THEORIES OF STREAMING DOUBLE REFRACTION

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I. Introduction

Most molecules are optically anisotropic because, in general, their polarizability is different in various directions. If, however, the molecules in an aggregate are completely randomly distributed, then the aggregate behaves as an isotropic medium. Any orientation, whether it is caused by artificial means or exists naturally, leads to anisotropy and thus gives rise to double refraction.

Orientation in liquids may be brought about by the application of electrical or magnetic fields, by the influence of acoustic waves, or by a hydrodynamic field. These influences give rise, respectively, to electric double refraction (Kerr effect), magnetic double refraction (Cotton–Mouton and Majorana effects), acoustic double refraction (Lucas effect), and dynamic or streaming double refraction (87) (Maxwell effect). Also included as an orientation effect is Wiener (162) or form (shape) double refraction (36, 37). This occurs in systems known as "Stäbchenmischkörper" and "Schichtenmischkörper," which give rise to positive and negative double refraction, respectively. The first system consists of a number of parallel isotropic rods, each small compared with the wavelength of light, immersed in a medium of refractive index different from that of the rods; the double refraction is often called "Stäbchendoppelbrechung." In the other system the rods are replaced by laminae and the double refraction is called "Schichtendoppelbrechung." In some cases, particularly in macromolecular solutions, orientation of the solvent molecules by the solute molecules may occur and this is another cause of double refraction. The phenomenon is called adsorption double refraction (157). Another type of double refraction is strain or deformation double refraction (photoelastic effect), which results from the action of an external force on a solid system and with which small deformations or internal displacements are associated. Several investigators have published reviews dealing with certain aspects of streaming double refraction. Boehm (4) gave many details about the apparatus, Edsall (30, 31) presented a general review up to 1942, Kanamaru and Tanaka (53) discussed some theoretical aspects, and Cerf and Scheraga (13) reviewed the results for macromolecular solutions. Peterlin and Stuart (106, 107) considered the general problem of artificial double refraction, including a discussion of streaming double refraction, and general articles have been written by Signer (131) and Eirich (34).

The purpose of this review is to present the theories given for the phenomenon. The period covered is from the date (1874) of the first theory up to the present day, although as far as the early theories are concerned, attention is given only to those parts which have provided a basis for, or are included in, modern theories.

II. Notation

The principal meanings of the symbols employed in this review are defined as follows:

$A_i = \alpha_i'(1 + L_i\varkappa_i)$ with $i = \xi, \eta, \zeta$; $B = \beta'(1 + L_\eta\varkappa_\eta)$,

A_m, A_s, A_b = average length of an uncharged, charged, and branched statistical chain element, respectively,

B = shape resistance of a flexible molecule,

C = resistance to rotation of a molecule ($= kT/D$),

D, D_a = diffusion constant and apparent diffusion constant,
E = electric vector of external field with components E_e,
E_i = electric vector of internal field,
F = distribution function,
G = velocity gradient,
H_o, H_p = functions of polarizability (Sadron's theory),
I = moment of inertia of particle,
$\mathcal{I}$ = imaginary part of optical factor Π,
J_o, J_p = functions of polarizability (Sadron's theory),
K_o, K_p = functions of polarizability (Sadron's theory),
L = hydrodynamic length of chain molecule,
L_1, L_2, L_3 = anisotropy factors (shape),
L_ξ, L_η, L_ζ = anisotropy factors (field),
$L_1' = 3L_1/4\pi$; $L_2' = 3L_2/4\pi$,
M_{jk} = average value of dipole moment ($j, k = 1, 2, 3$),
M = molecular weight
M_g = molecular weight of monomer unit
$[M]$ = Maxwell constant ($= \Delta n/n\eta G$ for liquids; $= \Delta n/n_o\eta_o Gc$ for solutions),
$[M]_{sp}$ = specific Maxwell constant $\left[= \left(\frac{\Delta n}{n_o \eta_o Gc}\right)_{\substack{G\to 0\\ c\to 0}} \right]$,
$[M]_m$ = molar Maxwell constant,
N = number of particles per unit volume (polydisperse system),
N_A = Avogadro's number,
N_m = number of statistical chain elements per molecule,
N_o = number of molecules per unit volume,
N_p = number of particles per unit volume (monodisperse system),
P, P_o, P_p = polarization, polarization due to solvent, and polarization due to particles,
$[P]$ = molar polarization,
R = gas constant per mole,
$\mathfrak{R}$ = real part of optical factor,
$\mathfrak{R}_i$ = frictional forces,
R_d = reduction factor (figure 15),
R_1, R_2, R_3 = deformation forces along axis of flexible molecule,
$S = (h_M - h_o)/kT$,
T = absolute temperature,
V = particle volume (for revolution ellipsoids $= 4\pi a_1 a_2^2/3$),
Y = elasticity coefficient,
Z = degree of polymerization,
a = radius of spherical particle,
a_1 = semi-major axis of ellipsoid,
a_2 = semi-minor axis of ellipsoid,
$b = (a_1^2 - a_2^2)/(a_1^2 + a_2^2)$ for ellipsoid; hydrodynamic length of monomer for chain molecules,
c = volume concentration ($= N_p V$)

c' = weight concentration ($= MN_2/N_{\mathrm{A}} = Mc/N_{\mathrm{A}}V$),
d = length of light path,
d_h = average thickness of statistical chain elements,
e, e_f = eccentricity factors,
$f(\sigma, b)$ = orientation factor,
g_1, g_2 = polarizability of ellipsoidal particle referred to external field,
h = distance between ends of an uncharged chain molecule; potential energy,
$\overline{h^2}, \overline{h_o^2}$ = mean square end-to-end distance of a chain molecule in a solution when flowing, and when stationary,
k = Boltzmann's constant,
l, l_f = eccentricity factors,
$l' = l(\epsilon - 1)/(\epsilon + 2)$,
m = dipole moment; real refractive index of particle,
n = real refractive index of solution,
n_o = refractive index of solvent,
n_x, n_y, n_z = principal refractive indices of flowing solution along Ox, Oy, Oz,
Σp = polarization/internal field ($= P_p/E_i$),
p_{ij} = tensor elements of Σp ($i, j = 1, 2, 3$); average moment/external field ($= M/E$),
q = number of monodisperse systems in a polydisperse system,
r = axial ratio,
s_{ij} = components of stress tensor ($i, j = 1, 2, 3$),
s_m = number of monomers in a statistical chain element,
t, t' = time,
u, v, w = components of particle velocity along O1, O2, O3,
y = delay potential/kT,
z = number of monomer groups in a branch,
α, β = polarizabilities of ellipsoid; $\bar{\alpha}, \bar{\beta}$ = mean values of α and β,
α', β' = relative polarizabilities of ellipsoid; $\bar{\alpha}', \bar{\beta}'$ = mean values of α' and β',
α_{ij} = induced moment due to unit field ($i, j = 1, 2, 3$),
γ_ξ, γ_η = mean polarizabilities of chain molecule,
δ_o = shape fluctuation ($\delta_o^2 = kT/2VY$),
ϵ, ϵ_o = dielectric constant of solution, and of solvent,
ζ = degree of branching of macromolecule,
η, η_o = dynamic viscosity coefficient of solution, of solvent,
η_i = internal viscosity coefficient of molecule,
$[\eta]$ = intrinsic viscosity or limiting viscosity number,
θ = orientation angle,
θ_i = intrinsic anisotropy; θ_f = form anisotropy,
κ_j = absorption index ($j = x, y, z$),
λ = wavelength,
λ_m, λ_o = frictional factor of molecule, of chain element,
μ = complex refractive index of particle,

μ_j = complex refractive index of solution ($j = x, y, z$),
ρ = density,
σ = gradient/diffusion constant ($= G/D$),
τ, τ_o, τ_d = relaxation time, orientation relaxation time, and deformation relaxation time,
τ' = macroconstellation changing time,
ϕ = orientation angle,
χ = extinction angle,
$\varkappa$ = relative optical susceptibility ($= P_i/\epsilon E_i = N_o p$),
$\psi = \chi - 90°$,
ω, ω_r = angular velocity of particle due to flow and due to repulsion,
$(\omega) = \pi/4 - \chi$,
$[\omega] = [(\omega)/\eta_o G]_{\substack{G\to 0\\ c\to 0}}$
Δ = phase difference,
$\Delta_i = (n_i^2 - 1)(n_i^2 + 2)$,
Θ = angle between directions of preferred orientation,
$\Lambda = N_p(\alpha' L_\xi + 2\beta' L_\eta)/3$,
$\Xi = \alpha' + 6\beta'$; function of molecular constants in Raman and Krishnan theory,
Π = optical factor,
$\Phi = (\alpha' L_\xi - \beta' L_\eta)$,
$\Psi = (\alpha' - \beta')$
$d\Omega = \sin\theta \, d\theta \, d\phi$ (solid angle)
Δn = birefringence ($= n_x - n_y$),
δn = eigen double refraction,
$\delta n'$ = birefringence in molecule induced by stress,
$\tan(\chi G)_o = \left(-\frac{\partial \chi}{\partial G}\right)_{\substack{G\to 0\\ c\to 0}}$
Ox, Oy, Oz = directions of principal refractive indices,
O1, O2, O3 = general coördinate system of reference,
$O\xi$, $O\eta$, $O\zeta$ = directions of particle axes.

III. Definitions of Extinction Angle and Flow Birefringence

Streaming double refraction occurs in pure liquids and Newtonian solutions at high rates of shear; it is most marked in non-Newtonian solutions containing asymmetrical molecules. The most satisfactory apparatus for its measurement is one in which the liquid is subjected to shear between two concentric cylinders, one of which rotates while the other is stationary (32, 33, 50). By this means a uniform velocity gradient may be produced across the annular gap. If the annular gap is viewed between crossed polarizing devices, so that the light travels parallel to the axes of the cylinders and is thus perpendicular both to the streamlines and to the velocity gradient, the field will appear dark when both cylinders are at rest. When one cylinder rotates shear forces arise, which cause the liquid to become optically biaxial, so that three different principal axes Ox, Oy, Oz,

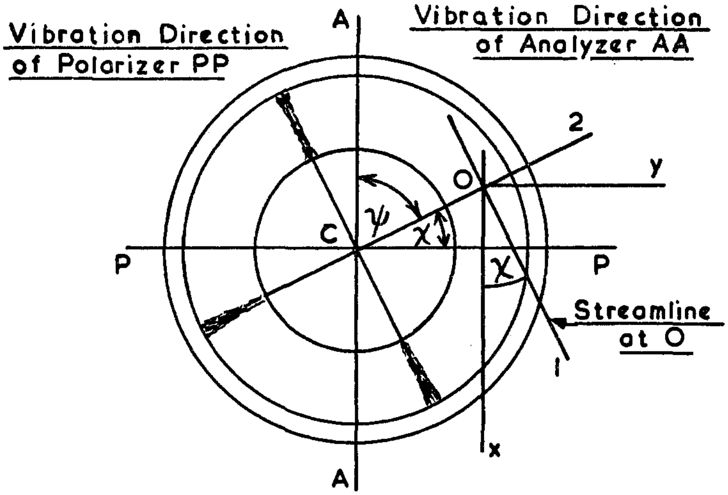


FIG. 1. View of the doubly refracting medium in the annular gap between concentric cylinders. ψ, angle of isocline; χ, extinction angle.

defining the extinction directions in the liquid, exist, together with three principal refractive indices n_x, n_y, and n_z. One of these axes, say Oz, coincides with the directions of the common axis of the cylinders and the other two, mutually perpendicular, lie in a plane perpendicular to this direction (51). The field of view now appears bright everywhere except for four regions equispaced around the gap corresponding to the directions Ox and Oy; they form the arms of a cross called the cross of isocline (figure 1). The position of the cross is specified by the "extinction angle" χ, which is defined as the smaller of the two angles between the vibration planes of the crossed polarizing devices and the arm of the cross. According to this definition χ lies always between 45° and 0°.

When linearly polarized light is passed through a length d of the doubly refracting liquid it is, in general, resolved into two linearly polarized components, one vibrating along Ox and the other along Oy. These emerge with a phase difference Δ (in radians) given by $\Delta = 2\pi d\Delta n/\lambda$, where Δn is the flow birefringence of the liquid given by $\Delta n = n_x - n_y$ and λ is the wavelength *in vacuo*. d is measured in the same units as λ. It is customary to designate a liquid as being optically positive or negative according to whether Δn is positive or negative.

IV. EARLY THEORIES (1873–1927)

The first published observations on flow birefringence were made in 1873, when Mach (85) observed double refraction in extremely viscous substances, such as strong metaphosphoric acid and Canada balsam, when poured into a beaker. The same method gave no results with less viscous liquids. In 1874 Maxwell (87) described a concentric cylinder apparatus used by him in 1866 in which flow birefringence could more easily be produced; his experiments were made on Canada balsam. In 1880 Quincke (113) described the existence of double refraction in unnamed liquids in the neighborhood of an immersed heated wire. The first real attempts to get quantitative measurements and to advance a theory were made by Kundt (81), who used an apparatus which was an improvement on Maxwell's. The double refraction was measured by observation of the movement of an interference band produced in a spectrum by a gypsum plate.

Kundt based his theory on the work of Stokes (135) dealing with incompressible liquids. According to Kundt each element of volume of a liquid in flow in the annular gap between two concentric cylinders is subjected to tensile and compressive stresses acting along two directions which are mutually perpendicular and inclined at 45° to the lines of flow. These stresses are each proportional to ηG, where η is the dynamic viscosity coefficient and G is the velocity gradient. Kundt assumed that these stresses produced double refraction in the liquid as in a solid and of magnitude proportional to the stress. The optic axes of the birefringent liquid were assumed to coincide with the directions of the stress. Thus the double refraction should be proportional to G and for all liquids the extinction angle χ should be 45°; any departure from this value was considered an anomaly and unexplainable. Several such cases were found. Kundt also introduced Maxwell's concept of fugitive elasticity (88) and relaxation time τ in a liquid and finally expressed the birefringence Δn as $K\tau G$, where K is a constant not considered in detail.

De Metz (89) and Umlauf (156) carried out a further set of experiments using an identical apparatus but measured the double refraction by a Babinet compensator; their results were similar to those of Kundt, but in addition they found that the double refraction decreased, although not directly, with temperature rise. They adopted Kundt's theory and concluded that viscosity was not primarily sufficient to determine the occurrence of double refraction and that the latter occurs only in oils or colloids. These deductions were supported by Almy (1), who found no trace of double refraction in water, and by Hill (47), who studied gum arabic in water. The theory was discussed by Havelock (44).

In 1901 Natanson (92) attempted to improve Kundt's theory and to investigate the significance of the constant K. He found that

$$K = \Pi r_1^2/(r_1^2 + 4v^2\tau^2)$$

where Π is an undefined optical factor, v is the linear velocity at any point distant r_1 from the center, and τ and G are as previously defined. Other attempts made by Zaremba (167) yielded a similar equation.

The apparently anomalous departure of χ from 45° was first considered by Schwedoff (126) who, after considering and rejecting the possibility that the optic axes do not always coincide with the axes of stress, decided that these latter axes do not always lie at 45° to the direction of flow. He derived an equation for χ in terms of a quantity proportional to the fugitive elasticity of the liquid. Later Natanson (93), assuming as in 1901 that the stress caused the double refraction, used the ideas given by Schwedoff to obtain the equation $\cot 2\chi = \pm\tau G$. Experimental results obtained by Zakrzewski (165, 166) were considered to confirm this equation and used to find values for τ; they were of the order of 10^{-5} sec. for colloids. Zocher (170) gave an alternative to the theory of Kundt by introducing the possibility that the double refraction was a result of orientation of particles which were asymmetrical with respect to shape as well as anisotropic with respect to optical properties. This idea was further developed by Graffi (41). On this hypothesis a particle subjected to laminar flow in the annular space between concentric cylinders will be orientated along the streamlines, because in any other position it will lie with its ends in layers of different velocities, which exert an orientating couple upon it. If the optic axis of the particle coincides with the direction of largest asymmetry, then, as can be seen from figure 1, values of χ of zero would be the rule; departures would be anomalous. This result was directly opposed to Kundt's prediction. One possible explanation of values of χ different from zero was one analogous to that considered, and rejected, by Schwedoff: namely, that the optic axis and the longest axis of geometrical asymmetry did not necessarily coincide. However, this simple explanation could not be sustained. For example, experiments with vanadium pentoxide, for which from other data it is known that the optical and geometrical axes do coincide, give values of χ varying from 0° to 45° according to the age of the preparation. Two other explanations were put forward by Zocher, the first being that possibly impulses due to Brownian motion might change the direction of the particles so that they did not lie along the flow lines, and the second that the particles were flexible. The first of Zocher's assumptions was later rejected (171). The second idea was developed by Pontremoli (109) but was subjected to doubt by the experiments of Vorlander (158–161), who found double refraction in noncolloidal liquids known not to be flexible. Pontremoli later tried unsuccessfully to combine the two ideas of orientation of anisotropic particles and deformation (110).

At this stage then there were two different conceptions for a theory of streaming double refraction: in one it was considered that the birefringence in a moving liquid could be calculated from that found in the same liquid at rest, but subject to tensions and compressions, and in the other it was decided that the resultant movement of particles in flow must be considered. The first had been treated in some detail; the latter had not been investigated. In addition, a distinction between rigid and flexible particles was visualized.

Theory of Raman and Krishnan

In 1928 Raman and Krishnan (114), after considering the experimental results of Vorlander and Walter (158), put forward a theory of orientation double refraction for liquids along the lines used by Langevin (82) and Born (5) to explain electric and magnetic double refraction. They assumed the liquid to consist of, or contain, highly asymmetric particles which were optically anisotropic. Then, starting as did Kundt, they considered the effect on the liquid of the tensile and compressive forces postulated by Stokes, but whereas Kundt supposed that the forces produced double refraction by strain, Raman and Krishnan assumed that these forces orientated the asymmetric molecules with

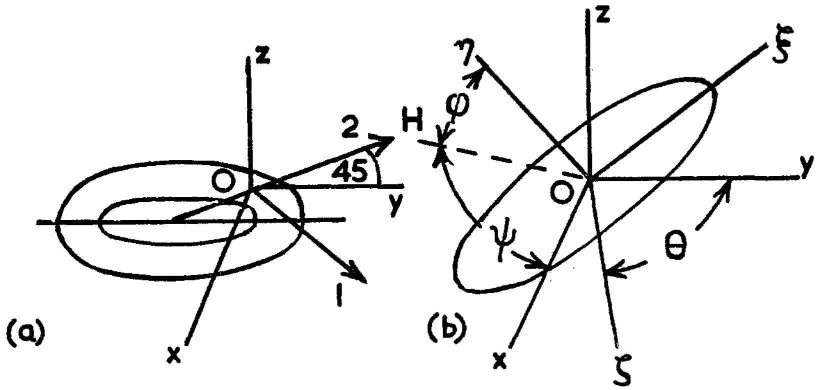


FIG. 2. Parameters for theory of Raman and Krishnan. (a) Position of coördinate system of reference with respect to any point O in the annular gap: Ox and Oy correspond to directions of compression and tension, respectively. (b) Position of axes Oξ, Oη, and Oζ of a molecule referred to axes Ox, Oy, Oz. OH is the line of intersection of the $\xi\eta$ plane with the xz plane; θ, ϕ, and ψ are the Eulerian angles.

The cosines of the angles between the axes are:

	x	y	z
ξ	$\gamma_{11} = -\cos\theta\cos\phi\sin\psi - \sin\phi\cos\psi$	$\gamma_{12} = \sin\theta\sin\psi$	$\gamma_{13} = -\cos\theta\sin\phi\sin\psi + \cos\phi\cos\psi$
η	$\gamma_{21} = \cos\theta\cos\phi\cos\psi - \sin\phi\sin\psi$	$\gamma_{22} = -\sin\theta\cos\psi$	$\gamma_{23} = \cos\theta\sin\phi\cos\psi + \cos\phi\sin\psi$
ζ	$\gamma_{31} = \sin\theta\cos\phi$	$\gamma_{32} = \cos\theta$	$\gamma_{33} = \sin\theta\sin\phi$

the largest molecular dimension along the direction of tension. This orientative tendency was opposed by thermal agitation, so that the resultant orientation was one of statistical equilibrium and the double refraction a result of this. The details of the mathematical treatment are as follows:

Consider the molecules to be rigid ellipsoids of revolution of axes $2a_1$, $2a_2$, $2a_3$. To define the orientation of the molecules consider a reference system of axes Ox, Oy, Oz situated as in figure 2(a); let the position of the axes of a typical molecule be as in figure 2(b).

According to Stokes, the tensile and compressive forces are each proportional to ηG per unit area, where η and G have their previous meanings. If there are N_o molecules per unit volume, the potential energy per molecule (h) is given by $h = K\eta G/N_o$, where K is a constant dependent on the orientation of the molecule with respect to the axes Ox, Oy, Oz of stress. Raman and Krishnan find that, owing to the tensile forces only,

$$K = -\ (b_1\gamma_{12}^2 + b_2\gamma_{22}^2 + b_3\gamma_{32}^2)$$

where γ_{12}, γ_{22}, and γ_{32} are as given in the caption to figure 2 and b_1, b_2, and b_3 are constants determined by the geometric form of the molecule. By the application of Boltzmann's theorem, the average potential energies $\bar{h}$ and $\bar{h}_o$ per molecule when the molecules are orientated by flow, and randomly orientated, respectively, are found. The decrease in potential energy per unit volume, i.e.,

$(\bar{h}_o - \bar{h})N_o$ is then given by

$$(\bar{h}_o + \bar{h})N_o = \frac{2}{45kT}[(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2](\eta G)^2/N_o \tag{1}$$

This is the work done in orientating the molecules.

An electric moment will be induced in a molecule when the field due to a light-wave is incident on it. For a unit field acting along the ξ axis let α_{11}, α_{12}, α_{13} be the induced moments along the ξ, η, and ζ axes, respectively; similarly, let α_{21}, α_{22}, α_{23} and α_{31}, α_{32}, α_{33} be the corresponding induced moments for unit field acting along the η and ζ axes, respectively. When the field E of the incident light-wave lies along the Ox axis, a molecule will acquire an induced moment whose component in this direction is m_x, where $m_x = \alpha_x E$. Here α_x is the polarizability in this direction and is a function of α_{ij} and γ_{ij} $(i, j = 1, 2, 3)$.

The polarizability $\bar{\alpha}_x$, averaged over all the molecules, is given by

$$\bar{\alpha}_x = \frac{\alpha_{11} + \alpha_{22} + \alpha_{33}}{3} + \frac{2\Xi\eta G}{N_o} \tag{2a}$$

where

$$\Xi = \frac{1}{45kT}[(b_1 - b_2)(\alpha_{11} - \alpha_{22}) + (b_2 - b_3)(\alpha_{22} - \alpha_{33}) + (b_3 - b_1)(\alpha_{33} - \alpha_{11})] \tag{2b}$$

Similarly, if the electric vector lies along the Oy axis, the average polarizability, $\bar{\alpha}_y$, is given by

$$\bar{\alpha}_y = \frac{\alpha_{11} + \alpha_{22} + \alpha_{33}}{3} - \frac{\Xi\eta G}{N_o} \tag{2c}$$

so that

$$\bar{\alpha}_x - \bar{\alpha}_y = 3\Xi\eta G/N_o \tag{3}$$

The same effect is produced by the compressive forces, so that for both forces acting together

$$\bar{\alpha}_x - \bar{\alpha}_y = 6\Xi\eta G/N_o \tag{4}$$

The connection between refractive index n and mean polarizability $\bar{\alpha}$, $[(\alpha_{11} + \alpha_{22} + \alpha_{33})/3]$, is taken to be

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N_o \bar{\alpha} \tag{5}$$

so that if n_x and n_y are the refractive indices along the directions Ox and Oy, respectively, then

$$\Delta n = n_x - n_y = \frac{(n^2 - 1)(n^2 + 2)}{n} \frac{\Xi}{\bar{\alpha}} \frac{\eta G}{N_o} \tag{6}$$

In order to express Ξ in terms of the optical constants and axial lengths of the molecule, the effective expansion per unit length of the aggregate along Ox due to orientation may be calculated; this multiplied by the force along Ox gives another expression for the work done per unit volume due to orientation. This is

$$\frac{1}{15kT}\,\frac{(b_1-b_2)(a_1-a_2)+(b_2-b_3)(a_2-a_3)+(b_3-b_1)(a_3-a_1)}{a_1+a_2+a_3}\,\frac{\eta^2G^2}{N_o} \tag{7}$$

The solution of the equation resulting when equations 1 and 7 are equated is

$$\frac{b_1-b_2}{a_1-a_2}=\frac{b_2-b_3}{a_2-a_3}=\frac{b_3-b_1}{a_3-a_1}=\frac{3}{2(a_1+a_2+a_3)} \tag{8}$$

Thus from equations 2b, 6, and 8,

$$\frac{\Delta n}{n\eta G}=\frac{(n^2-1)(n^2+2)}{10n^2N_okT}\left[\frac{(a_1-a_2)(\alpha_{11}-\alpha_{22})+(a_2-a_3)(\alpha_{22}-\alpha_{33})+(a_3-a_1)(\alpha_{33}-\alpha_{11})}{(a_1+a_2+a_3)(\alpha_{11}+\alpha_{22}+\alpha_{33})}\right]$$
$$=[M] \tag{9}$$

where $[M]$ is a constant called the Maxwell constant for a liquid. The principal deductions from this theory are as follows: (*1*) The angle of extinction χ equals 45° for all gradients. (*2*) If $a_1 > a_2 > a_3$, then Δn is positive or negative according to whether $\alpha_{11} > \alpha_{22} > \alpha_{33}$ or $\alpha_{11} < \alpha_{22} < \alpha_{33}$, respectively. (*3*) Δn is directly proportional to η and to G. The primary effect of temperature rise will be to lower η and hence Δn. (*4*) Δn is greater the greater the asymmetry of the molecule and increases with increasing optical anisotropy and with increasing refractive index. (*5*) Since n depends on wavelength, dispersion of double refraction should occur.

