
0101  7200  CLA
0102  1017  TAD TEMP
0103  4157  JMS PUNCH  ; PUNCH NO. OF CONSTANT BITS
0104  4157  JMS PUNCH
0105  1017  TAD TEMP
0106  1124  TAD M5
0107  7500  SMA
0110  7240  CLA CMA
0111  3017  DCA TEMP
0112  4127  JMS SET  ; RESET STACK AND COUNTER
0113  1017  GO1, TAD TEMP
0114  3014  DCA BITS
0115  1410  TAD I P1
0116  1002  TAD K4001
0117  7041  CIA
0120  4165  JMS FIXOUT
0121  2013  ISZ CNTR
0122  5113  JMP GO1
0123  5020  JMP BEGIN

0124  7773 M5, -5
0125  7777 K7777, 7777
0126  7600 M200, -200

/
0127 0000 SET, O
0130 7200 CLA
0131 1011 TAD PNT1
0132 3010 DCA P1
0133 1012 TAD NSAMP
0134 3013 DCA CNTR
0135 5527 JMP I SET

0136 0000 CLOCK, O
0137 1001 TAD TIMER
0140 3017 DCA TEMP
0141 3000 LOOP, DCA
0142 3000 DCA
0143 3000 DCA
0144 2017 ISZ TEMP
0145 5141 JMP LOOP
0146 5536 JMP I CLOCK

0147 0000 RUNOUT, O
0150 7200 CLA
0151 1126 TAD M200
0152 3017 DCA TEMP
0153 4157 JMS PUNCH
0154 2017 ISZ TEMP
0155 5153 JMP *-2
0156 5547 JMP I RUNOUT

0157 0000 PUNCH, O
0160 6021 PSF
0161 5160 JMP *-1
0162 6026 PLS
0163 7200 CLA
0164 5557 JMP I PUNCH

0165 0000 FIXOUT, O
0166 7110 CLL RAR
0167 2014 ISZ BITS
0170 5166 JMP *-2
0171 7004 RAL
0172 0003 AND K377
0173 4157 JMS PUNCH
0174 1124 TAD M5
0175 3014 DCA BITS
0176 5565 JMP I FIXOUT

0177 0000 STK, O
APPENDIX A.3

%COMMENT A.3 AUTOCORRELATION PROGRAM

%COMMENT COMPUTES AUTOCORRELATION FUNCTION, AND
%COMMENT TRANSFERS TO DIRECT-ACCESS FILE (DISK)

%COMMENT FILE REFERENCES
%COMMENT SQFILE01 IS BINARY DATA INPUT FILE (BINTEST ON B9383)
%COMMENT SQFILE11-SQFILE(10+NT) ARE NEWLY CREATED TAPE FILES
%COMMENT THEY ARE PERMANENT, ON B9384 (BINTEST1 ETC.)
%COMMENT DAFILE21-DAFILE(20+NT) ARE NEWLY CREATED DA FILES
%COMMENT THEY ARE PERMANENT, ON RCC318

%BEGIN
%COMMENT DECLARATIONS
%EXTERNALROUTINESPEC OPENSQ (%INTEGER CHAN)
%EXTERNALROUTINESPEC CLOSESQ (%INTEGER CHAN)
%EXTERNALROUTINESPEC READSQ (%INTEGER CHAN, %NAME BEGIN, END)
%EXTERNALROUTINESPEC WRITESQ (%INTEGER CHAN, %NAME BEGIN, END)
%EXTERNALROUTINESPEC OPENDA (%INTEGER CHAN)
%EXTERNALROUTINESPEC CLOSEDA (%INTEGER CHAN)
%EXTERNALROUTINESPEC WRITEDA (%INTEGER CHAN, %INTEGERNAME %C
%SECT, %NAME BEGIN, END)
%EXTERNALROUTINESPEC SET RETURN CODE (%INTEGER N)
%EXTERNALROUTINESPEC CPUPTIME
%EXTERNALROUTINESPEC DATE
%INTEGER I,J,K,L
%INTEGER NT,NS,N,MAXM
%INTEGER REF,TAPE, SERIES
%INTEGER RECCTR,CHK1,CHK0,BITS
%INTEGER SECT
%REAL SD,SKEW,KURT,INTENS,EXTRA,DELTA
%REAL MEAN,SUM2,SUM3,SUM4,ACC
%REAL TIME
%REAL CORRTAB,DCORRTAB
%REAL COVO,DCVO
%BYTEINTEGERARRAY DATA(1:192); !USUALLY ONLY 96, IMP <=100
%REALARRAY X(1:3600); !IMPLIES BLKSIZE=3600
%REALARRAY COV,DCOV,COV,DCOV,COV,DCOV(0:250); !MAXM<=249
%REALARRAY DADATA(1:550)

