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## Chapter 1

## INTRODUCTION

## 1.1 SOME FUNDAMENTAL ASPECTS OF THE FLOW OF POLYMER SOLUTIONS

## 1.1.1 Fluid flow

If an external stress,  $\sigma$ , is exerted on a fluid, deformation sets in and goes on until the stress is removed. A steady state can be reached in which the rate of deformation is constant because the deformation process is retarded by internal frictional forces (refs 1,2).

In this book, the plane simple-shear type of flow of polymer solutions will be dealt with in which there is a non-zero component of velocity in only a single direction. Let us define a Cartesian coordinate system with axes  $x$ ,  $y$  and  $z$ , and put a real fluid between two infinite parallel plates a distance  $h$  apart which are perpendicular to the  $y$  axis and of which only one is moving with a constant velocity in the  $x$  direction (Fig. 1.1a). There exists a transverse velocity gradient (shear-rate),  $\dot{\gamma}$ , in the fluid.

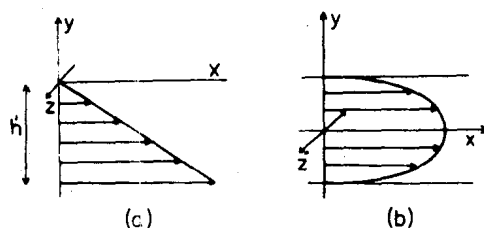


Fig. 1.1. The velocity profile of laminar flow between two parallel plates (a) and in capillary (b).

The velocity,  $\underline{v}$ , is given by eqn (1.1)

$$\underline{v} = (\dot{\gamma}y; 0; 0). \quad (1.1)$$

The higher the internal friction in the fluid, the higher is the stress which must be applied to maintain the velocity gradient. In this case the shear-stress is related to the shear-rate by eqn (1.2)

$$\sigma = \sigma_{xy} = \eta(dv_x/dy) = \eta \dot{\gamma} \quad (1.2)$$

where  $\eta$  is the viscosity coefficient or, simply, viscosity.

This simple shear-flow is achieved, e.g., in Couette cylinder viscometers (Couette flow), in capillary viscometers (Fig. 1.1b), and in cone-and-plate instruments (refs 1,2). Experiments in which the shear-rate is constant during one measurement yield the steady-state viscosity. If the shear-rate harmonically oscillates with an angular frequency, one obtains the dynamic viscosity.

### 1.1.2 The steady-state flow of polymer solutions

In a schematic representation of the dependence of  $\dot{\gamma}$  on  $\sigma$  for steady-state experiments (ref. 2), Newtonian flow is represented by a straight line passing through the origin of the coordinate system; the viscosity coefficient is then a constant. If the dependence is non-linear so that  $\eta$  depends on the shear-rate, we are concerned with non-Newtonian flow. There are several types of such behaviour.

For pseudoplastic and dilatant flow, the dependence of  $\dot{\gamma}$  on  $\sigma$  is linear at very low and at very high shear-rates (the first and the second Newtonian regions) while it is non-linear in the intermediate part. In the Newtonian regions, the viscosity coefficients ( $\eta_0$  for the first, and  $\eta_\infty$  for the second Newtonian region) are constant but not equal. If, in the intermediate part, the ratio  $\sigma/\dot{\gamma}$  is a decreasing function of  $\dot{\gamma}$  so that the viscosity coefficient (or, better, the apparent viscosity coefficient) decreases with increasing  $\dot{\gamma}$  (i.e.  $d\eta/d\dot{\gamma} < 0$ ), we are concerned with pseudoplastic flow; if  $d\eta/d\dot{\gamma} > 0$ , the flow is dilatant.

If flow does not set on until the yield value,  $\sigma_0$ , of the shear-stress has been overcome, it is called plastic flow. At  $\sigma < \sigma_0$ , the deformation of the system is elastic. If the dependence of  $\dot{\gamma}$  on  $\sigma$  is linear at  $\sigma > \sigma_0$ , we have Binghamian plastic flow. The ratio  $(\sigma - \sigma_0)/\dot{\gamma}$  is constant and is referred to as the plasticity,  $\eta_{pl}$ . If, on the other hand, the dependence is non-linear, the ratio  $(\sigma - \sigma_0)/\dot{\gamma}$  (the apparent plasticity) is not constant. We then have non-Binghamian plastic flow.