Although the experimental evidence supported conclusions 2 to 5 and for pure liquids deduction 1 is true, the first conclusion was incompatible with the data on colloids because the reasoning given above should apply to colloids as well as to pure liquids. No advantage is obtained by considering the possible deformation of the particles under such a stress system. In later papers Paldhikar (95) and Rao (115) gave further evidence purporting to support the general validity of the theory, but Narasimhamurty (91) some sixteen years later concluded that little agreement holds between theory and experiment.

V. Theories for Rigid Particles

A. THEORY OF HALLER

Haller (43), considering the known fact that for small gradients, colloidal particles gave extinction angles of 45°, which decrease to zero as the gradients increase, set out to investigate separately the behavior in flow of (*a*) rigid anisodimensional particles and (*b*) deformable particles. A deformable anisodimensional particle was not explicitly treated, it being inferred that it could be treated by consideration of the individual results of (*a*) and (*b*). In this section only the theory for rigid particles is presented; deformable particles are treated in Section VII,B.

The rigid anisodimensional particles are assumed to have the shape of ellipsoids of revolution, cylinders, or thin laminae. Such particles when subjected only to laminar flow execute a precessional motion. In figure 3(a) the orientation of an

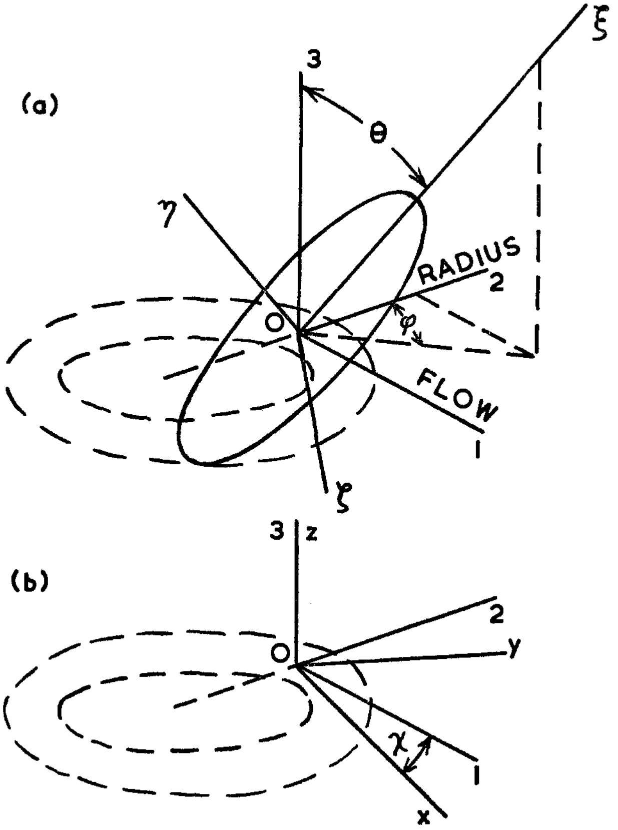


Fig. 3. Parameters giving orientation of (a) particle and (b) principal vibration directions.

ellipsoidal particle with reference to a three-dimensional coördinate system is shown. The particle is assumed to lie in the annular gap between two concentric cylinders. The motion of the particle is given by

$$\omega_\phi = \frac{\partial \phi}{\partial t} = \frac{G}{2}(1 - b \cos 2\phi) \tag{10}$$

$$\omega_\theta = \frac{\partial \theta}{\partial t} = \frac{bG}{4} \sin 2\theta \sin 2\phi \tag{11}$$

Here G is the velocity gradient and b is given by $b = (1 - \Gamma)/(1 + \Gamma)$, where Γ is the ratio of the maximum to the minimum rotational moment exerted on the particle.

If, when laminar flow is set up, the motion of all the particles in a liquid element of unit volume be considered, then, although the positions of the particles and the particles themselves will be continually changing, the number and orientations of the particles in the volume element are constant. The changes in orientation of the particles are considered to be due to the liquid flow and the diffusion caused by Brownian motion. The net result is that the particles move more slowly through some directions than others and so present a kinematic orientation. To calculate this orientation Haller finds a distribution function, F, which gives the frequency of the particles in the different positions; i.e., F is defined by the statement that $F\,d\theta\,d\phi$ shall be that fraction of the whole number of particles whose directions lie in the vanishingly small range between ϕ and $\phi + d\phi$ and θ and $\theta + d\theta$. Thus the change in distribution of the particles in the unit volume element per second due to the flow alone is given by

$$\left(\frac{\partial F}{\partial t}\right)_f = Gb\left[F \sin 2\phi\left(1 - \frac{1}{2}\cos 2\theta\right) + \frac{1}{2}\frac{\partial F}{\partial \phi}\left(\frac{1}{b} - \cos 2\phi\right) + \frac{1}{4}\frac{\partial F}{\partial \theta}\sin 2\phi \sin 2\theta\right] \qquad (12)$$

The corresponding change due to Brownian diffusion is

$$\left(\frac{\partial F}{\partial t}\right)_d = \frac{D}{2}\left[\frac{\partial^2 F}{\partial \phi^2} + \frac{1}{\sin^2 \theta} + \frac{\partial^2 F}{\partial \theta^2} + \frac{\partial F}{\partial \theta}\cot \theta + F\frac{1}{\sin \theta}\right] \qquad (13)$$

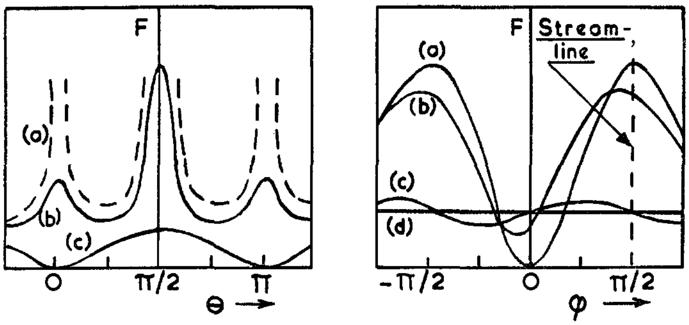
where D is the rotary diffusion constant of the particle. The latter is defined by the Einstein relationship $D = kT/C$, where C is the resistance to rotation of the molecule and k and T are as given in Section II. Values of D are given in Appendix 1. For a steady state

$$\left(\frac{\partial F}{\partial t}\right)_f + \left(\frac{\partial F}{\partial t}\right)_d = 0 \qquad (14)$$

which yields a differential equation for F.

Haller obtained solutions for F for two special cases in which the effect of the Brownian motion relative to the effect of the flow was either weak or strong. Weak Brownian motion corresponds to relatively large particles or small particles subjected to high gradients, and strong motion arises for small particles at low gradients. Haller's solutions were given in terms of constants which could not be evaluated but, from his results, graphs showing the general nature of the variation of F with θ, if ϕ is regarded as a constant, and the variation with ϕ, when θ is constant, have been drawn (figure 4). From figure 4(1) it is seen that particles in the plane $\theta = \pm n\pi/2$ ($n = 0, 1\ 2 \cdots$) have infinitely great values of F when there is no Brownian motion; this means that all other orientations with respect to the plane 2O1 are unstable. Immediately flow starts the particles move either into the 2O1 plane ($\theta = \pm \pi/2$) or at 90° to it ($\theta = 0$ or π); Haller states that about 71 per cent favor the orientation $\theta = \pm \pi/2$. From figure 4(2) it is clear that the longest dimensions of rod-shaped or ellipsoidal-shaped particles have a preferred orientation along O1. This also applies to the longest dimensions of lamellar particles. The value of F is independent of the flow gradient G.

With a small amount of Brownian motion, the variation of F is represented by curves (b) and (c) of figure 4. F now depends on G, but its maximum value is never as great as previously, which means that there is a smaller tendency to orientation in a given direction. The direction of preferred orientation is shifted



(1) φ, Constant

(2) θ, Constant(π/2)

Fig. 4. Variation of distribution function F for rod-shaped particles (Haller). In figure 4(1) curves (a), (b), and (c) hold for no, moderate, and strong Brownian motion, respectively. In figure 4(2) curve (a) holds for no Brownian motion and curves (b), (c), and (d) hold for increasing Brownian motion. χ, the angle of extinction, $= 90 - \phi$.

from $\phi = 90°$ towards $\phi = 45°$, corresponding to a rotation of the particle out of the O1 direction against the flow.

With strong Brownian motion the largest value of F occurs when $\theta = \pi/2$, and in this plane the preferred orientation for the longest dimension of ellipsoidal shaped particles ($\Gamma > 1$) is inclined at 45° to the O1 direction; for laminae ($\Gamma < 1$) the angle of inclination is 135°.

On the assumption that the directions of maximum orientation are the extinction directions in the liquid, this theory explains the change of χ from 45° to 0° as G increases, but the precise mode of change is not given. It also predicts a rise of double refraction with increasing gradient to a limit corresponding to complete orientation of the particles.

B. THEORY OF BOEDER

Boeder's theory (3) deals specifically with colloidal particles, which he assumed to be large ellipsoids of revolution with high axial ratio imbedded in a solution of small homogeneous molecules. The theory is developed with regard to a liquid contained in the annular gap between two concentric cylinders.

Starting with the assumption that the particles were subjected to an orientating influence due to flow and a disorientating effect due to Brownian motion he deduced, in a manner analogous to that used by Haller, an expression for the distribution function F of the major geometrical axes of the particles. Thus with the parameters shown in figure 3, Boeder defined the motion of the particles by the expressions

$$\omega_\phi = \frac{\partial \phi}{\partial t} = -G \cos^3 \phi \sin \theta \tag{15}$$

and

$$\omega_\theta = \frac{\partial \theta}{\partial t} = \frac{G}{4} \cos 2\theta \sin 2\phi \tag{16}$$

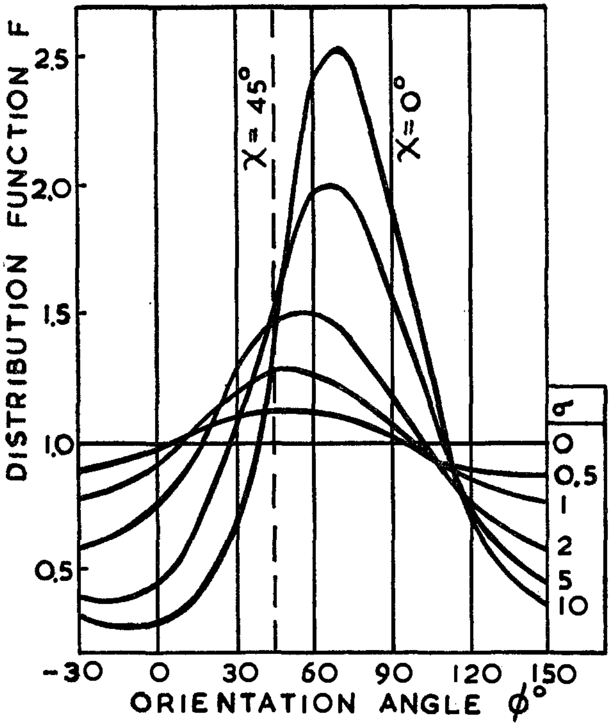


FIG. 5. Variation of distribution function F with ϕ for different values of σ (Boeder). χ, the angle of extinction, $= 90 - \phi$.

Then the variation with time of F due to the ordering effect of the flow is given by

$$\left(\frac{\partial F}{\partial t}\right)_f = G\left[F \sin 2\phi\left(\frac{\cos^2\theta}{2}+\frac{\sin 2\theta}{4}\right) - \cos^2\phi - \cos^2\phi\,\frac{\partial F}{\partial \phi}+\frac{1}{4}\sin 2\phi \sin 2\theta\,\frac{\partial F}{\partial \theta}\right] \quad (17)$$

which may be compared with equation 12.

The disordering effect of the Brownian motion is expressed by

$$\left(\frac{\partial F}{\partial t}\right)_d = D\left[\frac{\partial^2 F}{\partial \phi^2}\frac{1}{\sin^2\theta}+\frac{\partial^2 F}{\partial \theta^2}+\frac{\partial F}{\partial \theta}\cos\theta\right] \quad (18)$$

which is an equation similar to equation 13. Equations 17 and 18 give, with equation 14, a differential equation for F. Boeder gives the results of the integration in terms of a quantity σ, equal to G/D, and confined his results mainly to the two-dimensional case. For this $\theta = \pi/2$, and it is assumed that

$$\int_0^\pi F\,\mathrm{d}\phi = \pi$$

The solution is given to cover three ranges of values of σ.

(a) $\sigma = 0.5$ to $\sigma = 10$: This is solved by numerical integration and the solution given in the form of curves (figure 5); they have the same shape as those shown in figure 4(2).

(*b*) $\sigma < 0.5$:

$$F = 1 + \sigma \frac{\sin 2\phi}{4} - \sigma^2 \left(\frac{\cos 2\phi}{16} - \frac{\cos 4\phi}{64} \right) + \sigma^3 \left(\frac{9}{2^9} \sin 2\phi - \frac{3}{2^9} \sin 4\phi + \frac{1}{3.2^9} \sin 6\phi \right) \qquad (19)$$

(*c*) $\sigma > 10$:

$$F = \frac{2\mathrm{B}}{\sigma} \left[\frac{1}{2 \cos^2 \phi} + \frac{1}{\sigma} \frac{\sin \phi}{\cos^5 \phi} + \frac{1}{\sigma^2} \frac{(5 - 4 \cos^2 \phi)}{\cos^8 \phi} + \cdots \right] \qquad (20)$$

where B is a constant, which can be evaluated easily only for large values of ϕ to give

$$F = \frac{\pi \sigma^{1/3}}{4.976} \left[\frac{1}{(\phi \sigma^{1/3})^2} + \frac{2}{(\phi \sigma^{1/3})^5} + \frac{10}{(\phi \sigma^{1/3})^8} \right] \qquad (21)$$

In order to find the effect of the interaction of the electric field of an incident light-wave and the partially orientated system, Boeder next assumed that the liquid as a whole, or the particles, must be rendered anisotropic under flow. Accordingly the anisotropy can arise either because of a regular arrangement of the rod-shaped isotropic particles (Stäbchendoppelbrechung), or because of a change of shape (strain double refraction) of each particle which then becomes anisotropic. In addition the particles themselves might be anisotropic (eigen-doppelbrechung). Boeder points out that all three possibilities may exist together, but considers the possibility of "Stäbchendoppelbrechung" the least likely. The question whether the particle anisotropy is a deformation anisotropy or an eigen-anisotropy is undecided.

If now the particles are subjected to an external electric field of strength E, which produces an internal field E_i in the region of the particles, then each particle will become polarized by induction and assume an electric moment m which, if the average is taken over all the molecules, is given by $m = \alpha E_i$. Here α is the polarizability of the particle; it is a tensor. If P_p is the polarization of the liquid, i.e., the electric moment per unit volume resulting from the induced dipole moments of the particles, then $P_p = \Sigma p E_i$, where Σp is a tensor representing the sum of all the contributions of the individual polarizabilities of the N_p particles contained in unit volume. In calculating Σp, all the different orientations of the particles have to be considered. The tensor elements are given by

$$p_{ij} = \int_0^{2\pi} \int_0^{\pi} F \alpha_{ij}(\phi, \theta) \sin \theta \, d\theta \, d\phi \qquad (i, j = 1, 2, 3) \qquad (22)$$

where F is the distribution function and $\alpha_{ij}(\phi,\theta)$ is the polarizability for a particle in position (ϕ,θ) with respect to the coördinate system O1, O2, O3. By assuming that P_p is related to the field E_i by the Lorentz–Lorenz relationship

$$E_i = E + \frac{4\pi}{3} P$$

and that $E + 4\pi P_p = \epsilon E$, where ϵ is the dielectric tensor of the medium, Boeder was able to obtain an expression for ϵ in terms of the elements ϵ_{ij} $(i, j = 1, 2, 3)$ which refer to the coördinate system O1, O2, O3. For the two-dimensional case, this is

$$\epsilon = \begin{vmatrix} \epsilon_{11} & \epsilon_{12} & 0 \\ \epsilon_{21} & \epsilon_{22} & 0 \\ 0 & 0 & \epsilon_{33} \end{vmatrix}$$

where

$$\epsilon_{11} = 1 - \frac{4\pi}{N_p}\left[p_{11}\left(\frac{4\pi}{3}p_{22} - 1\right) - \frac{4\pi}{3}p_{12}^2\right]$$

$$\epsilon_{22} = 1 - \frac{4\pi}{N_p}\left[p_{22}\left(\frac{4\pi}{3}p_{11} - 1\right) - \frac{4\pi}{3}p_{12}^2\right]$$

$$\epsilon_{33} = 1 - \frac{4\pi p_{33}}{\left(\frac{4\pi}{3}p_{33} - 1\right)}$$

$$\epsilon_{12} = \frac{4\pi}{N_p}p_{12}; \qquad \epsilon_{12} = \frac{4\pi}{N_p}p_{21}$$

The tensor ϵ may be reduced to the diagonal form, with elements ϵ_x, ϵ_y, ϵ_z by a rotation $(90 - \chi)$ about the axis O3, where

$$\tan 2\chi = \frac{2\epsilon_{12}}{\epsilon_{11} - \epsilon_{22}} = \frac{2p_{12}}{p_{11} - p_{22}} = \frac{K}{H} \tag{23}$$

with

$$H = \int_0^{2\pi} F \cos 2\phi \, d\phi; \qquad K = \int_0^{2\pi} F \sin 2\phi \, d\phi$$

Now ϵ_x, ϵ_y, ϵ_z are the eigen-values of ϵ and are the principal values of the dielectric constant along the three principal directions Ox, Oy, Oz in the liquid. Two of these directions lie in the 2O1 plane and the third along the direction O3. The first two are identified with the principal vibration directions of the liquid so that χ is the extinction angle; its value is determined by the distribution function F.

If E, the external field, is due to a linearly polarized vibration of wavelength λ, then after traversing a length d of the medium, the phase difference Δ between the components along Ox and Oy of the emergent elliptically polarized beam is $2\pi d(\epsilon_x^{1/2} - \epsilon_y^{1/2})/\lambda$. This Boeder gives as

$$\Delta = \Pi[H^2 + K^2]^{1/2} = \Pi f(\sigma, b) \tag{24}$$

where Π is the optical factor, which is a function of the polarizability of the particles, and $f(\sigma, b)$, since it depends on F, is an orientation factor.

For values of σ between 0 and 10, Boeder gives the values of χ and $f(\sigma, b)$ in tabular form (table 1). If $\sigma < 0.5$ and > 10, then $\chi = \frac{1}{2}\tan^{-1} 4/\sigma$. In the

TABLE 1

Values of χ and $f(\sigma, b)$ given by Boeder (3)

σ	χ	$f(\sigma, b)$	σ	χ	$f(\sigma, b)$
0.0	45°		3.5	25°50′	2.000
0.5	41°27′	0.390	5.0	22°0′	2.400
1.0	38°15′	0.755	7.5	17°30′	2.770
2.0	32°13′	1.367	10.0	15°	3.020

former case $f(\sigma, b) \simeq (\sigma\pi/4)(1 - (\sigma^2/10))$, whereas for values of $\sigma > 10$, $H = 2\pi(1 - 2.22\sigma^{-1/3} + 0.568\,\sigma^{-1})$ and $K = 4.43\sigma^{1/3} - 2.79\sigma^{-1}$.

For the three-dimensional case and for small values only of σ, Boeder gives

$$\chi = \frac{1}{2}\tan^{-1} 6/\sigma = \frac{\pi}{4} - \frac{\sigma}{12}\left(1 - \frac{\sigma^2}{108} + \cdots\right) \tag{25a}$$

and

$$f(\sigma, b) = \frac{\sigma\pi}{10} \tag{25b}$$

It is seen that χ is greater than, and $f(\sigma, b)$ is less than, the corresponding values for two-dimensional motion.

C. THEORY OF W. KUHN

W. Kuhn (61) considered the particles in a solution to be either optically anisotropic and rigid, or isotropic and flexible. Only the former treatment is considered in this section. Rigid particles are orientated during flow and the method of treatment, and the results for long narrow rigid particles are almost identical with those of Boeder; unlike Boeder, however, Kuhn also deals with particles of small axial ratio.

In developing his theory, Kuhn did not use the concept of ellipsoidal particles but assumed that the particles, whatever their shape, could be represented by models from an arrangement of rigidly connected spheres. These are sometimes called the pearl necklace type of model. In figure 6 three such arrangements are shown. Kuhn, like Boeder, showed that each particle in a flowing solution executes an irregular rotational motion about its center of gravity in addition to translation, and thus assumes a preferred direction of kinematic orientation. He finds a distribution function, F, from a differential equation in the same manner as Boeder and Haller. The constants of integration are determined by imposing the condition that

$$\int_0^{2\pi} F\,d\phi = N_p$$

where N_p is the total number of particles per cubic centimeter.

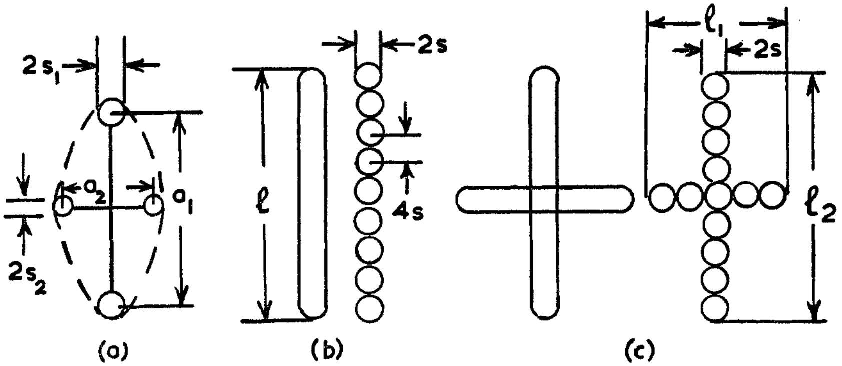


FIG. 6. Molecular models of W. Kuhn: (a) ellipsoidal molecule; (b) long narrow molecule; (c) free-draining molecule.

It is assumed that each particle possesses either eigen or form double refraction and that the total birefringence, which arises in the flowing solution, is given by

$$\Delta n = n_x - n_y = \int_0^{2\pi} [FH_1\{\sin^2\phi' - \cos^2\phi'\} + FH_2\{\cos^2\phi' - \sin^2\phi'\}]\, d\phi \tag{26}$$

In this equation n_x and n_y are the values of the refractive indices along the principal directions of vibration Ox and Oy, respectively (figure 3), and $\phi' = \phi + \chi$. The quantities H_1 and H_2 are functions of the polarizabilities of the particles and are defined by the equation

$$N_p(H_1 - H_2) = (n_x - n_y)_{\text{sat.}} = \Delta n_{\text{sat.}} \tag{27}$$

in which $(n_x - n_y)_{\text{sat.}}$ is the limiting value of the birefringence, which is assumed to exist when all the particles are completely orientated. The value of Δn is then found for the three different models of figure 6, which are supposedly suspended in a liquid of viscosity η_o and subjected to a flow gradient G.

1. *Model (a): ellipsoidal particle of small axial ratio*

Kuhn assumes that the rotational velocity, $\partial\phi/\partial t$, and the diffusion constant, D, of the particle are given by

$$\frac{\partial\phi}{\partial t} = -G\frac{a_1^2 s_1 \cos^2\phi + a_2^2 s_2 \sin^2\phi}{a_1^2 s_1 + a_2^2 s_2} \tag{28}$$

and

$$D = \frac{kT}{12\pi\eta_0(a_1^2 s_1 + a_2^2 s_2)} \tag{29}$$

where the symbols have the meanings given in Section II and figure 6.

In a later paper he takes $s_1 = s_2$, so that $2a_1$ and $2a_2$ become the major and minor axes, respectively.