%COMMENT OPEN FILES
OPENSQ(01); RECCTR=0 ;!NUMBER OF TAPES
READ(NT)
%CYCLE TAPE=1,1,NT
OPENSQ(10+TAPE)
OPENDA(20+TAPE)
SECT=1
READ(NS) ;!OPEN NEW TAPE FILE
;!OPEN NEW DA DATA FILE
;!NO. OF DATA SETS ON TAPE
%COMMENT READ DATA AND INITIALISE
%CYCLE SERIES=1,1,NS
NEWPAGE ; TIME=CPUTIME
READ(REF)
%PRINTTEXT 'DATE ' ; PRINTSTRING(DATE)
%PRINTTEXT ' SERIES REFERENCE NUMBER ' ; WRITE(REF,6)
NEWLINES(4)
READ(MAXM)
%PRINTTEXT ' NUMBER OF LAGS (=249)
READ(DELTA)
N=0 ; MEAN=0 ; SUM2=0 ; SUM3=0 ; SUM4=0
SD=0 ; SKEW=0 ; KURT=0 ; INTENS=0
EXTRA=0 ; CHK1=0 ; CHK0=0 ; BITS=0
%CYCLE I=1,1,192 ; DATA(I)=0 ; %REPEAT
%CYCLE I=1,1,3600 ; X(I)=0 ; %REPEAT
%CYCLE I=0,1,250
CDV(I)=0 ; DCOV(I)=0 ; CORR(I)=0 ; DCORR(I)=0
%REPEAT
%CYCLE I=1,1,550 ; DATA(I)=0 ; %REPEAT

%COMMENT UNPACK DATA SET
%CYCLE I=1,1,96
RECCTR=RECCTR+1
READSQ(01,DATA(1),DATA(96))
WRITESQ(10+TAPE,DATA(1),DATA(96))
L=96
%CYCLE J=1,1,L
1: ->2 %UNLESS DATA(J)=0
%IF N=0 %THEN ->4
%CYCLE K=0,1,20
->3 %UNLESS DATA(J+K)=0
%IF J+K=96 %THEN ->5
%REPEAT
->5
2: %IF N=0 %THEN %START
%IF J+4=96 %THEN %START
RECCTR=RECCTR+1
READSQ(01,DATA(97),DATA(192))
WRITESQ(10+TAPE,DATA(97),DATA(192))
L=192
->3
%FINISH
->3 %UNLESS DATA(J+3)=0
CHK1=DATA(J) ; CHK0=DATA(J+1) ; BITS=DATA(J+2)
EXTRA=512*CHK1/2**(8-BITS)
J=J+4 ; ->1
%FINISH
3: N=N+1 ; X(N)=DATA(J)+EXTRA ; MEAN=MEAN+X(N)
4: %REPEAT
%REPEAT

%COMMENT CALCULATE PARAMETERS
5: MEAN=MEAN/N
%CYCLE I=1,1,N
X(I)=X(I)-MEAN
SUM2=SUM2+X(I)**2 ; SUM3=SUM3+X(I)**3
SUM4=SUM4+X(I)**4
%REPEAT
SD = SQRT(SUM2/N)
SKEW = SUM3/SQRT(SUM2**3)
KURT = SUM4/SUM2**2
INTENS = SD/MEAN

%COMMENT DO AUTOCORRELATION FOR MAXM LAGS
- >6 %UNLESS N=1024 %OR N=2048 %OR N=3076
%CYCLE I=0,1,MAXM+1
ACC=0
%CYCLE J=1,1,N-I
ACC=ACC+X(J)*X(J+I)
%REPEAT
COV(I)=ACC/N
%REPEAT
DCOV(O)=2*(COV(O)-COV(1))
COVO=COV(O) ; DCOVO=DCOV(O) ; CORR(O)=1 ; DCORR(O)=1
%CYCLE I=1,1,MAXM
DCOV(I)=-COV(I-1)+2*COV(I)-COV(I+1)
CORR(I)=COV(I)/COVO ; DCORR(I)=DCOV(I)/DCOVO
%REPEAT