Time-dependent rheological properties are often observed with polymer solutions. We distinguish between thixotropy and rheopexy (negative thixotropy) (refs 1,2). In the former case, the viscosity diminishes with time, in the latter, it increases.

If viscosity measurements are performed at low concentrations, an important quantity called the intrinsic viscosity (limiting

viscosity number) can be evaluated. It is defined by eqn (1.3)

$$[\eta] = \lim_{c \rightarrow 0} [(\eta - \eta_s) / \eta_s c] \quad (1.3)$$

where  $\eta$  is the solution viscosity,  $\eta_s$  the solvent viscosity, and  $c$  the polymer concentration\*. The intrinsic viscosity is a characteristic function for the single molecule in solution. It depends on the molar mass, structure and conformation of the polymer molecules, on the solvent power, on temperature, and very often on the shear-rate and - in dynamic experiments - on the frequency.

The dimension of  $[\eta]$  is volume per unit mass so that this quantity has been aptly termed the "effective hydrodynamic specific volume" of the polymer in solution. It may be thought of as the sum of effective hydrodynamic volumes of the separate, non-interacting molecules that make up a gram of polymer.

In general, polymer solutions exhibit shear-rate-dependent viscosity, particularly at high  $\dot{\gamma}$ . This effect may arise from the properties of individual molecules and/or from intermolecular interactions. If only intermolecular interactions are involved, the effect vanishes at infinite dilution, and the intrinsic viscosity is independent of  $\dot{\gamma}$ . If the effect persists at infinite dilution, the intrinsic viscosity is a function of  $\dot{\gamma}$ .

Plastic flow and time-effects are observed only at finite concentrations, while the pseudoplastic type occurs also at infinite dilution.

### 1.1.3 The origin of additional frictional forces in solutions

The frictional force acting on the moving plate of area  $A$  (Fig. 1.1a) is

$$F \equiv \sigma A = \eta \dot{\gamma} A, \quad (1.4)$$

and the velocity of the displacement of the plate is

$$v = \dot{\gamma} h. \quad (1.5)$$

The work,  $W$ , dissipated per unit time and unit volume is

---

\*If the concentration  $c$  is expressed in  $\text{g/cm}^3$  (as will be done in this book), the dimension of  $[\eta]$  is  $\text{cm}^3/\text{g}$ . Very often, the intrinsic viscosity is expressed in  $\text{dl/g}$ .

$$W \equiv Fv/h'A = \dot{\eta}\dot{\gamma}^2. \quad (1.6)$$

It follows from eqn (1.6) that the increase in viscosity observed with polymer solutions is due to a greater amount of work necessary to maintain the velocity gradient constant, or - in other words - to overcome the frictional forces exerted by the dissolved molecules on the fluid.

The origin of the additional frictional forces can be understood on the basis of the following consideration. Let us introduce a spherical particle (of radius  $r_a$ ) in the flowing fluid. The particle endeavours to accommodate itself to the motion of the fluid as completely as possible. The centre of mass of the particle will assume the translational speed of the surrounding fluid, and the particle will experience uniform translation. It is convenient to introduce a Cartesian system of coordinates such that it takes part in the translational motion of the centre of mass, i.e. to identify the origin of the system with the centre of mass of the particle, and to study the behaviour of the particle with respect to this system.

Different parts of the particle are situated in different layers of the fluid which move with different velocities. The liquid tries to carry the particle so that the velocity at any point of the particle be the same as would be the velocity of the fluid in that point in the absence of the particle. That would be possible if the distances of these points could increase without limit. However, cohesive forces oppose this effect. The particle cannot follow the motion of the fluid exactly, and perturbs the flow. Here is the origin of the frictional forces.