For very large particles, for which $D \simeq 0$ and G/D is large,

$$F = \frac{N_p}{2\pi} \frac{(a_1 a_2 s_1 s_2)^{1/2}}{2(a_1^2 s_1 \cos^2 \phi + a_2^2 s_2 \sin^2 \phi)} \tag{30}$$

This is independent of G and is a maximum for $\phi = \pi/2$, so that $\chi = 0$. Then by equation 26

$$\Delta n = N_p(H_1 - H_2) \frac{s_1^{1/2} a_1 - s_2^{1/2} a_2}{s_1^{1/2} a_1 + s_2^{1/2} a_2} \tag{31}$$

For small particles, for which D is large and G/D is small,

$$F = \frac{N_o}{2\pi} \left[1 + \frac{G}{4D} \frac{a_1^2 s_1 - a_2^2 s_2}{a_1^2 s_1 + a_2^2 s_2} \sin 2\phi \right] \tag{32}$$

This is dependent on G and is a maximum for $\phi = \pi/4$, irrespective of whether the particle is rod-shaped or disc-shaped. The corresponding value of χ is 45° and Δn is given by

$$\Delta n = N_p(H_1 - H_2) \frac{3\pi G \eta_o}{2kT} (a_1^2 s_1 - a_2^2 s_2) \tag{33}$$

As G increases, F and Δn approach, but never reach, the values given by equations 30 and 31, respectively; χ decreases from 45° to a small value different from zero.

2. Model (b): ellipsoidal particle of large axial ratio (elongated or chain molecule)

In this case

$$\frac{\partial \phi}{\partial t} = -G \cos^2 \phi$$

and

$$D = 8kT/\pi \eta_o l^3$$

where l is the length of the particle.

For very large and for moderate values of σ, Kuhn uses Boeder's expressions for F (equations 21 and 20). These give a maximum at values of ϕ approaching $\pi/2$; the value $\pi/2$ occurs only for large values of σ and corresponds to a value of χ equal to zero and a birefringence given by equation 27. For small values of σ, Kuhn finds $\chi = 45°$ and

$$\Delta n = N_p(H_1 - H_2) \frac{\pi}{64} \frac{G \eta_o l^3}{kT} \tag{34}$$

where $N_p(H_1 - H_2) = V\delta n$, V is the volume occupied by the suspended particles per cubic centimeter of solution, and δn is their eigen double refraction.

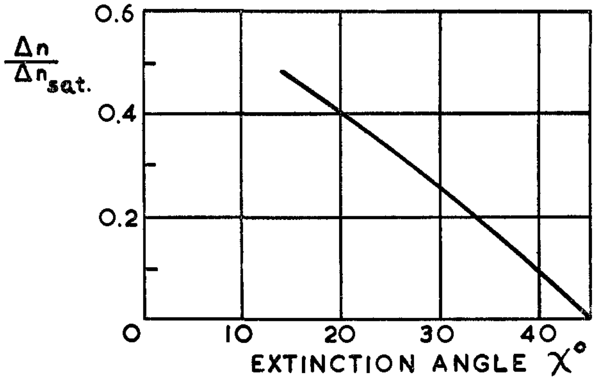


FIG. 7. Ratio of observed birefringence, Δn, to maximum birefringence, $\Delta n_{\mathrm{sat.}}$, for different values of χ (Kuhn (61)).

3. *Model (c)*

For this Kuhn modified equation 34 to get

$$\Delta n = N_p(H_1 - H_2)\frac{\pi G\eta_0}{64kT}(l_1^3 - l_2^3) \tag{35}$$

If $l_1 = l_2 = l$, then $\Delta n = 0$ and F has the constant value $N_p/2\pi$. This corresponds to no direction of preferred orientation with $\partial\phi/\partial t = -G/2$ and $D = 4kT/\pi$.

Kuhn states that the accepted values of $\partial\phi/\partial t$ and of D, obtained by Jeffery (48) and Gans (39), respectively, for rigid ellipsoids, are little different from those given by equations 28 and 29; for this reason he assumes the models to be satisfactory.

For molecules which may be represented by model (b), it is evident that if Δn is measured for small values of G/D, and if δn and V are known, then l can be found directly from equation 34. When δn is not known, then $\Delta n_{\mathrm{sat.}}$ may be found either from experimentally obtained graphs of Δn and χ against G, in which the value of $\Delta n_{\mathrm{sat.}}$ is that corresponding to the value of G for which $\chi = 0$ (extrapolated if necessary), or from the curve of figure 7. The curve enables $\Delta n_{\mathrm{sat.}}$ to be found if Δn is known for any value of χ, so that besides the particle length l, the eigen double refraction δn can also be found. Because in reality the problem is a three-dimensional and not a two-dimensional one, Kuhn considers the true value of l to be greater than that obtained by the above method.

D. THEORY OF SADRON

The theories of Kuhn, Haller, and Boeder all suffered from an inadequate treatment of the hydrodynamic motion of the flowing particles. Further, the optical behavior was incorrectly treated, in that the Lorentz–Lorenz relationship for the isotropic internal field in a medium due to an incident light-wave was used to connect the constants of the particles (e.g., polarizability) with the macroscopic measurable quantities (e.g., permittivity), whereas anisotropic internal fields are more probable. Sadron was the first to attempt a remedy of both defects, his theory being confined to the two-dimensional case.

Sadron (119, 120) assumes that in flow, rigid particles in solution precess in the manner already given by Boeder, but he replaces equation 15 by the equation given by Jeffery (48) to describe their motion. He then employs the method used by Langevin (82) for electric and magnetic double refraction of pure liquids to calculate the flow birefringence, but introduces an anisotropic field within the medium by applying the Lorenz method of consideration to an ellipsoid-shaped volume of dimensions equal to that of the particle. He considers first a monodisperse system of particles and then extends his theory to cover a polydisperse system.

1. Monodisperse system (119)

Each particle is taken to be an ellipsoid of revolution of axial ratio a_1/a_2 and such that this ellipsoid coincides with the ellipsoid representing its optical properties.

With reference to figure 3(a), the particles are assumed to lie in the plane $\theta = \pi/2$ and the rotational velocity ω_ϕ is given by

$$\omega_\phi = \frac{\partial \phi}{\partial t} = -G \frac{a_1^2 \cos^2 \phi + a_2^2 \sin^2 \phi}{a_1^2 + a_2^2} \tag{36}$$

Sadron then deduces that for the two-dimensional case the distribution F is (*cf.* equation 19)

$$F = \frac{N_p}{\pi}\left[1 + \frac{b\sigma}{4} \sin 2\phi\right] \tag{37}$$

where $b = (a_1^2 - a_2^2)/(a_1^2 + a_2^2)$ and the other symbols have their usual meanings. It is assumed that

$$\int_0^\pi F \, d\phi = \pi = N_p$$

The particles thus have a direction of preferred orientation and the medium becomes doubly refracting with principal vibration directions Ox and Oy parallel and perpendicular, respectively, to this direction (figure 3(b)). The extinction angle χ is given by the equation $\tan 2\chi = \text{constant} \times G/D$.

When the electric vector E of an incident light-wave is parallel to Ox and Oy, respectively, the polarizations P_x and P_y produced along Ox and Oy in the medium are given by

$$P_i = (P_o)_i + (P_p)_i \qquad (i = x, y) \tag{38}$$

where $(P_p)_i$ and $(P_o)_i$ are the polarizations in these directions due to all the suspended particles and the solvent molecules, respectively. For the solvent molecule let the azimuth of the major axis with respect to Ox be θ_o, the principal polarizabilities be α_o, β_o, and N_o be the number per cubic centimeter. The corresponding parameters for the particles are θ_p, α_p, β_p, and N_p. Then Sadron, assuming the solvent molecule to be influenced by an isotropic internal field of the general form $(E + (4\pi/3)P)$, deduces that

$$(P_o)_i = \left(E + \frac{4\pi}{3} P_i\right)(H_o)_i \qquad (i = x, y) \tag{39}$$

where

$$(H_o)_x = (\alpha_o \cos^2 \theta_o + \beta_o \sin^2 \theta_o)\mathrm{d}N \tag{40}$$

$$(H_o)_y = (\alpha_o \sin^2 \theta_o + \beta_o \cos^2 \theta_o)\mathrm{d}N \tag{41}$$

The field on the particles is taken as anisotropic and its values along the particle axes Oξ, Oη are given by $(E + L_iP)$, where $i = \xi, \eta$ and

$$L_i = \frac{4\pi}{3}(1 + e_i)$$

is a shape factor (see Appendix 2). Then

$$(P_p)_i = \left(E + \frac{4\pi}{3} P_i\right)(H_p)_i + \frac{4\pi}{3} P_i J_i \qquad (i = x, y) \tag{42}$$

where $(H_p)_x$ and $(H_p)_y$ are given by equations 40 and 41 with α_p, β_p, and θ_p replacing α_o, β_o, and θ_o.
Also

$$J_x = \int_0^\pi (e_\xi \alpha_p \cos^2 \theta_p + e_\eta \beta_p \sin^2 \theta_p)\mathrm{d}N \tag{43}$$

$$J_y = \int_0^\pi (e_\xi \alpha_p \sin^2 \theta_p + e_\eta \beta_p \cos^2 \theta_p)\,\mathrm{d}N \tag{44}$$

By equations 38, 39, and 42,

$$P_i = \left(E + \frac{4\pi}{3} P_i\right)(H_o + H_p)_i + \frac{4\pi}{3} P_i J_i \qquad (i = x, y) \tag{45}$$

or

$$P_i = E(H_o + H_p)_i + P_i(K_o + K_p)_i \tag{46}$$

where

$$K_o = \frac{4\pi}{3} H_o \text{ and } K_p = \int_0^\pi (L_\xi \alpha_p \cos^2 \theta_p + L_\eta \beta_p \sin^2 \theta_p)\,\mathrm{d}N$$

The connection between polarization, P, and refractive index, n, is given by $(n^2 - 1)E = 4\pi P$, so that

$$\frac{n_i^2 - 1}{n_i^2 + 2} = \frac{4\pi}{3} \frac{(H_o + H_p)_i}{1 - \frac{4\pi}{3} J_i} \qquad (i = x, y)$$

For small concentrations, and if Δ_i is written for $(n_i^2 - 1)/(n_i^2 + 2)$, then

$$\Delta_i \simeq \frac{4\pi}{3}\left(H_o + H_p + \frac{4\pi}{3} H_o J\right)_i \qquad (i = x, y) \tag{47}$$

It is further assumed that the solvent of refractive index n_o is not orientated during flow, so that $(H_o)_x = (H_o)_y = H_o$ and

$$\Delta_o = \frac{n_o^2 - 1}{n_0^2 + 2} = \frac{4\pi}{3} H_o \tag{48}$$

From equations 47 and 48,

$$\Delta_x - \Delta_y = \frac{4\pi}{3}[(H_p)_x - (H_p)_y + \Delta_o(J_x - J_y)] \tag{49}$$

Now θ_p is directly related to ϕ and F to $\mathrm{d}N$, so that using equation 37 the values of $(H_p)_i$ and J_i may be found.

Sadron gives

$$(H_p)_x = \frac{N_p}{2\pi}\left[\alpha_p + \beta_p + \frac{\sigma b}{2}(\alpha_p - \beta_p)\right] \tag{50}$$

$$J_x = \frac{N_p}{2\pi}\left[e_\xi \alpha_p + e_\eta \beta_p + \frac{\sigma b}{2}(e_\xi \alpha_p - e_\eta \beta_p)\right] \tag{51}$$

and $(H_p)_y$ and J_y are obtained by interchanging the polarizabilities α_p and β_p. From equation 49, finally,

$$\Delta n = \frac{\pi}{3}\frac{(n_o^2 + 2)^2}{n_o} N_p[(\alpha_p - \beta_p) + \Delta_o(e_\xi \alpha_p - e_\eta \beta_p)]b\sigma = \Pi b \frac{G}{D} \tag{52}$$

where Π, b, σ, and n_o have their usual meanings.[1]

Since

$$D = \frac{kT}{\eta_o V} f(r)$$

(see Appendix 1), equation 52 may be written in the form $y = Bx + C$, where

$$y = \frac{\Delta n}{N_p}\frac{1}{\eta_o G}\frac{n_o}{(n_o^2 + 2)^2}, \qquad x = \frac{n_o^2 - 1}{n_o^2 + 2}$$

$$B = \frac{\pi}{3}\frac{bV}{kTf(r)}(e_\xi \alpha_p - e_\eta \beta_p), \qquad C = \frac{\pi}{3}\frac{bV}{kTf(r)}(\alpha_p - \beta_p)$$

Thus a graph of y against x should be a straight line which, since $e_\xi < 0$ and $e_\eta > 0$, has a negative slope. The value of Δn can change from positive through zero to negative according to the value of n_o. Sadron illustrates this with the experimental results from Signer (figure 8), and in discussing the theory points out that if n is the value of n_o for which Δn is zero, then

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\alpha_p - \beta_p}{e_\xi \alpha_p - e_\eta \beta_p}$$

---

[1] The numerical factor $\pi/3$ in equation 52 appears incorrect, since the study of the original paper shows that a mistake has been made in copying an incorrect equation of Langevin and also there is apparently an error in the integration; the factor should read $4\pi/9$.

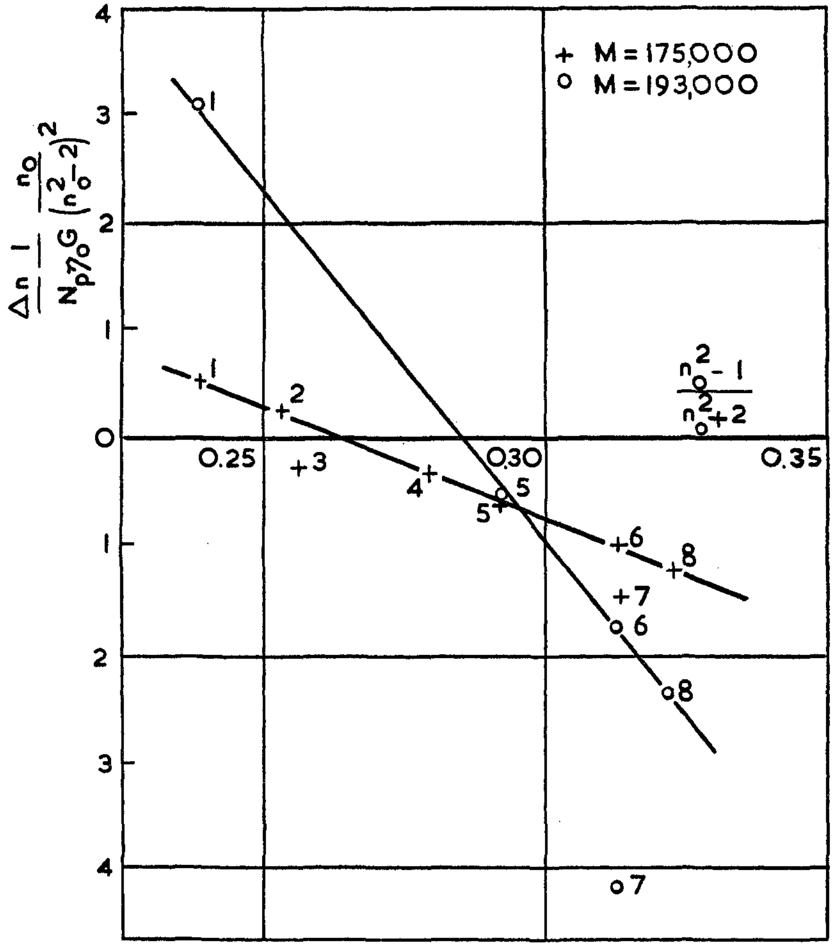


FIG. 8. Birefringence of solutions of polystyrene (molecular weights, M, of 175,000 and 193,000) in different solvents. Solvents are: (1) butyl acetate, (2) dioxane: H_2O (1:1), (3) pure dioxane, (4) decalin, (5) toluene, (6) ethylene bromide, (7) tetralin, (8) bromobenzene. From Sadron (119).

When n, α_p, and β_p are known, information on e_ξ and e_η, and hence the axial ratio r, can be found.

2. *Polydisperse system*

Sadron (120) considers a system composed of q monodisperse constituents each containing $(N_p)_k$ particles per unit volume of solution. It is assumed that the concentrations are low so that during flow each constituent is orientated as if it alone were present in solution and there are no interactive effects. The k^{th} system has a distribution function F_k, an extinction angle χ_k, a diffusion constant D_k and would, if alone present, give a birefringence $(\Delta n)_k$. The parameters are shown in figure 9.

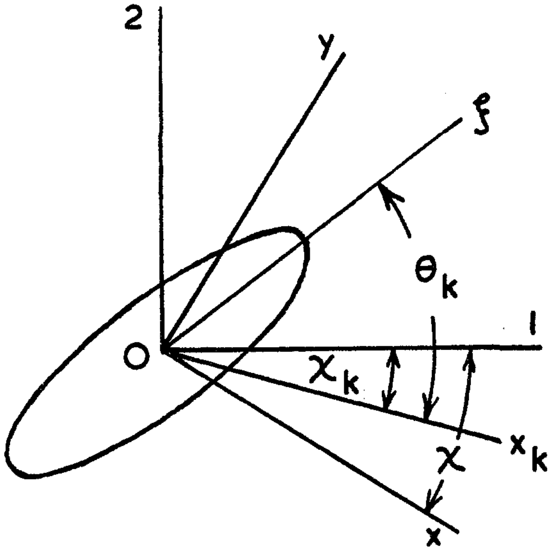


FIG. 9. Parameters for a polydisperse system (Sadron). Ox and Oy are the principal vibration directions of the solution, Ox_k is the direction of preferred orientation of type k particles, and O1 is the flow direction.

The polarization of the whole system when the incident light vector is parallel to Ox or Oy is obtained from equation 46, i.e.,

$$P_i = E\left[H_o + \sum_1^q H_p(\xi_k)\right]_i + P_i\left[K_o + \sum_1^q K_p(\xi_k)\right]_i \qquad (i = x,\ y) \tag{53}$$

where

$$[H_p(\xi_k)]_x = \frac{(N_p)_k}{2\pi}[(\alpha_p - \beta_p)_k S_k + (\alpha_p - \beta_p)_k Q_k \cos 2\xi_k] \tag{54}$$

and

$$[K_p(\xi_k)]_x = \frac{(N_p)_k}{2\pi}[(L_\xi \alpha_p + L_\eta \beta_p)_k S_k + (L_\xi \alpha_p - L_\eta \beta_p)_k Q_k \cos 2\xi_k] \tag{55}$$

with

$$S_k = \int_0^\pi F_k \, d\theta_k \quad \text{and} \quad Q_k = \int_0^\pi F_k \cos \theta_k \, d\theta_k$$

The terms $[H_p(\xi_k)]_y$ and $[K_p(\xi_k)]_y$ may be obtained from $[H_p(\xi_k)]_x$ and $[K_p(\xi_k)]_x$ by interchanging α_p and β_p. The subscript k indicates the k^{th} system, and θ_k is the aximuth of the major axis of a particle of the k^{th} system with respect to the corresponding direction of mean orientation.

From equation 53

$$\begin{aligned} P_x - P_y &= \frac{E}{(1 - K_o)^2}\sum_1^q [(1 - K_o)(\alpha_p - \alpha_p)_x + H_o(L_\xi \alpha_p - L_\eta P_p)]Q_k \cos 2\xi_k \\ &= \sum_1^q (P_x - P_y)_k \cos 2\xi_k \end{aligned} \tag{56}$$

where $(P_x - P_y)_k$ is the difference between the polarizations of the k^{th} system only caused by the electric vector being along Ox_k or Oy_k.

Sadron also shows that

$$\sum_1^q (P_x - P_y)_k \sin 2\xi_k = 0 \tag{57}$$

Equations 56 and 57 hold for a gradient G_k such that $G_k\eta_k = G\eta$, where η_k and η are the viscosity coefficients of the monodisperse and polydisperse systems, respectively. If the refractive indices of the polydisperse system and the monodisperse system are assumed equal, then these equations become

$$\Delta n = \sum_1^q (\Delta n)_k \cos 2\xi_k \tag{58}$$

and

$$0 = \sum_1^q (\Delta n)_k \sin 2\xi_k \tag{59}$$

where Δn is the double refraction of the whole system. Introducing χ, the extinction angle for the polydisperse system, by the relationship $\xi_k = \chi - \chi_k$, then

$$\Delta n^2 = \left[\sum_1^q (\Delta n)_k \sin 2\chi_k\right]^2 + \left[\sum_1^q (\Delta n)_k \cos 2\chi_k\right]^2 \tag{60}$$

and

$$\tan 2\chi = \frac{\sum_1^q (\Delta n)_k \sin 2\chi_k}{\sum_1^q (\Delta n)_k \cos 2\chi_k} \tag{61}$$

Experimental results on a mixture of two monodisperse constituents in solution for the two cases in which the constituents alone in solution exhibit flow double refraction of the same sign and of opposite sign are given by Sadron and Mosimann (123); they appear in good agreement with the results calculated from equations 60 and 61.

E. THEORIES OF PETERLIN AND STUART AND OF SNELLMAN AND BJORNSTAHL

For disperse systems consisting of colloidal particles or large molecules in a solvent, which under all conditions was assumed to be isotropic, Peterlin and Stuart (104) developed a continuum theory. In principle they followed the ideas of Boeder and Haller: namely, that the system becomes ordered and anisotropic when subjected to a flow gradient. They considered, however, particle motion in three dimensions and deduced accurate values for the distribution function F (97). In a manner analogous to that used by Sadron they introduced an anisotropic field, but they did not apply the Lorentz–Lorenz consideration to an ellipsoidal volume element of dimensions equal to that of the particle, but to one of much larger dimensions.

The theory of Snellman and Bjornstahl (133) is identical in concept. They used the results of Peterlin and Stuart for the behavior of the particles under flow but extended the optical considerations by taking into account the effect of absorption of light by the particles and by dealing in more detail with the internal field. This theory is presented in this review, and the equations of Peterlin and Stuart for the birefringence are presented as a special case.

A monodisperse system showing no optical activity is assumed in which the particles are taken to be identical, uncharged, rigid, homogeneous ellipsoids of revolution. The lengths of the major and minor axes are designated by $2a_1$ and $2a_2$, respectively, and the particle is supposed to have a mean radius of $(a_1a_2^2)^{1/3}$ and a volume of $(4\pi a_1a_2^2)/3$. The smallest dimension is taken to be greater than 10 A., so that the molecular structure of the solvent can be neglected, and the largest dimension less than 1000 A., so that the influence of the electric field of the incident light-wave may be treated quasi-statically (90). These limits are those also assumed by Peterlin and Stuart. Particle sizes are taken to be those when in solution, and in some cases they can be expected to differ from the "dried" particles because of possible changes due to solvation and swelling. The principal geometrical axes of the particles, the principal axes of dielectric susceptibility, and the principal axes of the absorption indices are taken to be coincident. The system is assumed to be so dilute that no interactive effects result, so that the total effect of all the particles can be taken as the sum of the effect of each particle. The polydisperse systems later considered are assumed to be composed of a number of groups of particles, each group having the properties given above and differing only in size. The theory applies essentially to a liquid in a concentric cylinder flow cell, although the concepts are of general validity.

Peterlin and Stuart, in studying the behavior of the particles, start from the established fact that the action of the flow gradient G is to cause them to precess. With reference to figure 3 the velocity of rotation of a particle orientated as shown has components $\partial\theta/\partial t$ and $\partial\phi/\partial t$, in the plane $3O\xi$ and about $O3$, respectively, given by

$$\omega_\phi = \partial\phi/\partial t = \frac{G}{2}(1 + b\cos 2\phi) \tag{62}$$

and

$$\omega_\theta = \partial\theta/\partial t = \frac{bG}{4}\sin 2\theta \sin 2\phi \tag{63}$$

These are Jeffery's equations. They differ from Boeder's equations (equations 15 and 16) but are almost identical with those due to Haller (equations 10 and 11). In this case, however,

$$b = \frac{(a_1^2 - a_2^2)}{(a_1^2 + a_2^2)} = \frac{r^2 - 1}{r^2 + 1} \tag{64}$$

where r is the axial ratio a_1/a_2. The effects of thermal agitation will be superimposed. Peterlin and Stuart use precisely the same method as Boeder and Haller to obtain a differential equation giving the distribution function F of the particles. This equation is

$$\frac{\partial F}{\partial t} = D\nabla^2 F - \operatorname{div}(F\omega) \tag{65}$$

where ω is the angular velocity of the particles with components ω_ϕ and ω_θ.

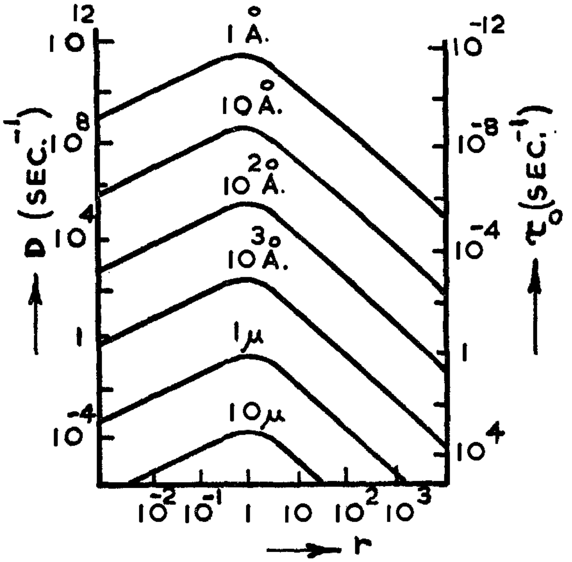


FIG. 10. Diffusion constant, D, and time of adjustment, τ_o, to steady state for ellipsoidal particles of different axial ratios r and mean radii $(a_1^{1/3}a_2^{2/3})$; calculated for viscosity of 0.01 poise at 20°C. After Peterlin and Stuart (106).