%COMMENT PRINT SERIES DATA
NEWLINES(2)
%PRINTTEXT 'TAPE NUMBER' ; WRITE(TAPE,6)
%PRINTTEXT 'FINAL BLOCK REF.' ; WRITE(RECTR,4)
NEWLINES(2)
%PRINTTEXT 'SERIES NUMBER' ; WRITE(SERIES,6)
NEWLINES(2)
%PRINTTEXT 'SERIES REFERENCE' ; WRITE(REF,6)
NEWLINES(4)
%PRINTTEXT 'NUMBER OF SAMPLES' ; WRITE(N,6)
NEWLINES(2)
%PRINTTEXT 'SAMPLE INTERVAL' ; PRINT(Delta,6,8)
%PRINTTEXT 'SECS' ; NEWLINES(2)
%PRINTTEXT 'SERIES MEAN' ; PRINT(MEAN,6,4)
%PRINTTEXT '(EXTRA = ' ; PRINT(EXTRA,3,0)
%PRINTTEXT ')'; NEWLINES(2)
%PRINTTEXT 'STANDARD DEVIATION' ; PRINT(SD,6,4)
NEWLINES(2)
%PRINTTEXT 'SKEWNESS' ; PRINT(SKEW,6,4)
NEWLINES(2)
%PRINTTEXT 'KURTOSIS' ; PRINT(KURT,6,4)
NEWLINES(2)
%PRINTTEXT 'INTENSITY' ; PRINT(INTENS,6,4)
NEWLINES(4)
%PRINTTEXT 'NUMBER OF AUTOCORRELATION LAGS' ; WRITE(MAXM,6) ; NEWLINES(2)
%PRINTTEXT 'STRAIGHT COVARIANCE - ZERO LAG' ; PRINT(COVO,6,4) ; NEWLINES(2)
%PRINTTEXT 'DIFFERENCED COVAR. - ZERO LAG' ; PRINT(DCOVO,6,4) ; NEWLINES(4)
%PRINTTEXT 'DATA STORED ON DAFILE' ; WRITE(20+TAPE,2)
%PRINTTEXT 'STARTING AT SECTION' ; WRITE(SECT,2)
%COMMENT TABULATE AND PLOT AUTOCORRELATION FUNCTION
NEWLINES(4); %PRINTTEXT 'STRAIGHT AND DIFFERENCED AUTOCORRELATION COEFFICIENTS';NEWLINES(3)
SPACES(26); %CYCLE I=-10;10
PRINT(I/10,2,1); SPACES(15)
%REPEAT; NEWLINE
%PRINTTEXT 'LAG  CORR  DCORR  T'
%CYCLE I=1;1,4; %PRINTTEXT '*****************************
%REPEAT
%CYCLE I=0;1;MAXM
CORRTAB=CORR(I); DCORRTAB=DCORR(I)
DADATA(20+I)=CORRTAB; DADATA(30+MAXM+1)=DCORRTAB
WRITE(I,3); SPACES(2); PRINT(CORRTAB,1,4); SPACES(2)
PRINT(DCORRTAB,14); SPACES(6)
CORRTAB=40*CORRTAB; DCORRTAB=40*DCORRTAB
%CYCLE J=-40;40
%IF J=INT(CORRTAB)THEN %START
 %PRINTTEXT 'X'; ->10
 %FINISH
%IF J=INT(DCORRTAB)THEN %START
 %PRINTTEXT '+'; ->10
 %FINISH
%IF J=0THEN %START
 %PRINTTEXT '*'; ->10
 %FINISH
SPACE
10:%REPEAT
NEWLINES
%REPEAT