These forces give rise to a torque which rotates the particle. The latter acquires an angular velocity  $\Omega$  of such magnitude

$$\Omega = \frac{1}{2} \dot{\gamma} \quad (1.7)$$

that the total torque is zero. The velocities at different points of the surface of the particle (points A,B,C,D in Fig. 1.2) differ in direction but not in absolute value, the latter being

$$u = \Omega r_a = \frac{1}{2} \dot{\gamma} r_a. \quad (1.8)$$

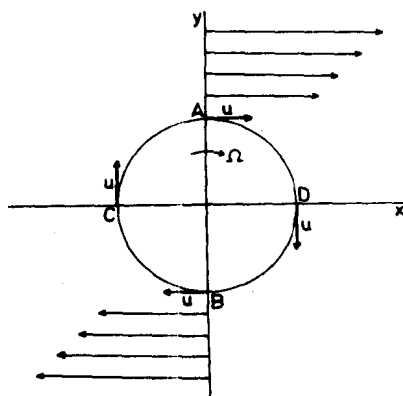


Fig. 1.2. A spherical particle in laminar flow.

In the absence of the particle, the velocity of the fluid,  $v^0$ , would be zero at points C and D, and it would be equal to  $\dot{\gamma}r_a$  at points A and B. Thus, there is a difference between the velocity of the points on the surface of the particle and the velocity which these points would have in the unperturbed fluid. For the points A, B, C, and D, the absolute value of this difference is

$$\Delta u = |v^0 - u| = \frac{1}{2} \dot{\gamma} r_a ; \quad (1.9)$$

for other points, it assumes other values but is always proportional to  $\dot{\gamma}r_a$ .

#### 1.1.4 The steady-state viscosity of polymer solutions

##### 1.1.4.1 General considerations

Theoretical interpretation of the flow properties of polymer solutions is based on the following ideas:

(i) The solvent is incompressible and its viscosity is Newtonian. The molecular structure of the solvent may be neglected, and the solvent is regarded as a continuous medium which exerts forces upon polymer molecules in the same way that a fluid exerts forces upon small suspended particles.

(ii) The macromolecules are represented by corresponding models to behave in a manner similar to that of the actual material (see 1.1.4.2).

(iii) The elements of the polymer chain are considered to be centres of resistance to flow, perturbing the fluid velocity at

the points of location of other elements. This effect leads to the intramolecular hydrodynamic interaction. At finite concentrations, there occurs the intermolecular hydrodynamic interaction. In concentrated solutions, the actual frictional forces are a consequence not only of frictional forces of isolated segments but also of long-range coupling of entangled chains.

(iv) When exposed to an external field of force, rigid molecules perform translational and rotational motions whereas flexible molecules also undergo deformation. These regular changes (in position, orientation, and in shape) will be disturbed by irregular motions of molecules and/or of their segments, which are characteristic of the Brownian motion.

According to the theory of Brownian motion, these effects (rotatory diffusion) can be thought of as being brought about by an additional force with components proportional to the components of the gradient of the distribution function which, in its most general form, gives the probability that the particle at a particular time will be located at some specified position with a specified orientation and velocity. Departures of the distribution function from equilibrium in the velocity field of the flowing solution contribute to viscosity. Since this term exhibits relaxation, its contribution is complex, and the solution can exhibit rigidity, vanishing for shears of zero frequency and approaching an asymptotic value at high frequencies.

#### 1.1.4.2 Models of macromolecules

Most theories of the flow properties of polymer solutions are based on the bead models.

The chain elements (of finite dimensions) are approximated, after Burgers (ref. 3), by points of force (beads, frictional centres). A proportionality relation is assumed to hold between the frictional force and the relative velocity of the beads. The proportionality constant is the friction coefficient of the bead,  $\zeta$ . The frictional centres are arranged in correspondence with the arrangement of chain units. A rigid array of frictional centres is a model for a rigid rod-like particle while a distribution function of interbead distance is adopted for random coils or worm-like chains.