In general F depends on θ, ϕ, and time, but according to Peterlin (97), a steady state is reached after a time τ_o, where $\tau_o = 1/6D$ (see figure 10). Then $\partial F/\partial t = 0$, so that by introducing the spherical coördinates θ and ϕ, equation 65 becomes

$$\frac{\partial^2 F}{\partial \theta^2} + \cot\theta \frac{\partial F}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 F}{\partial \phi^2}$$
$$= \frac{b\sigma}{2}\left[\frac{\sin 2\theta \sin 2\phi}{2}\frac{\partial F}{\partial \theta} + \left(\frac{1 + b\cos 2\phi}{b}\right)\frac{\partial F}{\partial \phi} - 3F\sin 2\phi \sin^2\theta\right] \tag{66}$$

where $\sigma = G/D$. This equation is similar to the equation deduced by Haller and identical with that due to Boeder if b is put equal to unity. Its solution, which must satisfy the conditions that F shall be finite at every point of the spherical surface and shall always be positive, has been given by Burgers (7) and Peterlin (97). The latter expresses F as a power series in b:

$$F = F_o + bF_1 + b^2F_2 + \cdots = \sum_{j=0}^{\infty} b^j F_j \tag{67}$$

where F_j is a function of σ, θ, and ϕ and is expressed in terms of a series of spherical harmonics. From the definition of F, the number, dN, of particles the axial directions of which lie within the solid angle dΩ (= sin θ dθ dϕ) is given by dN = F dΩ. It is assumed that with no flow (dN/dΩ) = F = 1, or

$$N_p = \int_0^{4\pi} F\, d\Omega = 4\pi$$

where N_p is the number of particles per unit volume and the final expressions for F are then given in the forms of limiting equations (see Appendix 3). From these the general behavior of F is deduced: for σ equal to zero it is a constant corresponding to random orientation; for small values of σ it has a maximum for values of ϕ near 45° and this maximum shifts towards values of ϕ of 90° as σ increases.

The optical behavior of the system is found by following the method used by Boeder. Thus Bjornstahl and Snellman (and Peterlin and Stuart) calculate the induced polarization P due to the electric field of the incident light-wave and, by relating this to the macroscopic quantities, refractive index, and concentration, deduce an expression for the birefringence. However, whereas Boeder considers the polarization, P, to be that resulting from the induced dipole moments of the orientated particles, namely P_p, Bjornstahl and Snellman follow Sadron in taking P to be the sum of P_p and the isotropic polarization, P_o, of the solvent, i.e.,

$$P = P_o + P_p \tag{68}$$

It is assumed that the light-wave has an electric vector E and it falls on the monodisperse system of permittivity ϵ, which consists of a number of anisotropic triaxial particles in a suspending medium (solvent) of permittivity ϵ_o. The

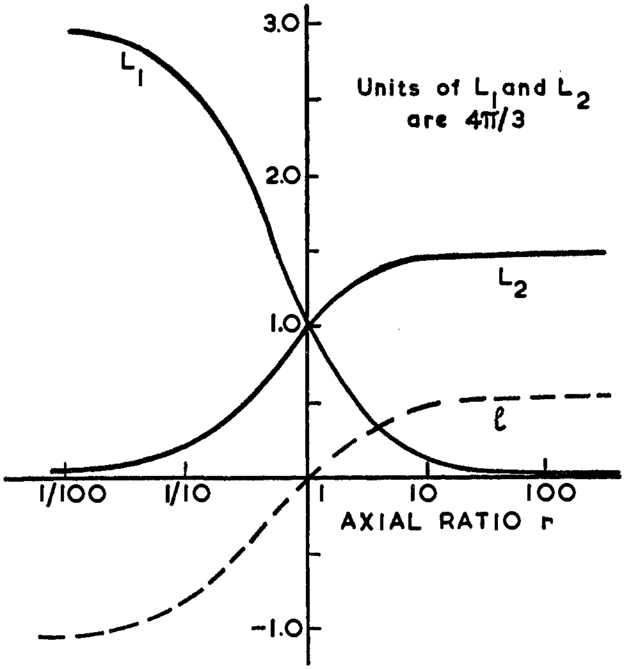


FIG. 11. Shape factors L_1 and L_2 (or L_ξ and L_η) as functions of axial ratio r. These factors are given by $L_1 = \frac{4\pi}{3}(1 - 2l)$ and $L_2 = \frac{4\pi}{3}(1 + l)$, and the variation of l with r is also shown (see Appendix 2).

polarizabilities and the permittivities of a particle along its axes Oξ, Oη, and Oζ (see figure 3) are taken to be α_ξ, α_η, α_ζ and ϵ_ξ, ϵ_η, ϵ_ζ, respectively.

The value of P_o due to the external field E is given by

$$4\pi P_o = (\epsilon_o - 1)E \tag{69}$$

To find P_p, the internal electric field acting on the particles is first found; this is anisotropic. Following Maxwell (86) the components of the internal field along the particle axes Oξ, Oη, and Oζ are taken as $E_\xi + L_\xi P_\xi$, $E_\eta + L_\eta P_\eta$, and $E_\zeta + L_\zeta P_\zeta$, respectively, where E_e ($e = \xi, \eta, \zeta$) are the corresponding components of the external field, P_e ($e = \xi, \eta, \zeta$) are the components of the polarization, and L_e ($e = \xi, \eta, \zeta$) are shape factors characterizing the asymmetry of the internal field (see figure 11 and Appendix 2).

The components along Oξ, Oη, and Oζ of the induced moment are given by

$$m_e = \alpha_e' (1 + L_e \varkappa_e)E_e = A_e E_e \qquad (e = \xi, \eta, \zeta) \tag{70}$$

where $\varkappa_e$ is the relative optical susceptibility of the particle given by $P_e/\epsilon E_e$; it is direction dependent. α_e' is the relative polarizability.

In the directions O1, O2, and O3, the components become

$$m_j = A_\xi E_\xi \cos(\xi j) + A_\eta E_\eta \cos(\eta j) + A_\zeta E_\zeta \cos(\zeta j) \qquad (j = 1, 2, 3) \tag{71}$$

Further, if E_1 is the component of E along O1, then

$$E_e = E_1 \cos(e1) \qquad (e = \xi, \eta, \zeta) \tag{72}$$

so that denoting the components along O1, O2, and O3 due to E_1 alone by m_{11}, m_{21}, m_{31}, respectively,

$$\begin{aligned} m_{11} &= [A_\xi \cos^2(\xi 1) + A_\eta \cos^3(\eta 1) + A_\zeta \cos^2(\zeta 1)]E_1 \\ m_{21} &= [A_\xi \cos(\xi 1)\cos(\xi 2) + A_\eta \cos(\eta 1)\cos(\eta 2) + A_\zeta \cos(\zeta 1)\cos(\zeta 2)]E_1 \\ m_{31} &= [A_\xi \cos(\xi 1)\cos(\xi 3) + A_\eta \cos(\eta 1)\cos(\eta 3) + A_\zeta \cos(\zeta 1)\cos(\zeta 3)]E_1 \end{aligned} \tag{73}$$

If ellipsoids of revolution of volume V are considered, then $\epsilon_\eta = \epsilon_\zeta$, $\alpha_\eta = \alpha_\zeta$, and $L_\eta = L_\zeta$, so that $A_\eta = A_\zeta$. For simplicity in writing, α_ξ' will be replaced by α' and α_η' by β'; also A and B will be used instead of A_ξ and A_η. Then equations 73 become

$$\begin{aligned} m_{11} &= [B + (A - B)\cos^2(\xi 1)]E_1 = \alpha_{11}E_1 \\ m_{21} &= [A - B]\cos(\xi 1)\cos(\xi 2)E_1 = \alpha_{21}E_1 \\ m_{31} &= [A - B]\cos(\xi 1)\cos(\xi 3)E_1 = \alpha_{31}E_1 \end{aligned} \tag{74}$$

Similarly, if E_2 and E_3 are the components of E along O2 and O3, respectively, then the corresponding components of the moment become

$$\begin{aligned} m_{12} &= \alpha_{12}E_2; \quad m_{13} = \alpha_{13}E_3 \\ m_{22} &= \alpha_{22}E_2; \quad m_{23} = \alpha_{23}E_3 \\ m_{32} &= \alpha_{32}E_2; \quad m_{33} = \alpha_{33}E_3 \end{aligned}$$

in which $\alpha_{12} = \alpha_{21}$; $\alpha_{13} = \alpha_{31}$, $\alpha_{32} = \alpha_{23}$ and α_{22}, α_{32}, and α_{33} are obtained from equations 74 by a cyclic interchange of indices.

Now if there are N_p ($= 4\pi$) particles per unit volume having a distribution function given by the solution of equation 66, then the average values M_{jk} of the components of the moment are given by

$$\left.\begin{aligned} M_{11} &= \frac{\int m_{11}\,\mathrm{d}N}{\int \mathrm{d}N} = \frac{\int m_{11}\,F\,\mathrm{d}\Omega}{4\pi} = p_{11}\,E_1 \\ M_{21} &= \frac{\int m_{21}\,\mathrm{d}N}{\int \mathrm{d}N} = \frac{\int m_{21}\,F\,\mathrm{d}\Omega}{4\pi} = p_{21}\,E_1 \\ M_{31} &= \frac{\int m_{31}\,\mathrm{d}N}{\int \mathrm{d}N} = \frac{\int m_{31}\,FD\Omega}{4\pi} = p_{31}\,E_1 \end{aligned}\right\} \tag{75}$$

The quantity p_{ij} ($i = 1, 2, 3,\ j = 1$) is the element of the tensor p representing the contribution of the polarizabilities (*cf.* equation 22). Similar expressions hold for M_{j2} and M_{j3} ($j = 1, 2, 3$). Bjornstahl and Snellman then introduced the facts that $\mathrm{d}\Omega = \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$ and the cosines of the angles ($\xi 1$), ($\xi 2$), and ($\xi 3$) are known in terms of θ and ϕ, to deduce the following equations:

$$\begin{aligned} 4\pi p_{11} &= \int_0^{\pi}\int_0^{2\pi} [A + (A - B)\sin^2\theta\sin^2\phi]\,F\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi \\ 8\pi p_{21} &= (A - B)\left[\int_0^{\pi}\int_0^{2\pi} \sin^2\theta\sin 2\phi\right]F\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi \\ 4\pi p_{22} &= \int_0^{\pi}\int_0^{2\pi} [B + (A - B)\sin^2\theta\cos^2\phi]\,F\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi \\ 4\pi p_{33} &= \int_0^{\pi}\int_0^{2\pi} [B + (A - B)\cos^2\theta]\,F\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi \quad \text{and} \quad p_{ji} = p_{ij} \end{aligned} \tag{76}$$

Now, in general, the polarization P_p in any direction in a medium of permittivity ϵ_o due to N_p particles each having an average component of dipole moment M in that direction caused by an external field E, is given by $P_p = \epsilon_o N_p M$, where, by equation 75, $M = pE$, i.e.,

$$P_p = \epsilon_o N_p p D = \epsilon_o \varkappa E \tag{77}$$

In the case considered here p is given by the symmetrical matrix

$$p = \begin{vmatrix} p_{11} & p_{21} & p_{31} \\ p_{22} & p_{22} & p_{32} \\ p_{31} & p_{32} & p_{33} \end{vmatrix} \tag{78}$$

If ϵ is the permittivity of the whole system, then by equations 68, 69, and 77,

$$(\epsilon - \epsilon_o) = 4\pi\epsilon_o N_p p = 4\pi\varkappa\epsilon_o \tag{79}$$

Bjornstahl and Snellman now assume that the particles are orientated symmetrically with respect to the flow plane so that $p_{31} = p_{32} = 0$. This condition prevails in a concentric cylinder flow cell. To find the directions Ox, Oy, Oz of the principal permittivities of the medium, the rules of tensor algebra are applied to the matrix (equation 78) to transform it to the diagonal form with elements p_x, p_y, and p_z. This is done by rotating the coördinate system O1, O2, O3 by $(90 - \chi)$ about the axis O3, where

$$\tan 2\chi = \tan 2(1x) = \frac{2p_{12}}{p_{11} - p_{22}} \tag{80}$$

and the elements p_x, p_y, p_z are given by

$$p_x = [(p_{11} + p_{22}) + \{(p_{11} - p_{22})^2 + 4p_{12}{}^2\}^{1/2}]_x \tag{81a}$$

$$p_y = [(p_{11} + p_{22}) - \{(p_{11} - p_{22})^2 + 4p_{12}{}^2\}^{1/2}]_y \tag{81b}$$

$$p_x = [p_{33}]_z \tag{81c}$$

The subscripts x, y, z to the brackets indicate that the values of the quantities considered are those for directions Ox, Oy, and Oz, respectively. Thus the values A and B which appear in the expressions for p_{11}, p_{22}, p_{12} in equation 81a are given from equation 70 by

$$A_x = \alpha_x'(1 + L_\xi \varkappa_x); \qquad B_x = \beta_x'(1 + L_\eta \varkappa_x) \tag{82}$$

Corresponding expressions hold in y and z. The angle χ is the extinction angle and its general value found by substitution from equation 76 into equation 80 is given by

$$\tan 2\chi = \frac{\displaystyle\int_0^\pi \int_0^{2\pi} F \sin^3\theta \sin 2\phi \, d\theta \, d\phi}{\displaystyle\int_0^\pi \int_0^{2\pi} F \sin^3\theta \cos 2\phi \, d\theta \, d\phi} \tag{83}$$

This equation agrees with equation 23 of Boeder when $\theta = 90°$.

The magnitude of the birefringence is found by finding the values of p_x, p_y, and p_z from equations 76 and 81 and hence evaluating the quantities $\varkappa_x$, $\varkappa_y$, and $\varkappa_z$. Then, finally,

$$\frac{\epsilon_x - \epsilon_y}{4\pi\epsilon_0} = \varkappa_x - \varkappa_y = N_p \Pi_{xy} f(\sigma, b) \tag{84}$$

and

$$\frac{\epsilon_x - \epsilon_z}{4\pi\epsilon_0} = \varkappa_x - \varkappa_z = N_p \Pi_{xz} f(\sigma, b) \tag{85}$$

where $f(\sigma, b)$ is a function of σ and b called the orientation factor, and Π_{xy} and Π_{xz} are optical factors given by

$$\Pi_{xy} = 4\left[\frac{\Psi(1 - \Lambda) + N_p\alpha'\Phi}{4(1 - \Lambda)^2 - (N_p \Phi f(\sigma, b))^2}\right]$$

$$\Pi_{xz} = \frac{\Psi(1 - \Lambda) + N_p \Phi(\alpha') + \dfrac{\sigma^2 b^2 \Xi}{840} - \dfrac{\sigma^2 b^2 \Xi(1 - \Lambda)}{420 f(\sigma, b)}}{2(1 - \Lambda)^2 - N_p \Phi(1 - \Lambda) f(\sigma, b)}$$

In these equations

$$3\Lambda = N_p(\alpha' L_\xi + 2\beta' L_\eta); \quad 3\alpha' = \alpha' + 2\beta'$$
$$\Phi = (\alpha' L_\xi - \beta' L_\eta); \quad \Xi = \alpha' + 6\beta'$$
$$\Psi = \alpha' - B'$$

For the quasi-stationary conditions under which these equations have been derived, permittivity may be replaced by the square of the refractive index. In the general case the refractive index is a complex index given by $\nu_j = n_j(1 - \kappa_j i)$, where $j = x, y, z$, and n_j and κ_j are the real refractive index and the absorption index of the solution, respectively. If $\epsilon_o = n_o^2$ and $\nu_x + \nu_y = 2\nu$, then by equation 84

$$\frac{\epsilon_x - \epsilon_y}{4\pi\epsilon_o} = \frac{\nu_x^2 - \nu_y^2}{4\pi n_o^2} = \frac{(\nu_x - \nu_y)2\nu}{4\pi n_o^2} = N_p\,\Pi_{xy} f(\sigma, b) \tag{86}$$

Thus if κ^2 is negligible, the birefringence Δn is given by

$$\Delta n = n_x - n_y = \frac{2\pi N_p}{n} n_o^2\, \mathcal{R} f(\sigma, b) \tag{87}$$

where $\mathcal{R}$ represents the real part of Π_{xy}.

This treatment also allows an expression for the dichroism of the solution to be found, since by considering the imaginary part $\mathcal{I}$ of Π_{xy}

$$-(n_x^2\kappa_x - n_y^2\kappa_y) = 2\pi N_p n_o^2 \mathcal{I} f(\sigma, b) \tag{88}$$

Expressions for $(n_x - n_z)$ and $-(n_x^2\kappa_x - n_z^2\kappa_z)$ can be deduced from which it is clear that the liquid in flow behaves as a biaxial crystal (51). With the usual method of observation in a concentric cylinder cell only the quantity $n_x - n_y$ can be measured.

The application of equations 83 and 87 to get expressions for χ and Δn requires the evaluation of F and $f(\sigma, b)$ and the determination of $\mathcal{R}$.

In the range $\sigma \leqslant 1.5$ and $b \leqslant 1$, Peterlin and Stuart find that

$$\chi = \frac{\pi}{4} - \frac{\sigma}{12}\left[1 - \frac{\sigma^2}{108}\left(1 + \frac{24b^2}{35}\right) + \cdots\cdots\right] \tag{89}$$

and

$$f(\sigma, b) = \frac{\sigma b}{15}\left[1 - \frac{\sigma^2}{72}\left(1 + \frac{6b^2}{35}\right) + \cdots\cdots\right] \tag{90}$$

Equation 89 is almost identical with equation 25a deduced by Boeder. For higher values of σ, no correspondingly simple expressions are available, but by use of an electronic computer F has been evaluated (40, 124) for all values of σ up to 200 and tables of χ and $f(\sigma, b)$ drawn up for various axial ratios. The results are reproduced in figure 12 and table 2. For the evaluation of $\mathcal{R}$ it is necessary to know α' and β' in terms of measurable quantities and to have values of L_ξ and L_η. According to Gans (38)

$$\epsilon_o\alpha' = \frac{\epsilon_o(\epsilon_\xi - \epsilon_o)V}{4\pi\epsilon_o + (\epsilon_\xi - \epsilon_o)L_1} = g_1 V \tag{91a}$$

$$\xi_o\,\beta' = \frac{\epsilon_o(\epsilon_\eta - \epsilon_o)V}{4\pi\epsilon_o + (\epsilon_\eta - \epsilon_o)L_2} = g_2 V \tag{91b}$$

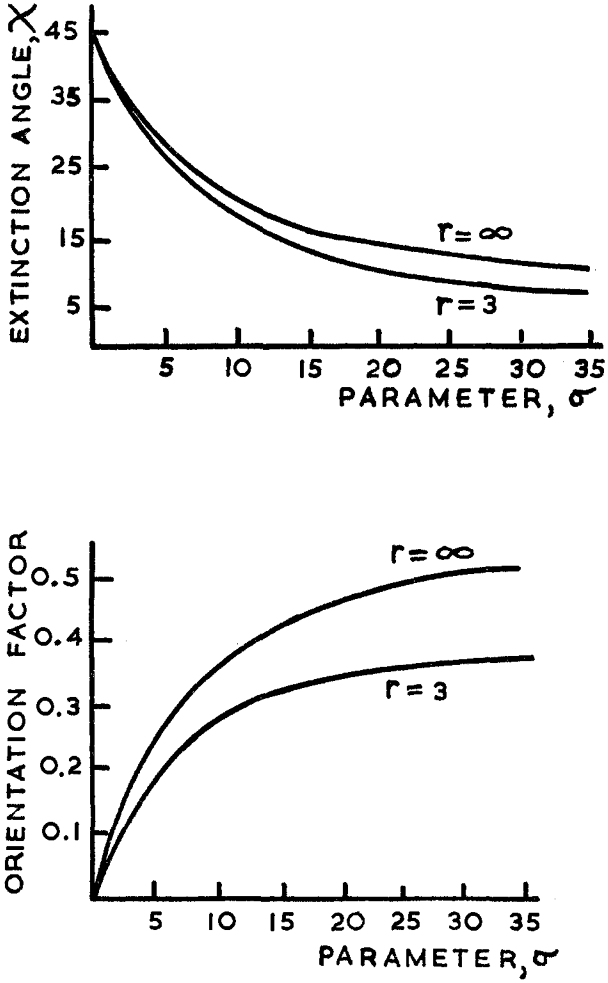


FIG. 12. Extinction angle, χ, and orientation factor, $f(\sigma, b)$ plotted against σ for different axial ratios r. After Scheraga, Edsall, and Gadd (124).

whence

$$g_1 - g_2 = \frac{3\epsilon_o}{4\pi}\left\{\frac{3\epsilon_o(\epsilon_\xi - \epsilon_\eta) + (\epsilon_\xi - \epsilon_o)(\epsilon_\eta - \epsilon_o)(L_1' - L_2')}{[3\epsilon_o + L_1'(\epsilon_\xi - \epsilon_o)][3\epsilon_o + L_2'(\epsilon_\eta - \epsilon_o)]}\right\} \tag{92}$$

In these equations $L_1' = 3L_1/4\pi$ and $L_2' = 3L_2/4\pi$, where L_1 and L_2 are the shape factors shown in figure 11, and if μ and m denote the complex and real refractive indices of the particle, respectively, and κ is its absorption index, then

$$\epsilon_\xi^{1/2} = \mu_\xi = m_\xi(1 - \kappa_\xi i); \quad \epsilon_\eta^{1/2} = \mu_\eta = m_\eta(1 - \kappa_\eta i) \tag{93}$$

Peterlin and Stuart considered the case when the concentration was low and no dichroism was present. Then, if $(g_1 - g_2)^{\mathfrak{R}}$ denotes the real part of $(g_1 - g_2)$,

$$\Delta n = \frac{2\pi N_p V}{n}(g_1 - g_2)^{\mathfrak{R}} f(\sigma, b) \tag{94}$$

where $f(\sigma, b)$ is given by equation 90.

TABLE 2A

Extinction angle, χ, as function of σ for various axial ratios r[a]

From Scheraga, Edsall, and Gadd (124), with r replacing p and σ replacing α

$\frac{r}{\sigma}$	1.00	2.00	3.00	4.00	5.00	7.00	10.00	16.00	25.00	50.00	∞
0.00	45.00	45.00	45.00	45.00	45.00	45.00	45.00	45.00	45.00	45.00	45.00
0.25	43.81	43.81	43.81	43.81	43.81	43.81	43.81	43.81	43.81	43.81	43.81
0.50	42.62	42.62	42.62	42.62	42.62	42.62	42.62	42.62	42.62	42.62	42.62
0.75	41.44	41.44	41.44	41.44	41.45	41.45	41.45	41.45	41.45	41.45	41.45
1.00	40.27	40.28	40.29	40.29	40.29	40.30	40.30	40.30	40.30	40.30	40.30
1.25	39.12	39.14	39.15	39.16	39.16	39.17	39.17	39.17	39.17	39.17	39.17
1.50	37.98	38.02	38.04	38.05	38.06	38.07	38.07	38.07	38.07	38.07	38.08
1.75	38.87	36.92	36.96	36.98	36.99	37.00	37.01	37.01	37.01	37.01	37.01
2.00	35.78	35.86	35.91	35.94	35.96	35.97	35.98	35.98	35.99	35.99	35.99
2.25	34.72	34.82	34.90	34.94	34.96	34.98	34.99	35.00	35.00	35.00	35.00
2.50	33.69	33.82	33.93	33.98	34.01	34.03	34.04	34.05	34.05	34.06	34.06
3.00	31.72	31.93	32.09	32.17	32.21	32.25	32.27	32.28	32.29	32.29	32.29
3.50	29.87	30.18	30.41	30.52	30.58	30.63	30.66	30.68	30.69	30.69	30.69
4.00	28.16	28.56	28.87	29.02	29.09	29.17	29.21	29.23	29.24	29.25	29.25
4.50	26.57	27.08	27.47	27.66	27.75	27.85	27.89	27.93	27.94	27.95	27.95
5.00	25.10	25.73	26.20	26.42	26.54	26.65	26.71	26.75	26.77	26.77	26.78
6.00	22.50	23.35	23.98	24.29	24.45	24.60	24.68	24.73	24.75	24.76	24.76
7.00	20.30	21.35	22.13	22.51	22.71	22.90	23.00	23.06	23.09	23.10	23.11
8.00	18.43	19.65	20.57	21.02	21.26	21.48	21.60	21.68	21.70	21.72	21.73
9.00	16.84	18.20	19.25	19.75	20.02	20.27	20.41	20.50	20.53	20.55	20.55
10.00	15.48	16.95	18.09	18.66	18.96	19.24	19.39	19.49	19.53	19.54	19.55
12.50	12.82	14.45	15.80	16.48	16.84	17.18	17.37	17.49	17.54	17.56	17.56
15.00	10.90	12.60	14.07	14.84	15.25	15.64	15.86	16.00	16.05	16.08	16.09
17.50	9.46	11.16	12.72	13.55	14.00	14.44	14.68	14.84	14.89	14.92	14.93
20.00	8.35	10.02	11.62	12.51	13.00	13.47	13.74	13.90	13.97	14.00	14.01
22.50	7.46	9.08	10.71	11.64	12.16	12.67	12.97	13.14	13.21	13.24	13.26
25.00	6.75	8.30	9.95	10.91	11.46	12.00	12.31	12.50	12.58	12.62	12.63
30.00	5.66	7.08	8.71	9.72	10.32	10.91	11.26	11.48	11.57	11.61	11.62
35.00	4.86	6.17	7.76	8.80	9.43	10.07	10.45	10.69	10.78	10.83	10.85
40.00	4.27	5.46	7.00	8.04	8.70	9.38	9.79	10.06	10.16	10.21	10.23
45.00	3.80	4.90	6.37	7.41	8.08	8.79	9.23	9.51	9.62	9.68	9.69
50.00	3.42	4.43	5.84	6.87	7.54	8.28	8.74	9.03	9.15	9.22	9.23
60.00	2.86	3.73	5.00	5.99	6.66	7.41	7.89	8.20	8.33	8.40	8.42
80.00	2.14	2.82	3.88	4.75	5.36	6.08	6.55	6.86	6.98	7.05	7.08
100.00	1.72	2.27	3.15	3.90	4.45	5.09	5.52	5.80	5.92	5.98	6.00
200.00	0.86	1.14	1.62	2.04	2.35	2.74	2.99	3.16	3.23	3.27	3.28

[a] Values of χ for σ-values above 60 are of uncertain validity.