%COMMENT FILE DATA ON DA FILE
DADATA(1)=REF; DADATA(2)=TAPE; DADATA(3)=SERIES
DADATA(4)=N; DADATA(5)=DELTA; DADATA(6)=MEAN
DADATA(7)=SD; DADATA(8)=MAXM
WRI TEDA(20+TAPE,SECT,DADATA(1),DADATA(2*MAXM+40))
SECT=SECT+1
NEWLINES(4)
%PRINTTEXT 'NEXT FILE SECTION IS'; WRITE(SECT,2)
%PRINTTEXT 'ON DAFILE'; WRITE(20+TAPE,2); NEWLINE
%PRINTTEXT 'CPU TIME FOR THIS SET'; PRINT(CPUTIME-TIME,3,0)
%PRINTTEXT 'SECS'
%REPEAT
CLOSES0(10+TAPE)
CLOSEDA(20+TAPE)
%REPEAT
CLOSES0(01)
SET RETURN CODE (100)
=%ENDOFPROGRAM
%COMMENT A.4 SPECTRUM PROGRAM
%COMMENT COMPUTES SPECTRAL DENSITY FUNCTION FROM ACF

%BEGIN

%COMMENT DECLARATIONS
%EXTERNAL LONGREALFNSPEC CPU TIME ; %REAL TIME ; TIME = CPU TIME
%EXTERNAL ROUTINESPEC OPENDA (%INTEGER CHAN)
%EXTERNAL ROUTINESPEC CLOSED A (%INTEGER CHAN)
%EXTERNAL ROUTINESPEC READDA (%INTEGER CHAN, %INTEGERNAME %C
SECT, %INTEGER BEGIN, END)
%EXTERNAL ROUTINESPEC WRITEDA (%INTEGER CHAN, %INTEGERNAME %C
SECT, %INTEGER BEGIN, END)
%EXTERNAL ROUTINESPEC DATE
%ROUTINESPEC AUTOSPEC (%REALARRAYNAME CDV)
%REAL DELTA, MEAN, SD
%REAL COVO, DCVO
%INTEGER FILE, SECT, I, J, K
%INTEGER OLDSECT, OLD FILE
%INTEGER RECORDING, RECTAPE, RECTR K, RECKSTART
%REALARRAY DADATA(1:1000), CORR, DCORR(0:250)
%INTEGER REF, TAPE, SERIES, N, MAXM
%INTEGER ENDER, WHICHSPEC

ODLF I LE=0 ; OLDSECT=0

%COMMENT UNPACK DATA FROM DAF ILE
1: READ(FILE) ; %IF FILE=0 %THEN %STOP ; !WHICH DAF ILE?
OPENDA (FILE)
2: READ(SECT) ; %IF SECT=0 %THEN %STOP ; !SECT. OF DAF ILE
%IF FILE=ODLF FILE %AND SECT=OLDSECT %THEN -> 6
OLDSECT=SECT ; OLD FILE=FILE
%CYCLE I=1,1,256 ; DADATA(I)=0 ; %REPEAT
%CYCLE I=0,1,256 ; CORR(I)=0 ; DCORR(I)=0 ; %REPEAT
COVO=0 ; DCVO=0
READDA(FILE, SECT, DADATA(1), DADATA(256))
REF=INT(DADATA(1)) ; TAPE=INT(DADATA(2))
SERIES=INT(DADATA(3)) ; N=INT(DADATA(4))
DELTA=DADATA(5) ; MEAN=DADATA(6) ; SD=DADATA(7)
MAXM=INT(DADATA(8))
COVO=DADATA(9) ; DCVO=DADATA(10)
%IF MAXM>113 %THEN %START
SECT=SECT+1
READDA(FILE, SECT, DADATA(257), DADATA(30+2*MAXM))
%FINISH

J=0
%CYCLE I=20,1,20+MAXM
CORR(J)=DADATA(I)
J=J+1
%REPEAT
J=0
%CYCLE I=30+MAXM,1,30+2*MAXM
DCORR(J)=DADATA(I)
J=J+1
%REPEAT
ZCOMMENT PRINT OUT SERIES DATA