The frictional centres are connected by links which experience no frictional interaction with the solvent. Rigid bars are used as links if the chain is not deformable (as with rigid rods) or if the

deformation need not be considered (as with flexible chains at very low, time-independent shear-rates). If, on the other hand, the deformation must be taken into account (e.g. with periodically varying shear-rates), springs are introduced into the model as links between the beads.

There exist different ways of treating the Brownian motion effect (refs 4,5). In one group of theories, Brownian motion (with rigid rods) and micro-Brownian motion (with flexible chains) is not considered explicitly. The detailed description of Brownian motion is replaced by a description based on the average velocities of the beads. To calculate the configurational averages, use is made of the equilibrium distribution of configurations.

In the other group of theories, the non-equilibrium distribution function of the frictional centres in the presence of frictional forces and of Brownian motion is explicitly calculated. It is obtained from the diffusion equation which describes the Brownian motion of the molecule under the influence of an external force field.

In the investigations of the shear-rate effects, the simple dumb-bell model is often employed to yield the first qualitative or semiquantitative insight (ref. 6). It considers the motion of the free ends only, which are connected by a rigid rod or by an elastic spring, and in which the frictional resistance is concentrated. This resistance results from the contribution of all the beads of which the chain is composed, under the assumption that, in laminar flow, the average velocities of beads symmetrically located are exactly opposite.

In recent theories advanced for rigid rods (ref. 7), worm-like chains (ref. 8), worm-like rings (ref. 9) and once-broken rods (ref. 10), the macromolecule is represented by a continuous cylinder (straight or worm-like) of contour length  $L$  and diameter  $d$ . It is probably a better approximation to the real polymer molecules than the array of discrete beads (ref. 11).

#### 1.1.4.3 The viscosity of solutions of non-interacting polymer molecules. The intrinsic viscosity

Representing the macromolecule by a set of  $n+1$  frictional centres (beads), and assuming that no interaction takes place between the macromolecules, we can calculate the total loss of energy as the sum of contributions from all the frictional centres.

Making this summation for chains endowed with a degree of flexibility, we must take into account the variability of configurations assumed by the molecules.

The frictional force exerted by the liquid on the  $j$ -th bead is  $-\underline{F}_j$ , and its component in the  $x$  direction is  $-F_{jx}$ . The work done in unit time by the fluid for the  $j$ -th bead is  $-\underline{F}_j \cdot \underline{v}_j^0$  (where  $\underline{v}_j^0$  is the original velocity of the liquid at the point of location of the  $j$ -th segment) or, with regard to eqn (1.1), to  $-\dot{\gamma} F_{jx} y_j$ . Taking the average over all configurations (configurational average)  $-\dot{\gamma} \langle F_{jx} y_j \rangle$ , summing the contributions from all the beads of the molecule, and multiplying the sum by the number of polymer molecules in unit volume  $cN_A/M$  (where  $N_A$  is the Avogadro number,  $c$  is the concentration and  $M$  the molar mass of polymer), we obtain the work dissipated per unit time and unit volume due to the presence of polymer molecules,  $-(cN_A/M) \dot{\gamma} \sum_j \langle F_{jx} y_j \rangle$ . According to eqn (1.6), this work must be equal to the difference  $(\eta - \eta_s) \dot{\gamma}^2$  so that

$$(\eta - \eta_s) \dot{\gamma}^2 = -(cN_A/M) \dot{\gamma} \sum_j \langle F_{jx} y_j \rangle. \quad (1.10)$$

The basic equation for the calculation of the intrinsic viscosity is readily obtained from eqns (1.3) and (1.10):

$$[\eta] = -(N_A/M\eta_s \dot{\gamma}) \sum_j \langle F_{jx} y_j \rangle. \quad (1.11a)$$

For some purposes, it is more convenient to write

$$[\eta] = -(N_A/M\eta_s \dot{\gamma}) \sum_j \langle (\underline{F}_j \cdot \underline{e}_x) (\underline{S}_j \cdot \underline{e}_y) \rangle \quad (1.11b)$$

where  $\underline{e}_x$  and  $\underline{e}_y$  are unit vectors defining the Cartesian system (with the origin in the centre of mass, with  $\underline{e}_x$  parallel to the stream lines of the unperturbed flow, and  $\underline{e}_y$  perpendicular to the phase boundary), and  $\underline{S}_j$  is the position vector of the  $j$ -th element relative to the centre of mass. An equation similar to (1.11) obtains if the distribution of discrete frictional centres is replaced by a continuous frictional force distribution (refs 7,8).