For small gradients $f(\sigma, b) \doteq b/15$, and since the volume concentration $c = N_pV$, or the weight concentration (expressed in grams per cubic centimeter) $c' = Mc/N_AV$, where M and N_A are the molecular weight and Avogadro's number, respectively.

$$[M]_{sp} = \frac{2\pi}{15n^2}(g_1 - g_2)^{\mathfrak{R}}\frac{b}{\eta_oD} \quad \text{(concentration in cm.}^3\text{ cm.}^{-3}\text{)} \tag{95a}$$

TABLE 2B

*Orientation factor, $f(\sigma, b)$ as function of σ for various axial ratios r**
From Scheraga, Edsall, and Gadd (124), with r replacing p and σ replacing α

$\frac{r}{\sigma}$	1.00	2.00	3.00	4.00	5.00	7.00	10.00	16.00	25.00	50.00	∞
0.00	0.00000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.25	0.00000	0.0100	0.0133	0.0147	0.0154	0.0160	0.0163	0.0165	0.0166	0.0166	0.0167
0.50	0.00000	0.0199	0.0266	0.0293	0.0307	0.0319	0.0325	0.0329	0.0331	0.0332	0.0332
0.75	0.00000	0.0298	0.0397	0.0437	0.0458	0.0476	0.0486	0.0492	0.0494	0.0495	0.0496
1.00	0.00000	0.0394	0.0525	0.0579	0.0606	0.0630	0.0643	0.0651	0.0654	0.0656	0.0656
1.25	0.00000	0.0489	0.0651	0.0718	0.0751	0.0781	0.0797	0.0807	0.0811	0.0813	0.0813
1.50	0.00000	0.0581	0.0774	0.0853	0.0892	0.0927	0.0947	0.0958	0.0963	0.0965	0.0966
1.75	0.00000	0.0671	0.0893	0.0984	0.1029	0.1069	0.1092	0.1105	0.1110	0.1113	0.1114
2.00	0.00000	0.0757	0.1007	0.1110	0.1161	0.1206	0.1231	0.1246	0.1252	0.1255	0.1256
2.25	0.00000	0.0840	0.1118	0.1231	0.1287	0.1338	0.1366	0.1382	0.1388	0.1392	0.1393
2.50	0.00000	0.0920	0.1223	0.1348	0.1409	0.1464	0.1494	0.1512	0.1519	0.1523	0.1524
3.00	0.00000	0.1069	0.1421	0.1565	0.1636	0.1700	0.1735	0.1756	0.1764	0.1768	0.1769
3.50	0.00000	0.1204	0.1601	0.1762	0.1842	0.1914	0.1954	0.1977	0.1986	0.1991	0.1992
4.00	0.00000	0.1326	0.1763	0.1941	0.2029	0.2108	0.2152	0.2177	0.2187	0.2192	0.2194
4.50	0.00000	0.1436	0.1909	0.2103	0.2198	0.2284	0.2331	0.2359	0.2370	0.2376	0.2377
5.00	0.00000	0.1534	0.2041	0.2249	0.2351	0.2444	0.2494	0.2524	0.2536	0.2542	0.2544
6.00	0.00000	0.1700	0.2268	0.2502	0.2617	0.2721	0.2778	0.2812	0.2825	0.2832	0.2834
7.00	0.00000	0.1835	0.2456	0.2712	0.2839	0.2954	0.3017	0.3054	0.3069	0.3076	0.3079
8.00	0.00000	0.1945	0.2613	0.2891	0.3028	0.3153	0.3222	0.3262	0.3278	0.3286	0.3289
9.00	0.00000	0.2035	0.2746	0.3044	0.3191	0.3326	0.3399	0.3443	0.3460	0.3469	0.3472
10.00	0.00000	0.2111	0.2860	0.3176	0.3334	0.3477	0.3556	0.3603	0.3621	0.3630	0.3633
12.50	0.00000	0.2253	0.3086	0.3444	0.3624	0.3788	0.3879	0.3933	0.3953	0.3964	0.3968
15.00	0.00000	0.2351	0.3254	0.3649	0.3848	0.4032	0.4133	0.4193	0.4216	0.4228	0.4232
17.50	0.00000	0.2421	0.3383	0.3810	0.4028	0.4229	0.4340	0.4406	0.4431	0.4444	0.4449
20.00	0.00000	0.2473	0.3485	0.3942	0.4177	0.4393	0.4513	0.4585	0.4612	0.4626	0.4631
22.50	0.00000	0.2513	0.3568	0.4052	0.4302	0.4533	0.4661	0.4737	0.4766	0.4782	0.4787
25.00	0.00000	0.2544	0.3637	0.4147	0.4412	0.4659	0.4796	0.4878	0.4910	0.4926	0.4932
30.00	0.00000	0.2589	0.3744	0.4299	0.4592	0.4867	0.5020	0.5113	0.5148	0.5166	0.5173
35.00	0.00000	0.2619	0.3823	0.4418	0.4736	0.5037	0.5206	0.5308	0.5347	0.5367	0.5374
40.00	0.00000	0.2640	0.3883	0.4513	0.4854	0.5181	0.5366	9.5478	0.5521	0.5543	0.5551
45.00	0.00000	0.2656	0.3930	0.4589	0.4952	0.5304	0.5505	0.5626	0.5673	0.5698	0.5706
50.00	0.00000	0.2667	0.3967	0.4653	0.5037	0.5413	0.5630	0.5763	0.5814	0.5841	0.5850
60.00	0.00000	0.2683	0.4021	0.4750	0.5169	0.5590	0.5838	0.5991	0.6051	0.6083	0.6094
80.00	0.00000	0.2699	0.4082	0.4868	0.5338	0.5826	0.6125	0.6314	0.6389	0.6429	0.6442
100.00	0.00000	0.2707	0.4114	0.4933	0.5434	0.5966	0.6298	0.6511	0.6596	0.6642	0.6657
200.00	0.00000	0.2718	0.4161	0.5034	0.5588	0.6199	0.6592	0.6850	0.6954	0.7010	0.7029

* Values of f for σ-values above 60 are of uncertain validity.

or

$$[M_{sp}] = \frac{2\pi}{15n^2}\frac{N_A V}{M}(g_1 - g_2)^{\mathcal{R}}\frac{b}{\eta_0 D} \quad \text{(concentration in g. cm.}^{-3}\text{)} \tag{95b}$$

In practice the refractive indices n and n_0 of the solution and solvent, respectively, may be assumed to have the same value. Clearly $[M]_{sp}$ is independent of concentration.

By equation 92,

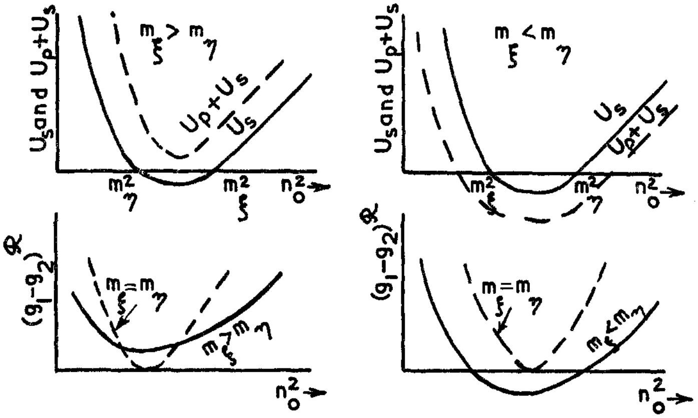
$$(g_1 - g_2)^{\mathcal{R}} = \frac{3}{4\pi}\frac{U_p + U_s}{W_\xi + W_\eta} \tag{96}$$

where

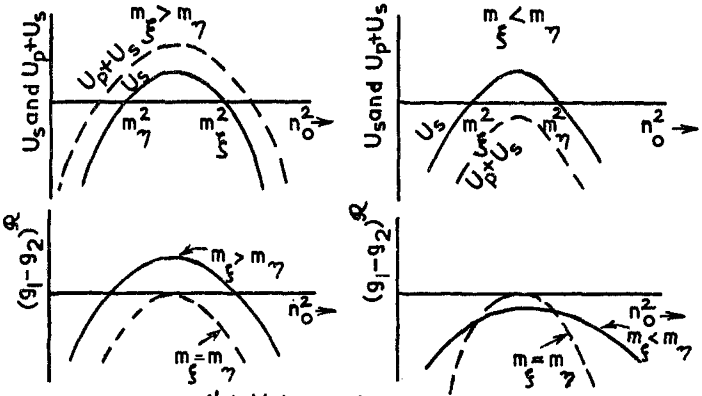
$$U_p = 3(m_\xi^2 - m_\eta^2);\ n_o^2 U_s = (m_\xi^2 - n_o^2)(m_\eta^2 - n_o^2)(L_2' - L_1')$$

$$n_o^2 W_\xi = 3n_o^2 + L_1'(m_\xi^2 - n_o^2);\ n_o^2 W_\eta = 3n_o^2 + L_2'(m_\eta^2 - n_o^2)$$

The values of U_p and U_s depend on the optical anisotropy (eigen anisotropy and shape (form anisotropy) of the particles, respectively, and the sum can be a positive or a negative quantity according to the value of n_o. The product $W_\xi W_\eta$ is, in practice, always positive, so that $(g_1 - g_2)^{\mathfrak{R}}$ can, under certain conditions, undergo a change of sign. The conditions are for elongated ellipsoids ($r > 1$, b positive) that m_ξ is less than m_η, and for disc-shaped particles ($r < 1$, b negative) that m_ξ is greater than m_η. If U_p is zero, i.e., isotropic particles, $(g_1 - g_2)^{\mathfrak{R}}$ is always positive when $r > 1$ and negative when $r < 1$. These facts, which are represented in figure 13, present certain similarities to form double refraction. The graph of Δn of a system of particles plotted against n_o^2 always



(a) Values for r>1



(b) Values for r<1

FIG. 13. Curves showing variation of $(g_1 - g_2)^{\mathfrak{R}}$ and parameters U_p and U_s for different values of solvent refractive index, n_o. (a) elongated elipsoids; (b) flattened ellipsoids.

takes the same form whatever the value of r, because Δn is proportional to $b(g_1 - g_2)^{\Re}$ and a change from $r > 1$ to $r < 1$ reverses the sign of b.

When dichroism is present, as in the case of a herapathite sol in flow, the expression for Δn is determined by the absorption coefficient. This was treated briefly by Snellman and Bjornstahl, who also indicated what would be the behavior of more highly concentrated solutions. For the latter case it was assumed that the eccentricity factor of the field is l_f, where

$$L_\xi = \frac{4\pi}{3}(1 - 2l_f) \text{ and } L_\eta = \frac{4\pi}{3}(1 + l_f)$$

(see Appendix 2). Then from equation 87,

$$\Delta n = \frac{2\pi N_p V}{n}\left\{(g_1 - g_2) - \frac{4\pi N_p V l_f}{3\epsilon_o}[4(g_1^2 + g_2^2) + g_1\, g_2]\right\}^{\Re} f(\sigma, b) \tag{97}$$

so that for small gradients

$$[M] = \frac{2\pi}{n^2}\left\{(g_1 - g_2) - \frac{4\pi l_f c}{3n_o^2}[4(g_1^2 + g_2^2) + g_1 g_2]\right\}^{\Re} \frac{b}{15\eta_o D} \tag{98}$$

where $\Re$ again denotes that the real part of the optical factor is to be taken. $[M]$ is concentration dependent, but it must be realized that with increasing concentration the hydrodynamic interaction of the particles increases, which leads to a decrease in D and an increase in $f(\sigma, b)$. This makes equation 98 of uncertain value; furthermore, as the concentration increases, so the possible validity of the initial assumptions decreases.

F. EXTENSIONS OF SNELLMAN–BJORNSTAHL THEORY

1. *Charged particles*

Charges on the particles will, in general, give rise to repulsive forces between them. These, if very high concentrations are present, could conceivably change the polarizabilities of the particles by bringing about a disturbance of their electronic structure. However, the concentrations for which equations 62 and 63 hold are such as to preclude this, and it is therefore assumed here that the only effect of the repulsive forces is to make the particles align themselves parallel to one another. Joly (52) has indicated how this effect may be treated.

It is assumed that the assembly of charged particles acquires an angular velocity ω_r, due to the repulsive forces, which is additional to the flow velocity, ω. Then, for steady motion, equation 65 is replaced by

$$D\nabla^2 F - \operatorname{div}(F\omega) - \operatorname{div}(F\omega_r) = 0 \tag{99}$$

where $F\omega_r$ is found to be given by

$$F\omega_r = B'\left[\frac{32kT}{9I}\right]^{1/2} f(S) \operatorname{grad} F \tag{100}$$

In this equation B' is a positive constant, I is the moment of inertia of the particle about its axis of rotation, and $f(S)$ is a function of S which is given by $S =$

TABLE 3

Values of the function $f(S)$

From Joly (52)

S	$f(S)$	S	$f(S)$	S	$f(S)$
0.0	0.0	1.1	0.298	3.0	0.415
0.1	0.105	1.2	0.321	3.5	0.4235
0.2	0.149	1.4	0.338	4.0	0.429
0.3	0.178	1.6	0.354	4.5	0.432
0.4	0.204	1.8	0.367	5.0	0.435
0.5	0.225	2.0	0.379	6.0	0.440
0.6	0.243	2.2	0.388	7.0	0.442
0.7	0.259	2.4	0.395	8.0	0.443
0.8	0.275	2.6	0.4035	9.0	0.4436
0.9	0.287	2.8	0.410	10.0	0.4438

$(h_M - h_o)/kT$. The quantity $h_M - h_o$ represents the potential barrier which a particle would have to jump in rotating through 180°. By substitution into equation 99 and rearrangement

$$\left[D - B'\left[\frac{32kT}{9I}\right]^{1/2} f(S)\right]\nabla^2 F - \text{div } F\omega = 0$$

or

$$D_a \nabla^2 F - \text{div } F\omega = 0 \qquad (101)$$

It is seen, therefore, that the effect of the charges is simply to reduce the diffusion constant from D to an apparent value D_a. Values of $f(S)$ as S increases from 0 to 10 are given by Joly (see table 3); for the two-dimensional case it is deduced that $D_a = D[1 - 2.25\, f(S)]$, an expression which probably holds approximately for three-dimensional motion.

2. Polydisperse systems

In order to find the effect for a suspension of a liquid of refractive index n_o containing q monodisperse systems, which do not mutually interact, each system, if it alone were present in suspension, is assumed to give rise to an extinction angle and birefringence given by equations 83 and 94. Then the q systems regarded as one system having $N(= \sum_1^q N_k)$ particles per unit volume may be shown to give rise to an extinction angle χ and birefringence $\Delta\nu$ given by

$$\tan 2\chi = \frac{\sum_{k=1}^{q} (\Delta\nu \cdot \nu)_k \sin 2\chi_k}{\sum_{k=1}^{q} (\Delta\nu \cdot \nu)_k \cos 2\chi_k} \qquad (102)$$

$$(\Delta\nu \cdot \nu)^2 = \left[\sum_{k=1}^{q} (\Delta\nu \cdot \nu)_k \cos 2\chi_k\right]^2 + \left[\sum_{k=1}^{q} (\Delta\nu \cdot \nu)_k \sin 2\chi_k\right]^2 \qquad (103)$$

in which $\Delta\nu_k$ and χ_k are the birefringence and extinction angle, respectively, of the k^{th} system. In practice the value of ν for the solution containing q monodisperse systems and that for a solution of the same concentration containing only one system are usually the same. The equations are also valid for charged particles.

3. The effect of optical activity

This problem was attempted by Bjornstahl (2). It was assumed that the activity changed with gradient, and by using a method involving the Poincaré sphere (49), relationships were obtained for the observed double refraction in terms of the double refraction with no activity and no absorption, of the degree of activity, and of the absorption indices. The theory lacks clarity and the results, even if correct, are too complicated to be of use.

VI. THEORIES FOR LIQUIDS

A. THEORY OF PETERLIN AND STUART

The theory of Raman and Krishnan (Section IV) would appear to apply both to colloidal solutions and to liquids composed of anisotropic molecules. A different theory has been presented by Peterlin and Stuart (105) along the lines of their earlier theory for rigid particles. They point out that the molecules cannot, as for gaseous molecules, be considered to be independent and initially in a state of random distribution, because in liquids a state of order is present. This order, which extends only to a distance of a few molecules from a given molecule, they call "Nahordnung" after a suggestion of Zernike (168). The two main effects of the "Nahordnung" are that the ordered environment of any molecule is characterized by a preferred direction in space which only slowly changes with time and that the internal field acting on a molecule is anisotropic. A schematic picture of "Nahordnung" is shown in figure 14.

To find the anisotropic field Peterlin and Stuart consider any molecule to be surrounded by a fictitious surface having the shape of an ellipsoid of revolution. The dimensions are taken to be large relative to the distances between the molecules and its major axis assumed to lie along the preferred direction of the

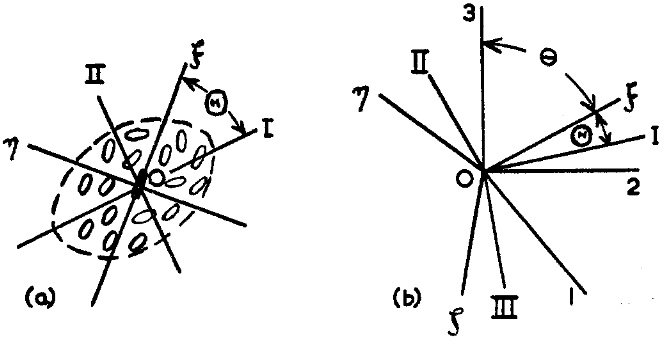


FIG. 14. (a) Schematic picture of the "Nahordnung." OI and OII are the directions of anisotropy of the internal field. (b) Parameters for the theory of Peterlin and Stuart for liquids (105).

"Nahordnung." Then the Lorentz relationship for the internal field is replaced by $E_j + L_jP_j$ (j = I, II, III) where

$$L_{\mathrm{I}} = \frac{4\pi}{3}(1 - 2l); \qquad L_{\mathrm{II}} - L_{\mathrm{III}} = \frac{4\pi}{3}(1 + l)$$

Thus

$$E_j + L_j P_j = \frac{\epsilon + 2}{3} l_j' E_j$$

where

$$l_{\mathrm{I}}' = 1 - 2l'; \;\; l_{\mathrm{II}}' = l_{\mathrm{III}}' = 1 + l'$$

with

$$l' = \frac{\epsilon - 1}{\epsilon + 2} l = \frac{n^2 - 1}{n^2 + 2} l$$

In these equations ϵ and n are the permittivity and refractive index of the medium and l is a function of the axial ratio of the fictitious ellipsoid.

The result of the existence of such a preferred direction in space is that free rotation of a molecule cannot occur, because rotation out of this preferred direction requires potential energy, h. This energy is a function of position and is called the delay potential; for polar and nonpolar molecules it is given by $h = -h_o \cos \Theta$ and $h = h \cos^2\Theta$, respectively, where Θ is as shown in figure 14.

Other possible effects of the "Nahordnung," which are mentioned but not considered by Peterlin and Stuart, are the deformation of the electron shells surrounding the molecules and a periodic variation of the "Nahordnung."

The molecules, which are taken as ellipsoids of revolution of axial ratio a_1/a_2, assume a kinematic orientation when subjected to flow with their orientation defined by a distribution function F. The magnitude of the induced double refraction is then found by differentiation of the equation giving the molar polarization $[P]$ of the liquid with the effects of the orientation of the molecules, the delay potential, and the field anisotropy taken into consideration.

Thus

$$[P] = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} = \frac{4\pi}{3} N_{\mathrm{A}} \bar{\alpha} \tag{104}$$

where M, ρ, and N_{A} are the molecular weight, the density, and Avogadro's number, respectively; $\bar{\alpha}$ is the mean apparent polarizability, i.e., the average value of all the induced molecular moments in a unit field.

Hence

$$\Delta n = \frac{4\pi}{3} N_{\mathrm{A}} \frac{\rho}{M} \frac{(n^2 + 2)^2}{6n} \Delta\bar{\alpha} \tag{105}$$

where $\Delta\bar{\alpha}$ is the sum for all molecules of the resolved parts of the differences of the principal polarizabilities along the directions O1 and O2 (figure 14 (b)) and which, according to Peterlin and Stuart, is given by

$$\begin{aligned} \Delta\bar{\alpha} &= (\alpha_1 - \alpha_2) \int F\,[\cos^2(\xi 2) - \cos^2(\xi 1)]\, d\Omega \qquad (106) \\ &= (\alpha_1 - \alpha_2) f(\xi 2, \xi 1) \end{aligned}$$

where $d\Omega = \sin\theta \, d\theta \, d\phi$ and the cosine terms are functions of θ and ϕ.

In finding the value of $f(\xi 2, \xi 1)$, it is considered that, because the kinematic orientation of the molecule in flow is determined by the motion of the whole ordered neighborhood, the delay potential does not influence F; neither does the anisotropy of the field. Even with the highest realizable values of G, which are between 10^4 and 10^5 sec.$^{-1}$, σ is only of magnitude 10^{-5} to 10^{-4} for molecules. Peterlin and Stuart consider therefore that F is given accurately by

$$F = 1 + \frac{\sigma b}{4} \sin 2\phi \sin^2 \theta$$

to give a value for $f(\xi 2, \xi 1)$ of $\sigma b/15$.

The polarizabilities α_1 and α_2 are really the optical polarizabilities of the molecules when they are in the gaseous state. They cannot be used for liquids because the delay potential and the anisotropic field come into play, but it is deduced that $(\alpha_1 - \alpha_2)$ must be replaced by $R_d(\alpha_1 - \alpha_2)$, where R_d is a reduction factor (<1) given by

$$R_d = 1 - \frac{l'}{2}\left(\frac{2\alpha_1 + \alpha_2}{\alpha_1 - \alpha_2}\right)(3g - 1) \tag{107}$$

The quantity g is a function of y, where $y = h/kT$. The values of R_d for different values of g and l' for polar and nonpolar molecules are shown in figure 15.