6: NEWPAGE
%PRINTTEXT 'DATE ' ; PRINTSTRING(DATE)
%PRINTTEXT ' SERIES REFERENCE NUMBER'
WRITE(REF,6) ; NEWLINES(2)
%PRINTTEXT ' TAPE NUMBER'
WRITE(TAPE,6) ; SPACES(20)
%PRINTTEXT ' NOMINAL FLOW RATE'
PRINT(DADATA(12),4,0) ; %PRINTTEXT ' LB./HR.' ; NEWLINE
%PRINTTEXT ' SERIES NUMBER'
WRITE(SERIES,6) ; SPACES(20)
%PRINTTEXT ' ACTUAL FLOW RATE'
PRINT(DADATA(13),4,1) ; %PRINTTEXT ' LB./HR.' ; NEWLINE
%PRINTTEXT ' SERIES REFERENCE'
WRITE(REF,6) ; SPACES(20)
%PRINTTEXT ' REYNOLDS NUMBER'
PRINT(DADATA(14),5,0) ; NEWLINE
%PRINTTEXT ' NUMBER OF SAMPLES'
WRITE(N,6) ; SPACES(20)
%PRINTTEXT ' FRICTION FACTOR'
PRINT(DADATA(15),2,4) ; NEWLINE
%PRINTTEXT ' SAMPLE INTERVAL'
PRINT(DELTA,6,8) ; %PRINTTEXT ' SECS.' ; NEWLINE
%PRINTTEXT ' SERIES MEAN'
PRINT(MEAN,6,4) ; SPACES(15)
%PRINTTEXT ' POLYOX CONCENTRATION'
PRINT(DADATA(16),31) ; %PRINTTEXT ' W.P.P.M.' ; NEWLINE
%PRINTTEXT ' STANDARD DEVIATION'
PRINT(SD,6,4) ; SPACES(15)
%PRINTTEXT ' % DRAG REDUCTION