It follows from eqn (1.11a) that the intrinsic viscosity is proportional to the sum of averages of products  $F_{jx} y_j$  where  $F_{jx}$  is the component of the statistical restoring force in the direction of flow, and  $y_j$  depends on the extension of the molecule in the direction of flow plane perpendicular to the flow. In order to

evaluate the viscosity or the intrinsic viscosity according to eqns (1.11), we need know the frictional force  $\underline{F}_j$  and the distribution function of distances  $\underline{S}_j$ .

#### 1.1.4.4 The hydrodynamic interaction

(a) Bead models. When calculating the frictional force exerted on the  $j$ -th element by the fluid, one must consider the fact that the distribution of velocities in the solution is not exactly that existing in the pure solvent because of the effect of the hydrodynamic interaction. The velocity of the fluid in the layer adhering to the dissolved particle is that of points on the surface of the particle,  $\underline{u}$ . In remote layers, it is equal to  $\underline{v}^0$ , the unperturbed velocity. In intermediate layers it is between  $\underline{u}$  and  $\underline{v}^0$ . That means that the original velocity is perturbed by the dissolved particle. If two or more particles (e.g. beads) are suspended in the fluid, the perturbations overlap, and the velocity of the fluid flowing around any of them is the sum of the unperturbed velocity and of the perturbations due to the presence of the other particles.

The problem of the hydrodynamic interaction is usually solved in terms of the Oseen approximation (refs 11,12). It was introduced into the hydrodynamics of polymer solutions, thirty years ago, by Kirkwood and Riseman (ref. 13) as a tool simplifying the solution of this problem. Recent studies (refs 14,15) have not disproved its practical value but have set bounds to its use.

Let  $\underline{v}_k$  be the velocity which the fluid would possess at the point of location of the bead  $k$  if that bead were absent, and  $\underline{u}_k$  be the velocity of this bead. Then a force  $\underline{F}_k$ ,

$$\underline{F}_k = \zeta(\underline{u}_k - \underline{v}_k) , \quad (1.12)$$

is exerted on the fluid by this bead. The translational friction coefficient of the bead  $\zeta$  depends on the fluid and on the chemical structure of polymer molecules. The perturbation of flow,  $\underline{v}^-(\underline{R}_{ks})$ , produced at the point  $k$  at a distance  $\underline{R}_{ks}$  from the locus  $s$  of application of the force  $\underline{F}_s$  can be calculated by the Oseen formula

$$\underline{v}^-(\underline{R}_{ks}) = \underline{T}(\underline{R}_{ks}) \cdot \underline{F}_s \quad (1.13)$$

where  $\underline{T}(\underline{R}_{ks})$  is the Oseen tensor,

$$\underline{T}(\underline{R}_{ks}) = (1/8\pi\eta_s R_{ks}) (\underline{E} + \underline{R}_{ks}\underline{R}_{ks}/R_{ks}^2). \quad (1.14)$$

$\underline{E}$  is the unity tensor, and  $R_{ks}$  is the distance between the beads  $k$  and  $s$  in a specified internal configuration of the molecule.

Combining eqns (1.13) and (1.14), we have

$$\underline{v}^-(\underline{R}_{ks}) = (1/8\pi\eta_s R_{ks}) (\underline{F}_s + \underline{R}_{ks}\underline{F}_s \cos \vartheta / R_{ks}). \quad (1.15)$$

The perturbation of flow is anisotropic, depending on the angle  $\vartheta$  between the vectors  $\underline{F}_s$  and  $\underline{R}_{ks}$ . The motion of a bead is accelerated if other beads move in the same direction (positive hydrodynamic interaction), and is slowed down in the opposite case (negative hydrodynamic interaction). The effect is maximum if the vectors are parallel, and minimum if they are perpendicular (Fig. 1.3).