Thus from equations 105 and 106 for a liquid containing N_o molecules per unit volume $(N_o = N_{\text{A}}\rho/M)$

$$\Delta n = \frac{2\pi}{3} \frac{(n^2 + 2)^2}{n} N_o(\alpha_1 - \alpha_2) \frac{\sigma b}{45} R_d \tag{108}$$

The Maxwell constant $[M]$ is given by

$$[M] = \frac{\Delta n}{n\eta G} = \frac{2\pi}{3}\left(\frac{n^2 + 2}{n}\right)^2 N_o(\alpha_1 - \alpha_2) \frac{b}{45\eta D} R_d \tag{109}$$

and the molar Maxwell constant $[M]_m$, which is taken to be equal to

$$\frac{1}{9} \frac{M}{\rho} \left(\frac{n}{n^2 + 2}\right)^2 [M]$$

by

$$[M]_m = \frac{2\pi}{27} N_{\text{A}} \frac{(\alpha_1 - \alpha_2)}{45\eta D} bR_d \tag{110}$$

For the more general case of molecules having the shape of a triaxial ellipsoid with principal polarizabilities α_1, α_2, and α_3 along the main geometrical axes of lengths $2a_1$, $2a_2$, and $2a_3$, respectively,

$$[M] = \frac{\pi}{3}\left(\frac{n^2 + 2}{n}\right)^2 N_o \frac{1}{45\eta}\left[\frac{(\alpha_1 - \alpha_2)b_{12}}{D_3} + \frac{(\alpha_2 - \alpha_3)b_{23}}{D_1} + \frac{(\alpha_3 - \alpha_1)b_{31}}{D_2}\right] R_d$$

where D_1, D_2, and D_3 are the diffusion constants for rotation about the three main axes and

$$b_{jk} = (a_j^2 - a_k^2)/(a_j^2 + a_k^2) \qquad (j, k = 1, 2, 3)$$

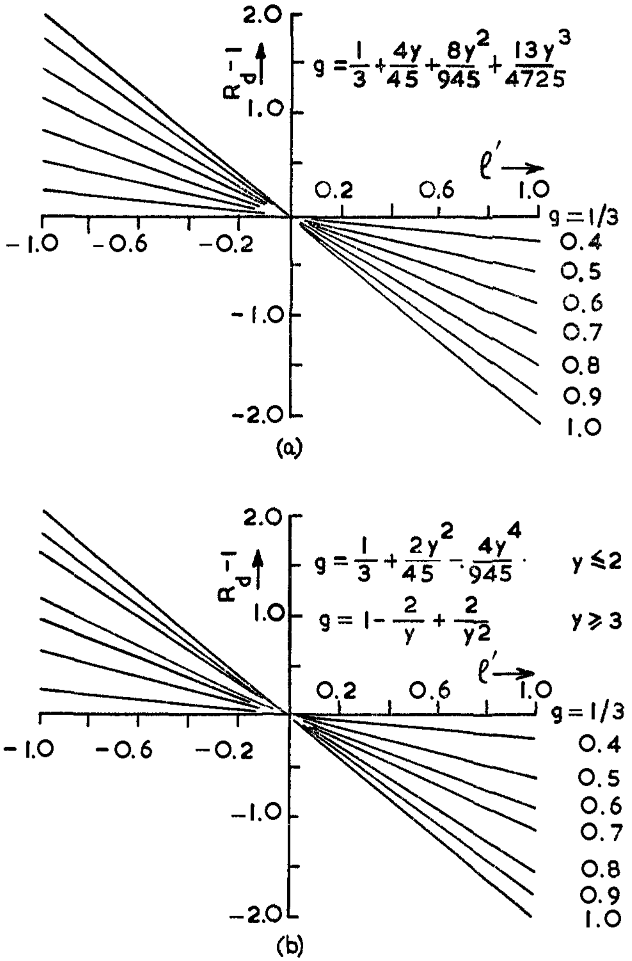


FIG. 15. Reduction factor, R_d, for various values of g and l' for (a) nonpolar and (b) polar molecules. The ordinate units are $(2\alpha_1 + \alpha_2)/(\alpha_1 - \alpha_2)$.

This equation for $[M]$ may be compared with equation 9 due to Raman and Krishnan, it being remembered that the diffusion constants are directly proportional to kT/η.

Peterlin and Stuart state that the value of R_d may be obtained from data on electric double refraction, magnetic double refraction, molar polarization, or molar refraction.

In a recent paper, Champion (25) has suggested that liquids such as carbon tetrachloride, for which the molecules would not be expected to show any orientation or distortion anisotropy, will give streaming double refraction due to the distortion of the radial distribution function during flow. The birefringence Δn is calculated from the variation of the polarization due to the distorted distribution function using the Bragg method (6). It is given by

$$\Delta n = \frac{2\pi}{n} N_o \alpha \frac{\Delta E}{E} \frac{3}{(3 - 4N_o \pi \alpha)} \tag{111}$$

where E is the external field, ΔE is the additional field due to the distorted function, N_o is the number of molecules per unit volume, and α is the polarizability of the molecule. Champion states that $\Delta n = 7 \times 10^{-8}$ for carbon tetrachloride for a gradient of 50,000 $\mathrm{sec.}^{-1}$

B. DISCUSSION

In deciding which of the two orientation theories for liquids is the better, the available experimental results may be examined. For the several cases where the data may be used for testing the theory of Raman and Krishnan little agreement is found (118); for the few cases where sufficient data are available for use with Peterlin and Stuart's theory, a much better agreement is indicated. Tolstoi (138) considered the values of the birefringence, Δn, and the angle of isocline, χ, in a liquid which was subjected simultaneously to hydrodynamic and electric fields. This idea was suggested much earlier by Taylor (137) to decide between the theories of Boeder and Kuhn. Tolstoi dealt with nonpolar ellipsoidal molecules having an anisotropic polarizability $\Delta\alpha$ and assumed that the field E was applied in the direction of the gradient G. It was shown that, with reference to figure 3, the rotational velocity ω_ϕ of the molecule in the plane 2O1 (i.e., $\theta = \pi/2$) was given by

$$\omega_\phi = \frac{\partial\phi}{\partial t} = \frac{G}{2}[1 + b' \cos 2(\phi - \phi')] \tag{112}$$

where

$$(Gb')^2 = (Gb)^2 + E^2\Delta\alpha/C$$

and

$$\tan 2\phi' = E^2\Delta\alpha/CGb \tag{113}$$

the quantities C and b having the meanings given in Section II.

Tolstoi then derived expressions for Δn and χ using the original theory of Peterlin and Stuart discussed in Section V,E. Thus

$$\Delta n = \frac{2\pi}{15n}(g_1 - g_2)^{\mathfrak{R}}\sigma b[1 + (E^2\Delta\alpha/CGb)^2]^{1/2} \tag{114}$$

and

$$\chi = \frac{\pi}{4} - \phi' - \frac{\sigma}{12}\left[1 - \frac{\sigma^2}{108} + \cdots\right] \tag{115}$$

Since for liquids σ is very small, equations 113, 114, and 115 enable it to be shown that

$$\left[\frac{\partial(\Delta n)}{\partial(E^2)}\right]_{\substack{E\to 0\\ G=\text{constant}}} = 0 \tag{116}$$

and

$$G \cot 2\chi = E^2 \times \text{constant} \tag{117}$$

Although Tolstoi does not mention the modified theory of Peterlin and Stuart involving the conception of a "Nahordnung," equations 116 and 117 will still apply.

Using the theory of Raman and Krishnan and assuming that the optical effects result from the electrical force in the direction of the gradient and the hydrodynamic force at 45° to this direction, Tolstoi finds the equations corresponding to equations 116 and 117 to be

$$\left[\frac{\partial(\Delta n)}{\partial(E^2)}\right]_{\substack{E\to 0\\ G=\text{constant}}} \neq 0 \tag{118}$$

and

$$G(\cot \chi - 1) = E^2 \times \text{constant} \tag{119}$$

Experiments with purified transformer oil gave results in good agreement with equations 116 and 117 but in marked disagreement with the deductions of equations 118 and 119. There is, however, need for further experiments along these lines.

The ideas of Champion have yet to be subjected to experimental verification. The difficulty would seem to be the detection of so small a birefringence at shear rates which easily cause parasitic birefringence in the apparatus.

VII. Theories for Flexible Particles

A. GENERAL

Early attempts at theories were made by Haller and by Kuhn with a pearl necklace type of model. Quantitative treatments for chain molecules were commenced in 1943.

The general concept of a chain molecule is that it is made up of a number (Z) of units called monomers; Z is known as the degree of polymerization. Each monomer is composed of a number of segments, and the molecule in solution is regarded as being curled up but subject to a continuous change of shape because of the almost free rotation of the segments around a given valency direction as axis. This rotation is caused by thermal agitation, and when the solution is at rest is opposed by the viscous resistance of the surrounding medium and by the resistance to change of shape offered by the molecule itself. The molecule is characterized by its "hydrodynamic length" L, which is the maximum length when the molecule is uncoiled without distortion of the valency angles and atomic distances, and by the distance h between its ends when it is coiled (figure 16). It is assumed that the properties of a suspension of such molecules are determined by the values of h of all the molecules.

W. Kuhn and H. Kuhn were the first to present a theory for dilute solutions of unbranched chain molecules. Simultaneously a theory was given by Hermans. These investigators considered the molecular shape to be that of a "random or statistical coil" (62). For this the chain molecule was supposed to consist of a number of small elements or chains, each one containing an equal number of units called monomer groups. It was assumed that the coil was freely draining—

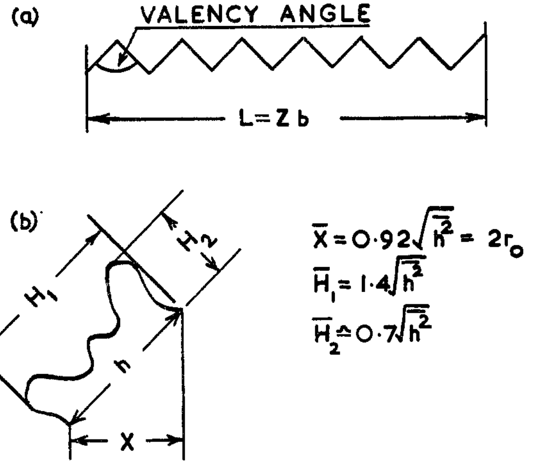


FIG. 16. Parameters for dimensions of unbranched molecule (Kuhn (73, 74, 75)). (a) Fully extended molecule; (b) randomly coiled molecule. L, Z, b, and h have their usual meanings (Section II); H_1, maximum coil diameter; H_2, cross-sectional diameter; x, maximum dimension in arbitrary direction; $\overline{X}$, average diameter. Regarded as a sphere of radius r_o and volume V_s, then $V_s = 4\pi r_o^3/3 = 0.41(A_m bZ)^{3/2}$; regarded as an ellipsoid of volume V_e, then $V_e = 0.36(A_m bZ)^{3/2}$.

i.e., it did not entrap solvent molecules or prohibit their movement through the coil—and that its behavior in flow was equivalent to that of a dumbbell-shaped particle. Later W. Kuhn and H. Kuhn introduced the concept of internal viscosity and imposed a limitation on free draining (69); the theory was extended by Peterlin (99). Other theories, in which different models were used, were given by Kramers and by Cerf, and further contributions have been made by Kirkwood and Zimm. Concentrated solutions have been treated by Peterlin and Lodge.

B. THEORY OF HALLER

Haller (43) considers the particles to be spherical and isotropic at rest and assumes that they are subject to external stresses due to the flow. These deform the particle into an elongated ellipsoid and cause internal stresses p_i which, however, are not identical with the external stresses p_e, because the particle is supposed to have an "internal viscosity," which, as the particle is deformed, causes additional internal stresses. The resultant internal stress is a combination of these two stresses, and the behavior of the particle in flow is characterized by the conditions for equilibrium between the external and the internal stresses. These ideas are developments of those given earlier by Natanson and Schwedoff. The double refraction which arises is taken as being essentially due to deformation.

Following Stokes the external stresses are taken to be a compression and tension acting on a direction defined by $\theta = \pi/2$ and $\phi = \pm \pi/4$, i.e., in the 2O1 plane at 45° to the direction of flow O1 (see figure 3). The internal stresses due to the "flow" or deformation of the particle are uncertain in magnitude but are

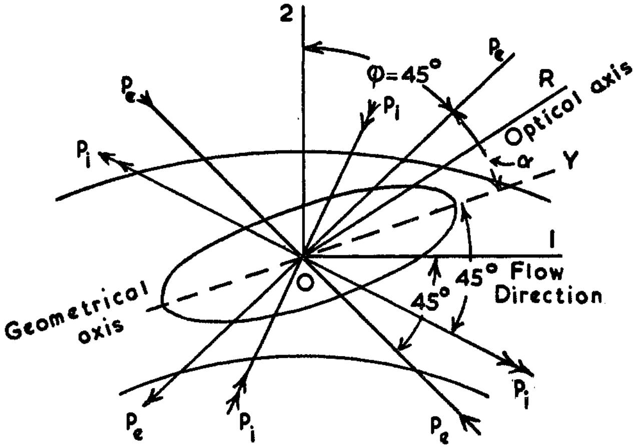


FIG. 17. Position of optical axis in a deformable particle (Haller). Op_e, directions of external hydrodynamic stresses; Op_i, directions of internal particle stresses.

considered to act at 45° to the major axis of the ellipse. The orientation of this axis depends on the external hydrodynamic stress and the internal particle stress.

The state of affairs is shown in figure 17. If the distortion is small, α is small: this corresponds to small gradients or very rigid particles and although p_e is regarded as finite, p_i is negligible. The axis OY is at 45° to O1. If the distortion is large, α approaches 45°; this corresponds to large gradients or flexible particles so that p_i is large. The axis OY then lies along O1. The axis OR of the induced double refraction does not entirely follow this pattern. For small gradients it is assumed to coincide with OY, but with larger gradients it is supposed to lag behind OY by an amount dependent on the nature of the particle. When α reaches its limit of 45°, the angle between OR and OY also reaches a limit but not 45°.

Thus the result of considering the deformability of the particle is that χ changes from 45° to a limiting value χ_o different from zero as G increases and there is no saturation value for the amount of double refraction. Haller points out that a number of lyophilic colloids show this behavior. He also mentions that streaming double refraction can arise in liquids possessing structural elasticity by deformation of the structure. The latter aspect has been considered by Ostwald (94).

C. THEORY OF W. KUHN

From a calculation using his theory for rigid particles Kuhn (61), using Signer's data (128), found that the eigen double refraction for rubber and polystyrene was so small that he was led to the conclusion that, in their normal state, the molecules of these substances must be almost optically isotropic. Further, since these substances when the particles were completely orientated by mechanical straining gave an appreciable amount of double refraction, Kuhn also concluded that flow double refraction must arise from a cause other than by orientation: namely, the effect of the stresses to which the particle is subjected when in the flow gradient. His theory, which deals first with elongated particles and then with spherical particles, is as follows:

For an elongated particle of length l (model b of figure 6) inclined at an angle $90 - \phi$ to the flow direction, it is deduced that there is an average force R_3 acting along the axis given by

$$R_3 = \frac{\pi}{16} \eta_o G l^2 \sin 2\phi \tag{120}$$

and a corresponding force acting perpendicular to this direction which, since the lateral dimension is small, is negligible. As ϕ varies with rotation of the particle, so the force is alternately tensile and compressive. If unit stress acting on a particle produces a birefringence of magnitude $\delta n'$, then the amount of birefringence δn_p given by each particle is expressed by

$$\delta n_p = \frac{1}{16 s^2} \delta n' l^2 \eta_o G \sin 2\phi \tag{121}$$

This arises irrespective of any preferred orientation of the particle and has a maximum for $\phi = 45°$. The total birefringence Δn due to all the particles, which is a result of the stresses induced in them and of the orientation of the particles with a distribution function F, is found from the equation

$$\Delta n = \frac{\pi}{16} l^2 \eta_o G \delta n' \int_0^{2\pi} F \sin 2\phi [\sin^2 \phi' - \cos^2 \phi'] \, d\phi \tag{122}$$

where χ is as in figure 3 and $\phi' = \phi + \chi$.

For moderate values of σ and using Boeder's value for F, Kuhn deduces from equation 122

$$\Delta n = V\left(\frac{l}{2s}\right)^2 \frac{\eta_o G}{8} \delta n' \left[\left(1 + \frac{\sigma^2}{2^7}\right) \sin 2\chi + \frac{3\sigma^3}{2^{10}} \cos 2\chi \cdots\right] \tag{123}$$

where V $(= \pi a^2 l)$ is the volume of the particle when it is in solution. For χ, Kuhn gives

$$\tan 2\chi = \frac{2^{10}}{2\sigma^3} + \frac{2^3}{3\sigma} + \cdots \tag{124}$$

For very small values of σ, i.e., with little preferred orientation, $F = N_p/2\pi$, so that by equation 124, $\chi = 45°$ and by equation 123,

$$\Delta n = \frac{N_p \pi l^3 G \delta n'}{32} = V\left(\frac{l}{2s}\right)^2 \frac{\eta_o G}{8} \delta n' \tag{125}$$

For very large values of σ, the angle χ approaches zero but Δn increases without reaching a constant value. Molecular lengths l can be found from equation 124, with D taken as $8kT/\pi\eta_o l^3$. Equation 125 has been used by Tsvetkov and Petrova (150) to find $(l/2s)$.

Kuhn considers that spherical particles are deformed into ellipsoids under flow. In this case the force acting perpendicularly to the major axis can no longer be neglected. For small values of σ, the angle χ is considered to to be 45° and equation 125 gives

$$\Delta n = V\eta_o G\delta n'/4$$

The double refraction is regarded as being almost entirely strain double refraction.

In discussing this theory for deformable particles Kuhn mentions that other factors occurring within the particle, such as Haller's internal viscosity, may arise. These may mean that the particle requires a finite time, τ', to change its shape, and, if so, this relaxation time would need to be considered. The decision whether the observed double refraction is due to orientation or extension must be made, according to Kuhn, after a consideration of the observed flow double refraction and the eigen double refraction obtained by straining the dry substance. Kuhn considers that if the particles break under the action of the hydrodynamic forces an abrupt change of value of Δn could be expected, the change varying according to whether the double refraction is due to orientation or to strain and is dependent upon the axial ratio before, and after, breakage.

D. THEORY OF W. KUHN AND H. KUHN (68, 69, 76)

In this theory the behavior of a molecule in a liquid is described as if two mass points, which are located at the ends of the coil and exert an elastic force upon each other, are diffusing in the liquid. The equilibrium distribution of the vector joining the end points is deformed under the influence of flow and a new stationary distribution is reached from which the viscosity and flow birefringence are calculated. To find the relative frequency at which the values of h occur in a suspension, at rest and when flowing, W. Kuhn (62, 70) considered the molecule as a "statistical coil" having the same values L and h as the real molecule and consisting, not of Z monomer units, but of N_m "statistical straight-chain elements" each of average length A_m. Each chain element is then supposed to consist of an average of s_m monomers, where the value of s_m is chosen so that the orientation of each element is independent of the other elements. The average external dimensions of the statistical coil (62, 64, 70, 76) are shown in figure 16 and defined in the caption. Then if b is the hydrodynamic length of the monomer,

$$L = Zb = N_m s_m b = N_m A_m \tag{126}$$

By purely statistical methods W. Kuhn (62, 70) calculated the probability for the occurrence of an end-to-end distance h for orientations random in space for a solution at rest and deduced that the mean value of the square of the spatial vector h is given by

$$\overline{h^2} = N_m A_m^2 = LA_m = ZbA_m \tag{127}$$

The resistance to changes of value of h is considered to be due to a statistical force R_1 and the resistance R_2 offered by the molecule itself. By using relationships between probability and entropy and between entropy and free energy the value of R_1 was given as (63)

$$R_1 = 2kT \left\{ \frac{3h}{N_m A_m^2} + \frac{1}{A_m} \left[\left(\frac{h}{N_m A_m} \right)^3 \frac{9}{5} + \left(\frac{h}{N_m A_m} \right)^5 \frac{297}{175} + \cdots \right] \right\} \tag{128}$$

which, since usually $h \ll N_m A_m$, becomes

$$R_1 \doteq kT \frac{6h}{N_m A_m^2} \tag{129}$$

The value of R_2 was expressed by the relationship (68)

$$R_2 = 2B \, \mathrm{d}H/\mathrm{d}t \tag{130}$$

where B is termed the shape resistance of the molecule (71). The latter is the chief factor deciding the time required by the molecule to change its configuration; the time τ'—called the macroconstellation changing time—required to double or halve h is given approximately by

$$\tau' = 2bA_m \frac{BZ}{kT}$$

Typical values are given in table 4.

The forces R_1 and R_2 and the thermal agitation give rise, in a solution at rest, to a kinematic equilibrium in the distribution of h.

W. Kuhn and H. Kuhn considered that the molecule in suspension may be (*1*) a loose structure through which the surrounding liquid can move freely, (*2*) a closely matted structure in which the solvent molecules lie completely immobilized between the coils, or (*3*) a structure allowing partial movement of the solvent. Cases 1 and 2 give rise to the "freely draining" molecule and "non-draining" molecule, respectively. The former has a small value for Z; the latter has a large value for Z and behaves somewhat as if the entire coiled-up molecule were contained in a closed skin, which separates the molecule and the liquid within, from the rest of the solution; for small flow gradients it acts as a rigid body. For the partially draining molecule the degree of immobilization of the solvent is expressed as a function of parameters which define the shape of the coil.

In flow any selected molecule will be subjected to the forces R_1, R_2, thermal

TABLE 4

Typical values of τ'

Substance	Solvent	A_m (×10^8)	b (×10^8)	BZ (10^{-6})	τ' (10^{-6} sec.)
Cellulose nitrate............	Butyl acetate	240	5.15	230	1300
Cellulose nitrate............	Cyclohexanone	200	5.15	10	47
Methylcellulose............	Water	130	5.15	2	6.4
Polystyrene................	Cyclohexanone	13	2.53	1000	160

agitation, and hydrodynamic flow forces. For simplicity W. Kuhn and H. Kuhn consider only two-dimensional motion. The theory is then as follows:

With reference to figure 18, assume a liquid flow in the direction O1. The molecule is regarded as having an "axis" defined by the vector h joining the end points and a center of gravity O at the midpoint of h. Owing to the flow forces, O assumes the translation speed of the surrounding liquid and superimposed is a rotary motion of h always in the same direction but not at a constant speed so that "the molecular axis" has directions of preferred orientation. To this motion is added a periodical dilatation and compression of the length h. Although the molecule is able always to participate in the rotation, it cannot completely realize the change in length of h shown in figure 18 due to the action of R_1 and R_2. Since, however, the liquid moves regardless of whether the molecule ends can follow, these ends attain finite speeds relative to the surrounding liquid and frictional forces $\mathcal{R}_3$ appear. To calculate these W. Kuhn and H. Kuhn replace the molecule by an elastic dumbbell model in which it is assumed that one-fourth of the original molecule is localized at each end of the dumbbell and the hydrodynamic effects of the intermediate chain parts are neglected. Then if the end of the model has a velocity v relative to the solvent, the force acting on the end in the direction of v is given by

$$\mathcal{R}_3 = v\eta_o\lambda_m L/4 \tag{131}$$

where η_o is the solvent viscosity, and λ_m is a frictional factor depending on the degree of immobilization of the solvent within the molecule and whether the motion of the molecule is one of translation or rotation. Initially, for freely draining molecules $\mathcal{R}_3$ was calculated as the resistance exerted on a sphere, so that λ_m was a purely numerical coefficient taken as $3\pi/2$. Later this was modified, but for the present it may be assumed to be a constant for a given molecule; it must be remembered that for considerations of flow double refraction the motion is mainly rotary.

In order to find the distribution function F, which determines the orientation of h, a method similar to that used by Peterlin and Stuart was used. The final differential equation, expressed in terms of h and ϕ (figure 18), is

$$\frac{\partial F}{\partial h^2} + \frac{\partial F}{\partial h}\left[\frac{2h}{\overline{h_o^2}} + \frac{1}{h} - 2\sigma' h \sin 2\phi\right] + \frac{1}{h^2}\frac{\partial^2 F}{\partial \phi^2} + 4\sigma' \cos^2\phi \frac{\partial F}{\partial \phi} + \frac{4F}{\overline{h_o^2}}$$
$$= \left(1 - \frac{D_t}{D_r}\right)\frac{\partial}{\partial \phi}\left(\frac{\partial F}{\partial \phi}\frac{1}{h^2} + 4\sigma' \cos^2\phi\right) \tag{132}$$

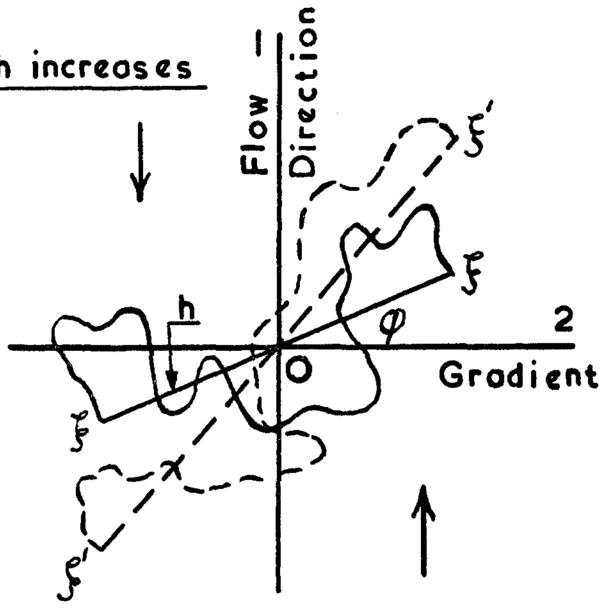
where

$$\overline{h_o^2} = \frac{2}{3} N_m A_m^2 = \frac{2}{3}\overline{h^2} \quad \text{and} \quad \sigma' = \frac{G}{16\mathrm{D}_t} \tag{133}$$

D_r and D_t are the translatory diffusion constants for motion of the end points along and perpendicular to h, respectively, and with the model considered here

$$D_t = \frac{2kT}{\lambda_m \eta_o L} \quad \text{and} \quad D_r = \frac{2kT}{\lambda_m \eta_o L + 8B} \tag{134}$$

(a) h increases



(b) h decreases

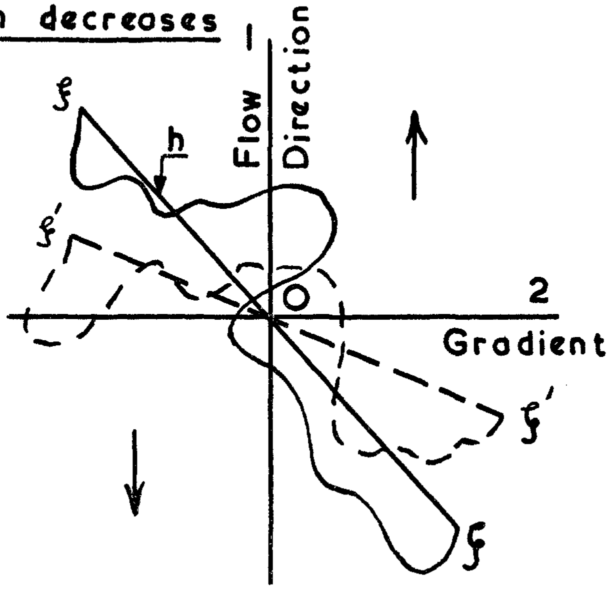


Fig. 18. Change in direction and length of end-to-end distance *h*. The arrows indicate motion of liquid surrounding the molecule as seen from a coördinate system which participates in the translation of the center of gravity. *h* revolves in an anticlockwise direction.