PRINT(DADATA(17),2,1) %UNLESS DADATA(17)=0
NEWLINES(2)
%PRINTTEXT ' NUMBER OF AUTOCORRELATION LAGS'
WRITE(MAXM,6) ; RECORDING=INT(DADATA(11))
RECTAPE=INT(RECORDING/100000)
RECTRK=INT(RECORDING/1000)-100*RECTAPE
RECSTART=RECORDING-100000*RECTAPE-1000*RECTRK
SPACES(20) ; %PRINTTEXT ' RECORDING TAPE'
WRITE(RECTAPE,2) ; %PRINTTEXT ' TRACK'; WRITE(RECTRK,1)
%PRINTTEXT ' STARTING AT'; WRITE(RECSTART,4)
NEWLINE
%PRINTTEXT ' INITIAL STRAIGHT COVARIANCE'
PRINT(COVO,6,4) ; NEWLINE
%PRINTTEXT ' INITIAL DIFFERENCED COVARIANCE'
PRINT(DCOVO,6,4) ; NEWLINES(2)
%PRINTTEXT ' TIME TO UNPACK AND PRINT DATA =
PRINT(CPUTIME-TIME,,1) ; %PRINTTEXT ' SECS.'
TIME = CPUTIME
%COMMENT DO REQUIRED SPECTRUM ANALYSIS
NEWLINES(6)
READ(WHICHSPEC)
! 0->SPEC BASED ON CORR, 1->SPEC BASED ON DCORR, 2->BOTH
%IF WHICHSPEC=0 %OR WHICHSPEC=2 %THEN %START
  %PRINTTEXT ' SPECTRUM BASED ON STRAIGHT AUTOCORRELATION'
  %PRINTTEXT ' COEFFICIENTS'
NEWLINES(2) ; AUTOSPEC(Corr)
NEWLINES(6) %FINISH
%IF WHICHSPEC=1 %OR WHICHSPEC=2 %THEN %START
  %PRINTTEXT ' SPECTRUM BASED ON DIFFERENCED AUTOCORRELATION'
  %PRINTTEXT ' COEFFICIENTS'
NEWLINES(2) ; AUTOSPEC(DCORR)
%FINISH
CLOSEDA(FILE)
->1
%COMMENT SPECTRUM SUBROUTINE
%ROUTINE AUTOSPEC(ZREALARRAYNAME COV)
%COMMENT COV MUST BE CORR OR DCORR IN THIS CASE
%COMMENT DECLARATIONS AND INITIAL CONDITIONS
%REAL MINLOG,MAXLOG,FREQ
%REAL C,VO,V1,V2
%INTEGER M,T,NT
%INTEGER MIN,MAX,STARS
%INTEGER BANDER
T=0 ; MAXLOG=0 ; MINLOG=100 ; MIN=100 ; MAX=0
READ(M) ; !FIRST AND HIGHEST TRUNCATION VALUE (<MAXM)
%REALARRAY W(1:4,1:M-1)
%REALARRAY SPEC,LOGSPEC(1:4,1:3*M)
%REALARRAY SPACER(1:4,1:3*M),TEMP(1:4)
%REALARRAY F,BAND,DF(1:4)
%REALARRAY FR,SP(1:480)
%INTEGERARRAY SYMBOL (1:4,1:3*M)
%INTEGERARRAY NU,NF,CODE,TP,FC(1:4)
%INTEGER S1<IP,TOTS
CODE(1)="X" ; CODE(2)="+" ; CODE(3)="*" ; CODE(4)="I"
NEWLINES(2) ; %PRINTTEXT 'TIME TO INITIALISE SPECTRUM = ' ; 
PRINT(CPUTIME-TIME,4,1) ; %PRINTTEXT ' SECS. ' ; TIME=CPUTIME
3: READ(M) ; %UNLESS T=0
%IF M=0 %THEN ->4
T=T+1
TP(T)=M ; !NUMBER OF TRUNCATION POINTS
NF(T)=3*M ; !NUMBER OF FREQUENCY POINTS
DF(T)=1/(2*DELTA*NF(T)) ; !DISTANCE BETWEEN FREQ. PTS.
BAND(T)=4/(3*M*DELTA) ; !BANDWIDTH FOR TVUE KEY WINDOW
NU(T)=INT((8*N)/(3*M)) ; !DEGREES OF FREEDOM
%COMMENT CALCULATE SPECTRA AND LOGSPECTRA
%CYCLE I=1,1,M-1
W(T,I)=0.5*(1+COS(I*M))
%REPEAT
%CYCLE I=1,1,NF(T)
C=COS(I/NF(T)) ; VO=0 ; V1=0
%CYCLE J=M-1,-1,1
V2=2*C*V1 - VO + W(T,J)*COV(J)
VO=V1 ; V1=V2
%REPEAT
SPEC(T,I)=2*DELTA*(COV(0)+2*(V1*C-VO))
%IF SPEC(T,I)<=0 %THEN LOGSPEC(T,I)=-100 %ELSE %C
LOGSPEC(T,I)=LOG(SPEC(T,I))/LOG(10)
%IF LOGSPEC(T,I)=-100 %THEN ->8
%IF LOGSPEC(T,I)>MAXLOG %OR T*I=1 %THEN MAXLOG=LOGSPEC(T,I)
%IF LOGSPEC(T,I)<MINLOG %OR T*I=1 %THEN MINLOG=LOGSPEC(T,I)
8: %REPEAT
NEWLINES(2) ; %PRINTTEXT 'TIME TO CALCULATE SPECTRUM ' ; 
WRITE(T,2) ; %PRINTTEXT ' WAS ' ; PRINT(CPUTIME-TIME,4,1)
%PRINTTEXT ' SECS. ' ; TIME=CPUTIME
->3 %UNLESS T=4
4: NT=T
%COMMENT PRINT SPECTRA AND LOGSPECTRA DATA
NEWLINES(4)