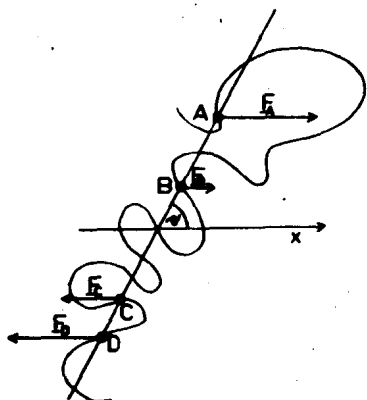


Fig. 1.3. The hydrodynamic interaction of beads.  
The curve represents the chain;  
A,B,C,D are frictional centres (beads).

Since the distances between elements situated on the same side from the centre of rotation of the molecule and moving in the same direction are smaller, the positive contribution to the hydrodynamic interaction is stronger, and the total effect of the hydrodynamic interaction is always positive.

The fluid velocity,  $\underline{v}_k$ , at the point  $k$  is the sum of the unperturbed velocity,  $\underline{v}_k^0$ , existing in the solvent in the absence of the polymer molecule and the summed Oseen perturbations from all the other chain elements, i.e.

$$\underline{v}_k = \underline{v}_k^0 + \sum_{\substack{s=-n \\ s \neq k}}^n \underline{v}^-(\underline{R}_{ks}) \quad (1.16)$$

From eqns (1.12), (1.13) and (1.14), we obtain

$$\underline{F}_k = \zeta (\underline{u}_k - \underline{v}_k^0) - \zeta \sum_{\substack{s=0 \\ s \neq k}}^n \underline{T}(\underline{R}_{ks}) \cdot \underline{F}_s \quad (1.17)$$

The anisotropy of the hydrodynamic interaction is very often neglected, and the Oseen tensor is replaced by its average,  $\langle \underline{T} \rangle$ , taken over the equilibrium configuration (refs 12,13). If the distribution of inter-bead distances is spherically symmetric, the average is

$$\langle \underline{T} \rangle = (1/6\pi\eta_s) \langle 1/R_{ks} \rangle \underline{E} \quad (1.18)$$

The use of the pre-averaged Oseen tensor keeps the mathematics within manageable limits but is a rather severe approximation as it introduces isotropy which is not present in the physical picture of the model.

(b) Cylinder models. In hydrodynamic calculations for the continuous cylinder model, the cylinder is replaced by a frictional force distribution,  $\underline{f}(s)$ , per unit contour length along the cylinder axis, as a function of the contour distance from one end,  $s$ . The source of hydrodynamic interaction originates on the axis and acts at the point on the cylinder surface. Therefore, calculating the distance of interaction,  $\underline{R}$ , one must consider not only the distance between the contour points J and K (denoted by  $\underline{R}$ ) but also the normal radius vector,  $\underline{r}$ , from the contour point J on the axis to a point P on the surfaces:  $|\underline{r}| = r = d/2$ . Since the frictional force distribution is a continuous function, the perturbation of flow due to the hydrodynamic interaction is given by the integral

$$\int \underline{T}(\underline{R}') \cdot \underline{f}(s) ds$$

(with limits appropriately chosen).

For an instantaneous configuration (or orientation) of the cylinder, the velocity  $\underline{v}(P)$  of the solvent at the point P relative to the velocity of this point,  $\underline{u}(P)$ , is defined as

$$\underline{v}(P) = \underline{v}^0(P) - \underline{u}(P) + \int \underline{T}(\underline{R}') \cdot \underline{f}(s) ds, \quad (1.19)$$

where  $\underline{v}^0(P)$  is the unperturbed velocity existing at the point P in the absence of the polymer molecule, and the Oseen-Burgers method

based on the non-slip condition is applied. This condition requires that the value of  $\underline{v}(P)$  averaged over a normal cross-section of the cylinder vanishes for all values of the contour distance:

$$\langle \underline{v}(P) \rangle_{(r)} = 0. \quad (1.20)$$

From eqns (1.19) and (1.20) one obtains an integral equation which is the basis for the determination of the frictional force for an instantaneous configuration:

$$\int_0^L \langle \underline{T}(\underline{R}') \rangle_{(r)} \cdot \underline{f}(s) ds = \langle \underline{u}(P) \rangle_{(r)} - \langle \underline{v}^0(P) \rangle_{(r)} \quad (1.21)$$