For small values of G, and arbitrary values of B, the solution of equation 132 is given as

$$F = \frac{N_p}{\pi h_o^2} \exp - \frac{h^2}{\overline{h_o^2}} [1 - \sigma'\overline{h_o^2} \sin 2\phi] \tag{135}$$

For moderate and small values of G and vanishingly small values of B,

$$F = \frac{N_p}{\pi \overline{h_o^2}} [1 + (\sigma' \overline{h_o^2})^2]^{-1/2} e^{-Ph^2} \tag{136}$$

where

$$P = \frac{1}{\overline{h_o^2}} \left[1 - \sigma'\overline{h_o^2} \frac{\sin 2\phi - \sigma'\overline{h_o^2} \cos 2\phi}{1 + (\sigma'\overline{h_o^2})^2} \right]$$

With very large values of B

$$F = \frac{N_p}{2\pi} f_1(\phi) f_2(h) \tag{137}$$

and if $\sigma' h^2$ is small

$$f_1(\phi) = 1 + \sigma' h^2 \sin 2\phi - (\sigma' h^2)^2 \left(\cos 2\phi + \frac{\cos 4\phi}{4} \right) + \cdots .$$

and

$$f_2(h) = \frac{\left[1 + \left(\frac{\sigma' h^2}{4} \right)^2 - \frac{7}{4} \left(\frac{\sigma' h^2}{16} \right)^4 + \cdots \right]}{\frac{\overline{h_o^2}}{2} \left[1 + \frac{1}{2} (\sigma'\overline{h_o^2}) - \frac{21}{8} (\sigma'\overline{h_o^2})^4 + \cdots \right]} e^{-h^2/h_o^2}$$

Since the viscosity of a solution of chain molecules is dependent on their behavior in flow, the considerations above may be utilized in obtaining expressions for the intrinsic viscosity. In this review intrinsic viscosity, $[\eta]$, is taken to be the quantity $[(\eta - \eta_o)/\eta_o c]_{c \to 0}$, where η is the viscosity of the solution, η_o that of the solvent, and c unless otherwise stated is the concentration expressed in grams per 100 cc. W. Kuhn and H. Kuhn find that with the distribution functions given by equations 135 and 136, the intrinsic viscosity for small gradients and arbitrary values of B, and for arbitrary gradients and small values of B, is given by

$$[\eta] = \frac{\lambda_m}{48} \frac{N_A}{10^2} \frac{Z}{M_g} \frac{A_m^2}{s_m} b = \frac{\lambda_m}{48} \frac{N_A}{10^2} \frac{Z}{M_g} A_m b^2 \tag{138}$$

In this equation, the concentration c is given by

$$c = 10^2 Z M_g N_p / N_A = 10^2 M N_p / N_A \tag{139}$$

where N_A is Avogadro's number and M and M_g are the molecular weights of the molecule and the monomer, respectively.

Using equation 137, for large values of B

$$[\eta] = \frac{\lambda_m}{48} \frac{N_A}{10^2} \frac{Z}{M_g} \frac{A_m^2}{s_m} b \left[1 - 2(\sigma'\overline{h_o^2})^2 + \frac{473}{16} (\sigma'\overline{h_o^2})^4 \cdots \right] \tag{140}$$

1. *Magnitude of double refraction*

To find the double refraction of the flowing liquid, it is necessary first to consider the dependence of the optical anisotropy of a molecule on h. This has been done by Kuhn and Grun (67), who regarded each statistical chain element as optically anisotropic with polarizabilities α_1 and α_2 along and perpendicular to its axis (figure 19), and then by considering the whole molecule found its mean polarizabilities γ_ξ and γ_η in directions along the perpendicular to h. For values of $h \ll L$, they give

$$\gamma_\xi = \frac{N_m}{3}(\alpha_1 + 2\alpha_2) + \frac{2}{5}\frac{h^2}{N_m A_m^2}(\alpha_1 - \alpha_2)$$

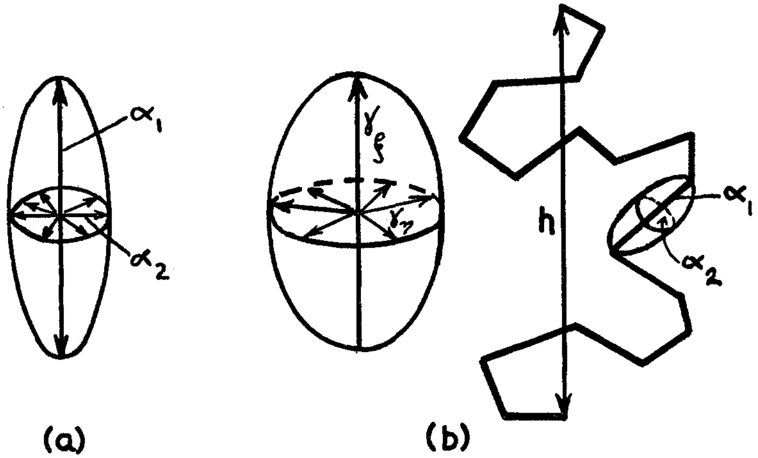


FIG. 19. (a) Optical polarizability of a statistical chain element represented as an ellipsoid of revolution with axes α_1 and α_2. (b) Chain consisting of N_m statistical elements of length A_m. The optical polarizability can be described by an ellipsoid of revolution with axes γ_ξ and γ_η (equation 141).

and

$$\gamma_\eta = \frac{N_m}{3}(\alpha_1 + 2\alpha_2) - \frac{1}{5}\frac{h^2}{N_m A_m^2}(\alpha_1 - \alpha_2)$$

so that

$$\gamma_\xi - \gamma_\eta = \frac{3}{5}(\alpha_1 - \alpha_2)\frac{h^2}{N_m A_m^2} = \theta_i \frac{h^2}{\overline{h^2}} \qquad (141)$$

in which θ_i is written for $3(\alpha_1 - \alpha_2)/5$. For larger values of h,

$$\gamma_\xi - \gamma_\eta = N_m(\alpha_1 - \alpha_2)\left[\frac{3}{5}\left(\frac{h}{N_m A_m}\right) + \frac{36}{175}\left(\frac{h}{N_m A_m}\right)^4 + \frac{108}{875}\left(\frac{h}{N_m A_m}\right)^6 + \cdots\right]$$

W. Kuhn, H. Kuhn, and Buchner (77) give values of $\alpha_1 - \alpha_2$ for the special cases where each chain element can be considered as an elongated or flattened ellipsoid of revolution. These values are obtained from equation 91 if α' and β' are taken as α_1 and α_2, respectively.

The contribution to the polarizability of the whole medium by each molecule depends not only on the magnitude of h but also on its orientation. The total contribution of all the molecules is therefore determined by using the distribution function given by the solution of equation 132, and since polarization is related directly to refractive index, an expression for the birefringence Δn may then be found.

For a liquid of refractive index n_o containing molecules with a large shape resistance B subjected to any flow gradient, Δn is given by

$$\Delta n = n_x - n_y = \frac{8\pi}{15n_o}\left(\frac{n_o^2 + 2}{3}\right)^2 N_p(\alpha_1 - \alpha_2)\sigma'\overline{h^2}\,[S_1^2 + T_1^2]^{1/2} \tag{142}$$

where

$$S_1 = \frac{\sigma'\,\overline{h^2}f_1\,(\sigma'\overline{h^2})}{f(\sigma'\overline{h^2})}\,; \qquad T_1 = \frac{f_2(\sigma'\overline{h^2})}{f(\sigma'\overline{h^2})}$$

and n_x and n_y are the refractive indices along and perpendicular to the direction of preferred orientation of the molecular axes; they are the principal refractive indices of the medium. The functions f_1, f_2, and f are given by W. Kuhn and H. Kuhn as complicated integrals. For small values of B and any gradient, $S_1 = \frac{2}{3}\sigma' h^2$ and $T_1 = 1$, whereas for any value of B and small gradients, $S_1^2 + T_1^2 = 1$. These results are shown graphically in figure 20, where the variation of $[\eta]$ with G is also given.

The specific Maxwell constant $[M]_{sp}$ is given by

$$[M]_{sp} = \frac{4\pi}{5}\left(\frac{n_o^2 + 2}{3n_o}\right)^2 \frac{\alpha_1 - \alpha_2}{kT}\,\frac{\lambda_m}{48}\,\frac{N_A}{10^2}\,\frac{Z}{M_g}\,A_m\,b^2 \tag{143}$$

$$= \frac{4\pi}{5}\left(\frac{n_o^2 + 2}{3n_o}\right)^2 \frac{\alpha_1 - \alpha_2}{kT}\,[\eta] \tag{144}$$

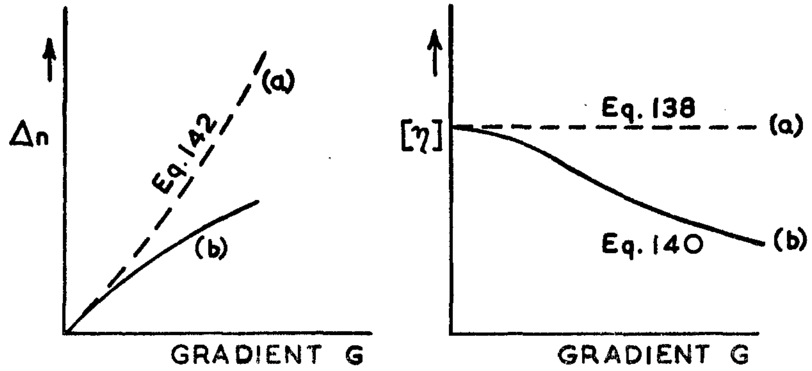


FIG. 20. Variation of birefringence, Δn, and intrinsic viscosity, $[\eta]$, with gradient for (a) vanishing shape resistance (soft molecule) and (b) large shape resistance (rigid molecule).

2. Value of extinction angle (χ)

The number (dN) of particles, having arbitrary values of h, which are orientated at an angle between ϕ and $\phi + d\phi$ is given, for arbitrary values of G and B, by

$$dN = \left[\frac{N_p}{2\pi}\int_{h=0}^{\infty} f_2(h)\right] f_1(\phi)\, d\phi = F(\phi)\, d\phi$$

The function $F(\phi)$ and hence dN has a maximum value for a value ϕ_m of ϕ given by $-\cos 2\phi_m = S_1/T_1$. At any instant most of the particles are orientated at this angle and in this direction the maximum amount of uncoiling occurs, giving rise to maximum polarizability of the medium. Thus $(90_m - \phi)$ is the extinction angle χ, whence

$$-\cot 2\phi_m = \cot 2\chi = \tan\left(\frac{\pi}{2} - 2\chi\right) = \frac{S_1}{T_1} \tag{145}$$

so that

$$\chi = \frac{\pi}{4} - \frac{1}{2}\tan^{-1} S_1/T_1 \tag{146}$$

W. Kuhn and H. Kuhn evaluate S_1 and T_1 to get

$$\tan 2\left(\frac{\pi}{4} - \chi\right) = \cot 2\chi = \beta\,\frac{2}{3}\,\sigma'\overline{h^2} \tag{147}$$

where $\beta = 3$ for stiff (large B) and $\beta = 1$ for soft (small B) molecules. These results are illustrated in figure 21.

Thus

$$\left[\frac{\cot 2\chi}{\eta_o G}\right] = \beta\,\frac{\lambda_m}{48kT}\,\frac{A_m{}^2}{s_m}\,bZ^2 \tag{148}$$

Further, if the parameters (ω) and [ω] be introduced where

$$(\omega) = \frac{\pi}{4} - \chi \quad\text{and}\quad [\omega] = [(\omega)/\eta_o\, G]_{\substack{G\to 0\\ c\to 0}}$$

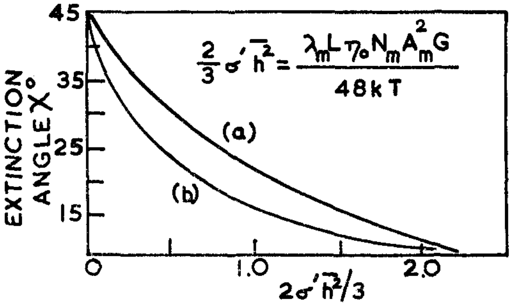


FIG. 21. Variation of χ with gradient for (a) vanishing shape resistance (soft molecule) and (b) large shape resistance (rigid molecule).

then using equation 138,

$$\left[\frac{\cot 2\chi}{\eta_o G}\right]_{\substack{G\to 0\\ c\to 0}} \simeq \left[\frac{2(\pi/4 - \chi)}{\eta_o G}\right]_{\substack{G\to 0\\ c\to 0}} = 2[\omega] = \beta \times 10^2 \frac{M}{RT}[\eta] \tag{149}$$

Equations 138 and 148 hold for all degrees of immobilization of the solvent in the chain molecule provided a suitable value for λ_m is used. Although attempts have been made to calculate λ_m theoretically, notably by Debye and Bueche (29) and by Kirkwood and Riseman (59, 60), an empirical relationship was derived by W. Kuhn and H. Kuhn by means of experiments on macroscopic models (73, 74, 75). These were made from wire of length L bent into N_σ circular segments of length B_σ, it being considered that these were preferable to the original N_m straight segments of length A_m. At first (73, 74, 75) it was found that $N_\sigma = 0.789N_m$ and $B_\sigma = A_m/0.789$, which gave for a partially draining coil of thickness d_h

$$\lambda_m^{-1} = -0.05 + 0.12 \log_{10}(A_m/d_h) + 0.037(Zb/A_m)^{1/2} \tag{150}$$

Later (79, 80) these relationships were regarded as erroneous and replaced by $N_\sigma = 1.532N_m$ and $B_\sigma = A_m/1.532$; whence

$$\lambda_m^{-1} = -0.08 + 0.12 \log_{10}(A_m/d_h) + 0.052(Zb/A_m)^{1/2} \tag{151}$$

which takes the values $0.052(Zb/A_m)^{1/2}$ and $-0.03 + 0.12\log_{10}(A_m/d_h)$ for large and small values of Z, i.e., for nondraining and freely draining molecules. If the value given by equation 151 is substituted in equation 143 the dependency of $[M]_{sp}$ on Z is given; in general for intermediate and very high values of Z, it is approximately proportional to Z and $Z^{1/2}$, respectively. The linear variation is borne out by the results of Wissler (163) on methyl cellulose, whereas the results of Signer and Gross (129) on polystyrene agree roughly to a square-root variation.

In assessing the value of equation 151 it must be observed that, as obtained by Kuhn, it applies strictly only for pure constant rotation of the molecule. In streaming double refraction experiments the conditions are somewhat different and equation 151 can at best be regarded only as an approximation. However, equations 144 and 149, which do not contain λ_m, are more reliable and should hold irrespective of whether the molecules are freely draining, nondraining, or partially draining.

In discussing their theory for the elastic dumbbell model W. Kuhn and H. Kuhn (73, 74, 75) regard equations 143 and 148, with the value of λ_m given by equation 151, as being essentially true for the three-dimensional case, and when allowance is made for the lateral dimensions of the coil; they consider only small changes in the numerical factors are involved. The final expressions given (79, 80) are, with the usual notation,

$$[\eta] = \frac{0.43}{(-1.6 + 2.3\log(A_m/d_h) + N_m^{1/2})} \frac{N_A}{10^2} \frac{Z}{M_0} \frac{A_m^2 b}{s_m} \tag{152}$$

$$[M]_{sp} = \frac{24\pi}{43}\left(\frac{n_o^2 + 2}{3n_o}\right)^2 \frac{\alpha_1 - \alpha_2}{kT}[\eta] \tag{153}$$

$$\left[\frac{\cot 2\chi}{\eta_o G}\right]_{\substack{G\to 0\\ c\to 0}} = 2[\omega] = \beta \frac{40}{43} 10^2 \frac{M}{RT}[\eta] \tag{154}$$

From equation 154, the quantity

$$T\left(-\frac{\partial\chi}{\partial G}\right)_{\substack{G\to 0\\ c\to 0}}$$

which henceforth will be written as $T \tan (\chi G)_o$, is given by

$$T \tan (\chi G)_o = \beta \frac{20}{43} 10^2 \frac{M}{R} [\eta]\eta_o \tag{155}$$

and since a variation of η_o from small to large values is equivalent to the variation of B from large to small values, a graph of $T \tan (\chi G)_o$ against η_o should take the form shown in figure 22 (curve 4). Cerf (22), when discussing this theory, states that a different method of calculation gives the equation

$$T \tan (\chi G)_o = 0.45 \times 10^2 \frac{M}{R} [\eta]\eta_o + 0.04 \frac{B}{k} A_m b \tag{156}$$

which leads to a different curve.

Kuhn, Katchalsky, and Kunzle have attempted to treat the effects of electric charges on flexible molecules (54, 55, 66, 78), and W. Kuhn and H. Kuhn have considered branched molecules (72). It is found that coiled-chain molecules whose chains contain a large number of ionizable groups undergo a change of shape when any of the groups acquire electric charges. This change is caused by the electrostatic repulsive field which brings about some uncoiling of the

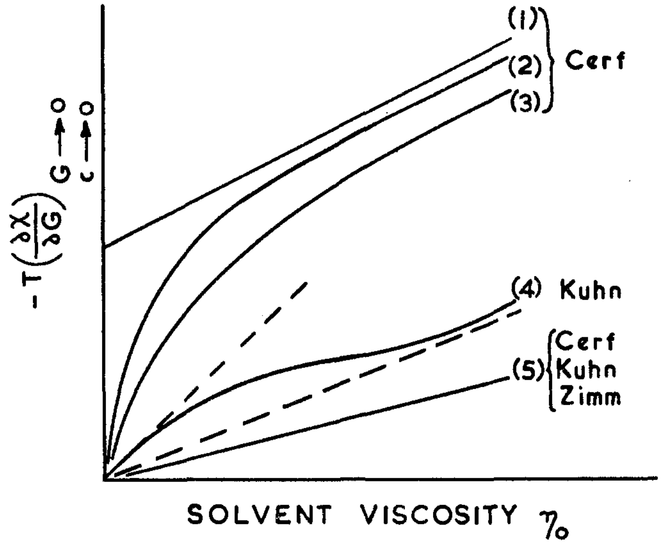


FIG. 22. Variation of $T(-\,\delta\chi/\delta G)_{\substack{G\to 0\\ c\to 0}}$ with solvent viscosity for different theories at very small concentration. Curve (1), elastic sphere model, $\delta_o = 0$, equations 189, 192; Rouse model, equation 196. Curve (2), elastic sphere model, $\delta_o = 0.1$, equation 187. Curve (3), elastic sphere model, $\delta_o = 0.2$, equation 187. Curve (4), elastic dumbbell model: the curve lies between the dotted lines which are the curves given by equation 155 for stiff and soft molecules. Curve (5), rigid particle (Cerf, equations 190 and 197; Kuhn, equation 192, Zimm, equation 202).

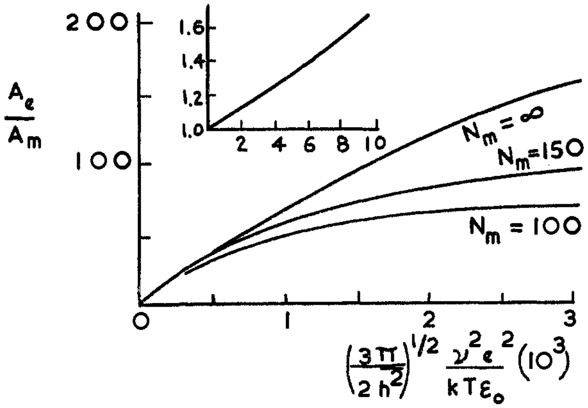


FIG. 23. Ratio of chain lengths of charged and uncharged molecules as a function of charge (Kuhn (54)).

molecule and leads to a mean square end-to-end distance $\overline{h_e^2}$ and average chain length A_e different from $\overline{h^2}$ and A_m. It is then considered that, in such cases, any equations in which $\overline{h^2}$ and A_m occur still hold if these quantities are replaced by $\overline{h_e^2}$ and A_e, respectively. An expression for the ratio A_e/A_m, which also equals $\overline{h_e^2}/\overline{h^2}$, as a function of $(3\pi)^{1/2}\nu^2 e^2/(2\overline{h^2})^{1/2}kT\epsilon_0$ is given by Kuhn, where ν is the number of groups ionized, e is the charge on each group, and ϵ_0, k, and T have their usual meanings; it is shown graphically in figure 23.

An additional effect of the charges is to change $(\alpha_1 - \alpha_2)$, which may decrease as ν increases (e.g., in aqueous solutions of polymethacrylic acid) and even change sign from positive to negative (e.g., polyacrylic acid).

The work of Signer (130) and of Yang, Foster, and Stacy (134, 164) on branched molecules indicates that such molecules have a smaller optical anisotropy and smaller dimensions than unbranched ones of the same molecular weight and degree of polymerization Z. W. Kuhn and H. Kuhn (72) define the degree of branching by the expression $\zeta = Z/z$, in which z is the number of monomers in a branch, and show that the molecule behaves as an unbranched molecule composed of chain elements of length A_b which, provided $\zeta \geqslant 3$, is related to A_m by the equation

$$\left(\frac{A_b}{A_m}\right)^{3/2} = \left[\frac{2\ln(\zeta+1)/2}{\zeta\ln 2}\right]\left[\frac{43}{40+\zeta} + 6.3\,\frac{\zeta}{40+\zeta}\right]$$

This relationship is shown graphically in figure 24.

In a review paper Kuhn, Kuhn, and Buchner (77) considered briefly the case in which the elastic dumbbell model was not entirely satisfactory: namely, for macromolecules which, at low gradients, may behave as a spherelike cluster (121) of radius r_o. The model in this case was taken to be two dumbbells in the form of a cross, and the material of the molecule assumed to have an internal viscosity coefficient η_i. Because of this viscosity the molecule has a "deformation relaxation time", τ_d', defined as the time taken to change its deformation from any value dV to dV/e, where e is the base of logarithms. $\tau_d' = (2\eta_i + 6\eta_o)/Y$,

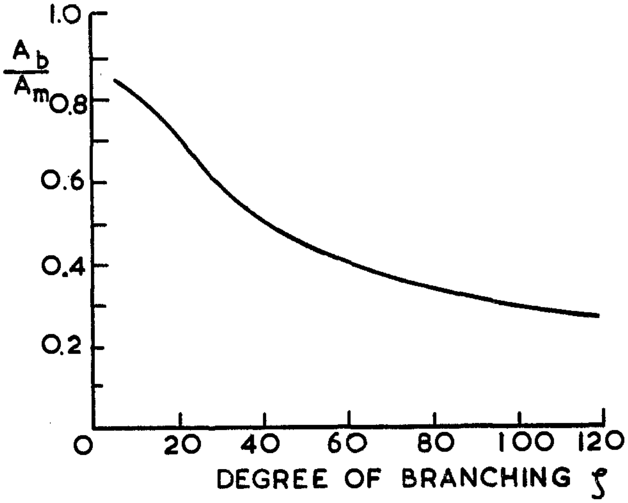


FIG. 24. Ratio of chain lengths of branched and unbranched molecules as a function of the degree of branching (Kuhn (72)).

where Y is the coefficient of elasticity of the material. This value compared with the time

$$\tau_o' = \frac{1}{D} = \frac{8\pi\eta_o r_o^3}{kT}$$

which the sphere takes to rotate through 90° due to thermal agitation determined the ultimate behavior of the particle in flow. For $\tau_d' \gg \tau_o'$ it was orientated, and for $\tau_o' \gg \tau_d'$ it was deformed. In dealing with the latter case Kuhn first gave an expression for the strain double refraction exhibited by an elastic material consisting of a number of statistical elements immersed in a medium of refractive index n_o and viscosity η_o and subjected to a force X.