ZPRINTTEXT 'SAMPLE INTERVAL = ' ; PRINT(DELTA,1,8)
ZPRINTTEXT ' SECS.' ; NEWLINES(2)
%CYCLE T=1,1,NT
WRITE(TP(T),3) ; ZPRINTTEXT ' TRUNCATION POINTS.'
SPACES(6) %UNLESS T=NT ; %REPEAT ; NEWLINE ; %CYCLE T=1,1,NT
WRITE(NF(T),3) ; ZPRINTTEXT ' FREQUENCY POINTS.'
SPACES(7) %UNLESS T=NT ; %REPEAT ; NEWLINE ; %CYCLE T=1,1,NT
PRINT(DF(T),3,2) ; ZPRINTTEXT ' C.P.S. INTERVAL.'
SPACES(6) %UNLESS T=NT ; %REPEAT ; NEWLINE ; %CYCLE T=1,1,NT
PRINT(BAND(T),3,2) ; ZPRINTTEXT ' C.P.S. BANDWIDTH.'
SPACES(5) %UNLESS T=NT ; %REPEAT ; NEWLINE ; %CYCLE T=1,1,NT
WRITE(NU(T),3) ; ZPRINTTEXT ' DEGREES OF FREEDOM.'
SPACES(5) %UNLESS T=NT ; %REPEAT ; NEWLINES(2)
%CYCLE T=1,1,NT
ZPRINTTEXT ' NF  FREQ  SPEC LOGSPEC '
%REPEAT ; NEWLINES(2)
%CYCLE I=1,1,NF(1)
%IF I=1 %THEN %START
FREQ=-DF(1)/2
%CYCLE T=1,1,NT
F(T)=DF(T)/2 ; FC(T)=1
%REPEAT
%FINISH
FREQ=FREQ+DF(1)
%CYCLE T=1,1,NT
TEMP(T)=1000 ; SPACER(T,I)=1000 ; SYMBOL(T,I)=0
%IF F(T)-FREQ >= DF(1)/2 %THEN SPACES(30) %ELSE %START
WRITE(FC(T),3) ; PRINT(F(T),4,2) ; SPACE
PRINT(SPEC(T,FC(T))13) ; SPACE
PRINT(TEMP(T)1,I) ; SPACE
SPACES(2) %UNLESS TEMP(T)=-100
F(T)=F(T)+DF(T) ; FC(T)=FC(T)+1
%FINISH
%REPEAT
%CYCLE J=1,1,NT
%CYCLE T=1,1,NT
%IF TEMP(T)<SPACER(J,1) %THEN %START
%IF NT>1 %THEN %START
%CYCLE M=J,1,NT-1
SPACER(J+1,I)=SPACER(J,1)
SYMBOL(J+1,1)=SYMBOL(J,1)
%REPEAT
%FINISH
SPACER(J,1)=TEMP(T) ; SYMBOL(J,1)=CODE(T)
TEMP(T)=1000
%FINISH
%REPEAT
%REPEAT
NEWLINE
%REPEAT
NEWLINES(2) ; ZPRINTTEXT 'TIME TO PRINT SPECTRA = ';
PRINT(CPUTIME-TIMEZi, 1)
%PRINTTEXT ' SECS.' ; TIME=CPUTIME
%COMMENT PLOT OVERLAID LOGSPECTRA
NEWLINES(10)
MAX=INTPT(MAXLOG)+1 ; MIN=INTPT(MINLOG)
SPACES(10) ; STARS=INTPT(80/(MAX-MIN))
%CYCLE I=M IN,1,MAX
WRITE(I,I) ; SPACES(STARS-2) %UNLESS I=MAX
%REPEAT ; NEWLINE
SPACES(10) ; %PRINTTEXT 'T'
%CYCLE I=M IN,1,MAX-1
%CYCLE J=1,1,STARS-1 ; %PRINTTEXT '*' ; %REPEAT
%PRINTTEXT 'T' ; %REPEAT
%PRINTTEXT ' BANDWIDTHS ' ; NEWLINE
BANDER=0
%CYCLE I=1,1,NF(1)
F(1)=(I-1/2)*DF(1)
PRINT(F(1),4,2) ; SPACES ; %PRINTTEXT _?
SKIP=O ; TOTS=O
%CYCLE T=1,1,NT
%IF T=1 %THEN %START
%IF SPACER(T,I)=100 %THEN TOTS=O %ELSE %C
TOTS=INT(STARS*(SPACER(T,I)-MIN))
SPACES(TOTS)
PRINTSYMBOL(SYMBOL(T,I))
->5
%FINISH
%IF SPACER(T,I)=1000 %THEN ->7
SKIP=INT(STARS*(SPACER(T,I)-MIN)) - TOTS
%IF SKIP=0 %THEN ->5
TOTS=TOTS+SKIP
SPACES(SKIP-1)
PRINTSYMBOL(SYMBOL(T,I))
5: %REPEAT
7: %IF BANDER=0 %THEN %START
SPACES(STARS*(MAX-MIN)+2-TOTS)
%CYCLE T=1,1,NT
%IF F(I)<=BAND(T) %THEN %START
PRINTSYMBOL(CODE(T))
BANDER=BANDER+1
%FINISH
%IF F(I)>BAND(T) %THEN SPACE
SPACE
%REPEAT
%IF BANDER=0 %THEN BANDER=1 %ELSE BANDER=0
%FINISH
NEWLINE
%REPEAT
NEWLINES(2) ; %PRINTTEXT 'TIME TO PLOT SPECTRA = '
PRINT(CPUTIME-TIME,4,1) ; %PRINTTEXT ' SECS.' ; TIME=CPUTIME
NEWLINES(2)
%END

%END OF PROGRAM
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REFERENCES

45. Harrison, M. Reported in Ref. 39 (Reiss & Hanratty).
57. International Critical Tables 5:15.
61. Grant, J. "Sutton's Volumetric Analysis".