#### 1.1.4.5 Orientation and deformation of polymer molecules

For a qualitative description of the orientation and deformation effects of shear forces in laminar flow, it is convenient to adopt the dumb-bell model, and for a further simplification of the matter, to consider only the dumb-bells lying in the x-y plane.

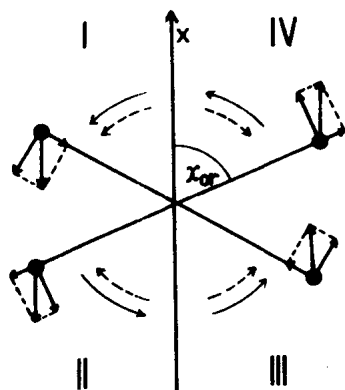


Fig. 1.4. An elongated rigid particle in laminar flow. Rotation by shear forces denoted by  $\longrightarrow$ , rotatory diffusion by  $\dashrightarrow$ .

In Fig. 1.4, arrows represent the differences of the unperturbed velocities of the liquid in the centre of the dumb-bell and in the points occupied by the frictional centres. They also represent the force exerted on the frictional centre by the liquid. This force depends on the angle between the direction of flow and the axis of the dumb-bell (orientation angle  $\chi_{or}$ ). It assumes largest values if particles are oriented perpendicularly to the flow direction ( $\chi_{or} = 90^\circ$ ), while lowest values correspond to the parallel

orientation ( $\chi_{or} = 0^\circ$ ).

The frictional force can be resolved into radial and tangential components. The tangential components at two frictional centres of a dumb-bell are equal in magnitude, but of opposite direction; acting as a torque, they cause rotation of the particle. Obviously, the tangential component is the larger, the larger is  $\chi_{or}$  so that the rotation is not uniform. Consequently, the particle spends shorter time periods in those regions of orientation where the velocity of rotation is high. For an ensemble of particles, there exists a non-uniform distribution function of orientational angles which gives the probability of finding a particle oriented in the direction defined by  $\chi_{or}$  or - in other words - the number of particles per unit volume oriented in the corresponding direction.

The orientation is opposed by random thermal motions, which tend to destroy the non-uniform distribution of  $\chi_{or}$  and restore the uniform one. We have to do with a current of rotating particles which is proportional to the gradient of the distribution function of orientation. It has the same physical background as diffusion in systems characterized by a concentration gradient, and it is therefore referred to as rotatory diffusion. It is characterized by the rotatory diffusion coefficient,  $D_r$ , or by the relaxation time of orientation,  $\tau_{or} = 1/6D_r$ . This quantity has the following physical meaning: an imposed preferred orientation reverts to random orientation with a time decay proportional to  $\exp(-t/\tau_{or})$ .

According to Fig. 1.4 the diffusion current in the even quadrants is opposite to the rotatory motion caused by the shear-rate whereas the directions of both motions are the same in the odd quadrants. Therefore, the resulting angular velocity is lower in the even quadrants. A stationary distribution of  $\chi_{or}$  angles is set up which is more or less different from the uniform distribution at the state of rest. The distribution is a function of the ratio of the relative intensities of hydrodynamic and thermal motions of the axes of the particles, expressed by the ratio  $\dot{\gamma}/D_r$  (ref. 16).

The effect of the radial component of the frictional force depends on the rigidity of the particle. For rigid, undeformable particles, the radial component is destroyed by the rigidity of the particle. With coiling, deformable molecules, this component is not compensated and, therefore, causes deformation. The molecule dilates when passing the even quadrants, and is compressed in odd ones. Within one rotation about its axis, the molecule is twice dilated and twice compressed. Since it spends a shorter period of time in