Thus

$$n_{\parallel} - n_{\perp} = \frac{2\pi}{5} n_o \left(\frac{n_o^2 + 2}{3n_o}\right)^2 \frac{\alpha_1 - \alpha_2}{kT} X$$

where α_1, α_2, k, and T have their usual meanings and $n_{\parallel}$ and $n_{\perp}$ are the refractive indices parallel and perpendicular to the force. For a sphere, X was given as $2\eta_o G$; for a solution containing N_p spheres per cubic centimeter each of volume V, the birefringence Δn was given as

$$\Delta n = (n_{\parallel} - n_{\perp}) N_p V$$

For a chain molecule considered as a nondraining sphere $V = 0.41(A_m Z b)^{3/2}$, so that finally

$$[M]_{sp} = \frac{4\pi}{5}\left(\frac{n_o^2 + 2}{3n_o}\right)^2 \frac{\alpha_1 - \alpha_2}{kT}\, 0.41\, \frac{N_A}{10^2} \frac{Z^{1/2}}{M_o} (A_m b)^{3/2} \tag{157}$$

The problem was treated in greater detail by Cerf (see Section VII,K).

E. THEORY OF PETERLIN

Peterlin (99, 102) introduced the effects of hydrodynamic interaction between the chain elements and of their volume into the theory of W. Kuhn and H. Kuhn for a partially draining coil. It was first assumed that each statistical element could be replaced by a sphere of radius a for the purpose of calculating the hydrodynamic resistance and the chain was then regarded as $(N_m - 1)$ small dumbbells instead of one large one. Assuming next that the second virial coefficient B is a measure of the volume occupied by the segments and their interaction, Peterlin deduced that $\overline{h^2} = A_m{}^2 N_m{}^{1+\epsilon}$, where ϵ is a function of B and only becomes appreciable for large values of Z. Then

$$[\eta] = \frac{\lambda_g}{24[\pm 1 + CN_m{}^{(1-\epsilon)/2}]} \frac{N_A}{10^2} \frac{Z}{M} N_m{}^{(1+\epsilon)} A_m{}^2 \simeq \frac{\lambda_g}{24} \frac{N_A}{10^2} \frac{Z}{M} \frac{N_m{}^{(1+3\epsilon)/2}}{C} A_m{}^2 \tag{158}$$

$$\frac{\Delta n}{c\eta_o n_o G} = \frac{4\pi}{5} \left(\frac{n_o{}^2 + 2}{3n_o}\right)^2 \frac{\alpha_1 - \alpha_2}{kT} [\eta]\{1 + f([\eta]\eta_o\,(G)\} \tag{159}$$

In these equations $C \simeq 2.3a/A_m$, the quantity λ_g is the frictional resistance of each element, and for infinitely dilute solutions and low gradients the function $f([\eta]\eta_o G)$ is zero. The extinction angle χ is given by equation 149, so that both $[M]_{sp}$ and cot 2χ are proportional to $Z^{3(1+\epsilon)/2}$ or $M^{3(1+\epsilon)/2}$.

As the concentration increases equations 149 and 159 no longer hold and the viscosity η of the solution, defined by $\eta = \eta_o + c[\eta]\eta_o$, becomes dependent on G. This departure is due to interactive forces between the molecules, and Peterlin suggests that these forces can be allowed for by treating the molecules in the same manner as in a very dilute solution, but by making the shearing stress orientating the molecules $\eta^* G$ instead of $\eta_o G$, where η^* is an effective viscosity. The latter is defined by $\eta_G = \eta_o + c[\eta]\eta^*$, where η_G is the viscosity of the solution at the prevailing gradient. This point of view would seem to exclude very concentrated solutions and natural melts. Then for moderately concentrated solutions (order of grams per 100 cc.)

$$\frac{\Delta n}{n_o} = \frac{4\pi}{5} \left(\frac{n_o{}^2 + 2}{3n_o}\right)^2 \frac{\alpha_1 - \alpha_2}{kT} (\eta_G - \eta_o)G \left\{1 + f\left(\frac{\eta_G - \eta_o}{c} G\right)\right\} \tag{160}$$

$$RT \cot 2\chi = \beta \left(\frac{\eta_G - \eta_o}{c}\right) MG \times 10^2 = \beta \times 10^2 MG[\eta]\eta^* \tag{161}$$

A graph of Δn against $(\eta_G - \eta_o)G$, when the function f is zero, or of $\Delta n/(\eta_G - \eta_o)G$ against $(\eta_G - \eta_o)G/c$, when f is finite, should give coincident curves (straight lines) for all concentrations. Discrepancies may occur, however, owing to the fact that the anisotropy of the internal field may change with concentration and produce a shift in the Δn curve. Similarly, a single curve should result if χ is plotted against $(\eta_G - \eta_o)G/c$, although since χ is very much influenced by polydispersity the system must be accurately monodisperse. Peterlin uses the results of Schmidli (108, 125) for nitrocellulose and of Tsvetkov, Frisman, Petrova, and Poddubnyi (141, 143, 151, 152) for polystyrene and polyisobutylene to test the theory and finds a satisfactory agreement.

F. THEORY OF HERMANS

Hermans (45) presented a theory for three-dimensional motion identical in concept with the two-dimensional theory of W. Kuhn and H. Kuhn. It was limited to small gradients and freely draining molecules and gave entirely similar results. Thus,

$$[\eta] = \frac{2}{3}\,\frac{N_A}{10^2}\,\frac{Z}{M_g}\,\frac{A_m^3}{s_m^2} \tag{162}$$

$$[M]_{sp} = \frac{8\pi}{15}\left(\frac{n_o^2+2}{3n_o}\right)^2\frac{\alpha_1-\alpha_2}{kT}\,\frac{N_L}{10^2}\,\frac{Z}{M_g}\,\frac{A_m^3}{s_m^2} \tag{163}$$

$$\left[\frac{\cot 2\chi}{\eta_o\, G}\right]_{\substack{G\to 0\\ c\to 0}} = \frac{2}{3}\,\frac{A_m^3\, Z^2}{s_m^2\, kT} = \frac{10^2 M[\eta]}{RT} \tag{164}$$

Comparison with equations 138, 143, and 149, when λ_m equals $3\pi/2$ and $A_m = s_m b$, shows differences only in the numerical factors. Hermans discusses this and concludes that no decision can be made as to which values are preferable, because neither theory has considered the effect of hydrodynamic interaction between the chain elements. A method of introducing this was indicated in a paper on sedimentation velocities (46).

Snellman (132), in discussing the Kuhn–Hermans theory, considers the optical treatment to be incorrect and states, without proof, that the term $(n_o^2 + 2)^2/9$ in equations 143 and 163 must be replaced by the volume of the chain element and that $(\alpha_1 - \alpha_2)$ is given by

$$(\alpha_1 - \alpha_2) = \frac{n_o^2}{4\pi}\left[\frac{m_1^2 - 3m_2^2 + n_o^2 + (m_1\, m_2/n_o)^2}{n_o^2 + m_2^2}\right]$$

where m_1 and m_2 are the principal refractive indices of the Kuhn chain element. The extinction angle is given by equation 164 but with the numerical factor ⅓ instead of ⅔.

G. THEORY OF STUART AND PETERLIN

A theory which was similar to the Kuhn–Hermans theory was suggested by Peterlin (98) and extended later in collaboration with Stuart (136). Only the two-dimensional case for small gradients was considered and the anisotropy of the internal field was neglected. The molecules were taken to consist of a number of rigid chain elements joined randomly together to form a rigid entity. The expressions derived for $[M]_{sp}$ and $[\omega]$ are

$$[M]_{sp} = 3\pi\left(\frac{n_o^2+2}{3n_o}\right)^2\frac{\alpha_1-\alpha_2}{kT}\,\frac{\lambda_o}{48}\,\frac{Z}{10^2}\,\frac{A_m^2}{s_m}\,\frac{1}{V_o} \tag{165}$$

$$[\omega] = \frac{\lambda_o}{16kT}\,N_m^2 A_m^2 = \frac{\lambda_o}{16kT}\,\frac{A_m^2}{s_m^2}\,Z^2 \tag{166}$$

where λ_o and V_o are the frictional coefficient and volume, respectively, of a chain element, and the remaining quantities are as previously defined.

H. THEORY OF KRAMERS

Kramers (56) gave a more detailed theory than Hermans but based it on similar principles. The methods of Riemannian geometry were used and only freely draining molecules considered. The model chosen to represent the molecule resembled a pearl necklace and consisted of N_m spherical particles of equal mass with every two successive particles connected by links which were assumed to be rigid rods of length A_m and of zero mass. The hydrodynamic force which a liquid exerts on each particle was taken to be $\lambda_o v$, where v is the particle velocity relative to the liquid and λ_o is a frictional constant. Karmers considered that either the two links which meet in a particle are completely free to rotate with respect to one another, i.e., they are analogous to the statistical chain elements of Kuhn, or that the valency angle between two successive links is fixed with and without the possibility of free rotation. In both cases he investigated the statistical behavior of the individual links when in a flowing liquid and then deduced the behavior of the whole model. For this purpose it was assumed that the equations of motion are those of a molecule in a liquid at rest subjected to a field of force possessing potential energy and the molecular distribution was found by application of Boltzmann's law. An attempt was made to take into account the interaction between two links, but this consideration was incomplete in that a link was considered only to be affected by the two neighboring links.

In treating the optical behavior an expression was deduced for the polarization tensor p per molecule, which was then related to the dielectric constant ϵ in any direction in the liquid by the expression $\epsilon = \epsilon_o + 4\pi N_p p$, where ϵ_o is the dielectric constant of the solvent. Kramers gave p as a symmetrical matrix with elements p_{ij}, in which for a molecule possessing a large number of links

and

$$\left.\begin{aligned} p_{11} &= p_{22} = p_{33} \simeq N_m\, a \\ p_{31} &= p_{32} = 0 \\ p_{21} &= C\,\frac{\lambda_o\, A_m{}^2 N_m{}^2 G b}{180kT} = C\,\frac{\delta\eta G b}{5kT} \end{aligned}\right\} \tag{167}$$

The quantities a and b are optical anisotropy factors for the molecule, $\delta\eta$ is the contribution per molecule to the viscosity, G, k, and T have their usual meanings, and C is a numerical factor, which for a molecule whose links possess free rotation is almost unity and with partially free rotation may be as high as 3. No final expressions for the double refraction of the solution or the extinction angle χ were given.

I. THEORIES OF ČOPIČ AND OF TSVETKOV

In these theories it is suggested that flow double refraction is a result of the eigen anisotropy of the undeformed molecule, its asymmetrical shape, and the anisotropy resulting from deformation.

Čopič (27) appears to use the model of Kramers and the hydrodynamic considerations of Hermans. In treating the optical behavior he pays particular attention to the influence of the internal field on the optical anisotropy of the solution and finally (28, 103) replaces equation 141 by

$$\gamma_\xi - \gamma_\eta = \theta_i \frac{h^2}{\overline{h^2}} + \theta_f \frac{h}{\overline{h^2}} \tag{168}$$

where θ_i and θ_f are the intrinsic and form anisotropies of the particles. These are defined by

$$\theta_i = \frac{3}{5}(\alpha_1 - \alpha_2); \quad \theta_f \left(\frac{9M}{4\pi\rho \mathrm{N_A}}\right)^2 \frac{1}{\overline{h^2}^{\,3/2}} \left[\frac{n_o(n^2 - n_o^2)}{n^2 + 2n_o^2}\right]^2$$

in which n and ρ are the refractive index and density of the solute molecule and the other symbols have their usual meanings. Then, for soft molecules, χ is given by equation 164 and the birefringence by

$$\frac{\Delta n}{c\eta_o n_o G} = C\,[0.86\theta_f + \theta_i(1 + \beta^2)^{1/2}][\eta] \tag{169}$$

where

$$C = \frac{4\pi}{3}\left(\frac{n_o^2 + 2}{3n_o}\right)^2 \frac{1}{kT} \quad \text{and} \quad \beta = \frac{M}{RT}[\eta]\,\eta_o G$$

For stiff molecules equation 169 holds but with the term β^2 omitted. χ is given by

$$\frac{\cot 2\chi}{\eta_o G} = \frac{7}{3}\,[(\theta_i + 0.63\theta_f)/(\theta_i + 0.73\theta_f)]\,\frac{\mathrm{M}}{RT}\,[\eta]10^2 \tag{170}$$

Tsvetkov (139–153) takes as his model for the molecule in solution an ellipsoid of revolution completely entrapping the solvent; it has a volume V, a density ρ, and an axial ratio a_1/a_2. The double refraction for small values of G is considered to be due to orientation effects but deformation effects quickly enter as G increases. It is assumed that the treatment of Peterlin and Stuart is applicable and that Δn is given by equation 94 but with $V(g_1 - g_2)$ taken to be $\gamma_\xi - \gamma_\eta$, where

$$\gamma_\xi - \gamma_\eta = \theta_i\left(\frac{n_o^2 + 2}{3}\right)\frac{\overline{h_o^2}}{\overline{h^2}} + \left(\frac{n^2 - n_o^2}{4\pi n_o\,\rho N_A}\right)^2 \frac{M^2}{V}(L_2 - L_1) \tag{171}$$

In equation 171 L_1 and L_2 are shape factors (figure 11), $\overline{h^2}$ is the mean square distance between the ends of the undeformed chain molecule, and $\overline{h_o^2}$ is the value of $\overline{h^2}$ when the molecule is deformed. If, for small values of G, no deformation is present, then $\overline{h_o^2} = \overline{h^2}$, so that $[M]_{sp}$ is found from equation 95b to be

$$[M]_{sp} = \frac{2\pi b N_A}{225\eta_o DM}\left(\frac{n_o^2 + 2}{n_o}\right)^2(\alpha_1 - \alpha_2) + \frac{(L_2 - L_1)bM}{120\eta_o\,\pi \mathrm{D V}\rho^2 \mathrm{N_A}}\left(\frac{n_o^2 - n_o^2}{n_o^2}\right)^2$$

$$= \frac{1}{n_o}\,[[n]_e + [n]_f] \tag{172}$$

where $[n]_e$ and $[n]_f$ are due to the eigen anisotropy and form anisotropy, respectively. Tsvetkov assumes that $D = RT/4M\eta_o[\eta]$, so that

$$\frac{[M]_{sp}}{[\eta]} = \frac{0.11b}{kT}\left(\frac{n_o^2 + 2}{n_o}\right)^2(\alpha_1 - \alpha_2) + \frac{b(L_2 - L_1)}{30\pi\rho^2 N_A\,T}\left(\frac{n^2 - n_o^2}{n_o^2}\right)^2\frac{M^2}{V} \tag{173}$$

The value for χ when G is small is obtained from equation 89 and is given by

$$\left[\frac{(\pi/4 - \chi)}{G}\right]_{G\to 0} = \frac{1}{12D} = \frac{C}{12kT} \tag{174}$$

where C is the resistance to rotation of the molecule. Tsvetkov states that this should remain constant as G increases, but if this is not so then deformation must occur. Then (139, 141, 143, 151, 152),

$$\tan 2\chi = \tan 2\chi_o + 6kT/GC \tag{175}$$

where χ_o is the limiting value of χ ($\neq 0$) as G approaches infinity.

One immediate deduction from this theory is that the variation of $[n]_f$ with n_o is parabolic, which has been shown experimentally (140), and it is possible for $[n]_e$ to increase with G more quickly than $[n]_f$.

J. THEORY OF KIRKWOOD

Kirkwood and Riseman (59) criticized the theory of Kramers on the grounds that the hydrodynamic interactions of the monomer units were not considered sufficiently and each particle was supposed to offer the same resistance to solvent flow that it would offer if the other particles were not present to perturb the flow in its neighborhood. They attempted to formulate a theory for viscosity and to give expressions for the rotary diffusion constants (60) in which these defects were remedied. The model used consisted of an array of N_m identical structural units attached to a flexible framework. Their final equations for the intrinsic viscosity, $[\eta]$, and diffusion constant, D, of dilute solutions were expressed in terms of two parameters b and λ' which could be evaluated. Thus

$$[\eta] = \frac{N_A\lambda' b^2}{3600\eta_o M_o} Z\left[\left(\frac{6}{\pi^2}\right)\sum_{k=1}^{\infty}\frac{1}{k^2}\frac{1}{1+\lambda_o(Z/k)^{1/2}}\right] \tag{176}$$

$$D = \frac{N_A kT}{400M\eta_o [\eta]} \tag{177}$$

in which macromolecule concentrations are in grams per 100 cc., b is the effective hydrodynamic distance between chain elements, λ' is the friction constant associated with the chain elements, and

$$\lambda_o = \lambda'[(6\pi^3)^{1/2}\eta_o b]^{-1}$$

The other symbols have their usual meanings. An approximate form of equation 176 has also been given by Peterlin (100). Extensions to the theory were made by Kirkwood (57), who derived a generalized diffusion equation for partially draining macromolecules in flow and later (58) indicated its application to the birefringence problem. Expressions for the elements of the polarizability tensor were given, but not in a form which enabled usable expressions for Δn and χ to be deduced.

Schoenberg, Riseman, and Eirich (127) used some of the results of Kirkwood's work in treating their experimental data on flow double refraction. They assumed that the molecule behaved as a rigid particle and used an empirical equation to give χ: namely, $\tan 2\chi = mD/G$, where m is a number and D is given by equation 177. Thus,

$$\left[\frac{\cot 2\chi}{\eta_o G}\right]_{\substack{c\to 0\\ G\to 0}} = 2[\omega] = \frac{4}{m}\, 10^2 \frac{M}{RT} [\eta] \tag{178}$$

Values of m have to be determined from a knowledge of molecular weight values obtained by another method, e.g., osmosis; its value is about 2.

K. THEORY OF CERF (8–24)

Cerf first treated the double refraction effects arising from a suspension of spherical deformable particles and then dealt with the case when the particles were chain molecules.

1. Spherical particles

A monodisperse, dilute solution was considered, using as a model an elastic sphere of radius 50 to 500 A. which was assumed to be homogeneous and isotropic with regard to its elastic properties. Initially the sphere was regarded as impermeable, but later (17, 19) it was decided that the results held good for permeable spheres.

The effect of the flow is to change the spheres into ellipsoids with their elasticity attempting to restore the spherical shape. Cerf assumed that both deformation and restoration of shape are opposed by the internal viscosity η_i of the material of the particle, as suggested by Haller, and that superimposed is the effect of thermal agitation, which manifests itself by causing fluctuations in particle shape. Under these combined influences the deformed ellipsoids assume a state of kinematic equilibrium with their major axes inclined to the streamlines at a finite angle.

In developing the theory, Cerf introduces the quantities τ_o and τ_d, which are the times required to establish the orientation of the molecule supposed rigid, and the lifetime of the ellipsoidal configuration, respectively; they differ from the quantities τ_o' and τ_d' used by Kuhn. Cerf takes τ_o as $1/6D$, where D is the rotary diffusion constant of the ellipsoid and gives (18) τ_d as $2.5\,(\eta_o + 0.4\eta_i)/Y$, where Y is the coefficient of elasticity. In general, for any value of the ratio τ_d/τ_o both orientation and deformation occur. The spheres, initially of radius a, are supposed to become ellipsoids having axes $2a_1$, $2a_2$, and $2a_3$, where $a_1 = a(1 + \delta)$, $a_2 = a$, and $a_3 = a(1 - \delta)$. The ellipsoids execute a precessional motion, their angular velocity for two-dimensional flow being given by (19)

$$\frac{\partial\phi}{\partial t} = \frac{G}{2}\left[1 + \cos 2\phi\left(b - \frac{1}{\tau_d}\frac{5}{4}\frac{\eta_o}{Y\delta}\right)\right] \tag{179}$$

and their change in deformation with time by

$$\frac{\partial\delta}{\partial t} = -\frac{1}{\tau_d}\left(\delta - \frac{5}{4}\frac{\eta_o G}{Y}\sin 2\phi\right) \tag{180}$$

In these equations $b = (a_1^2 - a_3^2)/(a_1^2 + a_3^2) \doteq 2\delta$, and ϕ is as shown in figure 3(a). The change $\partial\delta/\partial t$ is zero when $\phi = \pi/4$ and the value, δ_h, of δ is then $5\eta_o G/4Y$. The distribution function, F, of the major axes is found from the differential equation,

$$\delta_o^2\nabla^2 F + 4\tau_d D \frac{\partial^2 F}{\partial\phi^2} + 4F(1 + G\tau_d \delta \sin 2\phi + 2\frac{\partial F}{\partial\delta}(\delta - \delta_h \sin 2\phi)$$

$$- \frac{\partial F}{\partial\phi}[G\tau_d + \cos 2\phi(2G\delta + \delta_h/\delta)] = 0 \quad (181)$$

the solution to which is given as

$$F = \frac{2}{\pi\delta_o^2} e^{-(\delta/\delta_o)^2}\left[1 + \frac{2\delta \cos 2\phi(G\delta_o^2\tau_d + \delta_h)}{\delta_o^2\tau_d(1 + 4D\tau_o)}\right] \quad (182)$$

where

$$\delta_o^2 = \overline{\delta^2} = \frac{kT}{2VY} \quad (183)$$

The quantity δ_o is regarded as the measure of the fluctuations in shape due to thermal agitation; V is the particle volume.

In calculating the optical effects it is assumed that the directions of the principal refractive indices coincide with the principal axes of the deformation ellipsoid. Finally, using Boeder's method of treatment, for small gradients, Cerf gets

$$\chi = \frac{\pi}{4} - \frac{G}{2}\frac{\tau_d\tau_o}{\tau_d + \tau_o} \quad (184)$$

$$[M]_{sp} = \frac{1}{n_o^2 Y}\left[5\alpha + 2\left(\frac{\bar{n} - n_o}{\bar{n}}\right)^2\right]\left[\frac{(\eta_o/\eta_i) + 4\delta_o^2/5}{(\eta_o/\eta_i) + 4\delta_o^2/3}\right] \quad (185)$$

where n_o is the refractive index of the solvent; α characterizes the anisotropy acquired by the sphere when deformed and is given by $2(n_o - n_2)Y/5\bar{n}\eta_o G$, in which n_1 and n_2 are the principal refractive indices of the material of the sphere and $\bar{n}$ its mean index.

By equation 184,

$$\frac{1}{2\tan(\chi G)_o} = \frac{1}{\tau_d} + \frac{1}{\tau_o} \quad (186)$$

or in terms of η_o, η_i, and Y,

$$\frac{1}{2\tan(\chi G)_o} = \frac{\eta_i + \frac{4}{3}\frac{\eta_i}{\eta_o}\delta_o^2[\eta_i + 2.5\eta_o]}{(\eta_i + 2.5\eta_o)}\frac{Y}{\eta_i} \quad (187)$$

If $\tau_o > \tau_d$ and $\delta_o < 0.1$, the effect is mainly one of deformation and equations 186 and 187 give

$$\tan(\chi G)_o = \frac{1.25}{Y}(\eta_o + 0.4\eta_i) = \frac{\tau_d}{2} \quad (188)$$

whence

$$T\tan(\chi G)_o = B\eta_o + C \quad (189)$$

in which B and C are constants. The Maxwell constant is given by equation 185 with the term in the second bracket set equal to unity.

If $\tau_0 < \tau_d$, the effect is one of orientation of a rigid particle, whence by equation 186,

$$T \tan (\chi G)_o = \frac{\tau_o T}{2} = \frac{T}{12D} = \text{constant} \times \eta_o \qquad 190$$

An expression for $[M]_{sp}$ is not in this case given by Cerf.

Equations similar to equations 186 and 188 were derived by Kuhn, Kuhn, and Buchner (77) for elastic spheres; they are

$$\frac{1}{2 \tan (\chi G)_o} = 6 \left(\frac{1}{\tau_o} + \frac{1}{4\tau_d} \right) \qquad (191)$$

$$\tan (\chi G)_o = \frac{2}{Y} \left(\eta_o + \frac{\eta_i}{3} \right); \quad \tan (\chi G)_o = \frac{\tau_o}{12} \qquad (192)$$

(deformation) (orientation)

2. Chain molecules

In considering the effect of chain molecules, Cerf emphasizes that selection of a model is complicated, since among other things, the molecular configurations have not a center of symmetry or an axis of revolution and the molecule may possess varying degrees of permeability. Initially Cerf used an ellipsoidal molecule and attempted to extend the theory of Peterlin and Stuart. Later he considered the dumbbell model of W. Kuhn and H. Kuhn, but could not reconcile this model with the case when the chain molecule behaves as a spherelike cluster. Finally, Cerf considered that chain molecules may be treated by taking the mean volume V, which is occupied by the most probable configuration of the chains, and regarding it as being limited by a spherical surface. The sphere was taken as being made up of the material of the chain but swollen with solvent. The value of χ is given by equation 184, but $[M]_{sp}$, as given by equation 185, has to be modified to take into account the influence of the solvent on the mean refractive index $\bar{n}$. Cerf does this by replacing $\bar{n}$ by n^*, where $Vn^* = n - (1 - V)n_o$. Here it should be mentioned that many statements on Cerf's theory in the paper by Cerf and Scheraga (13) have been superseded by later work.

To explain why, with chain molecules, the limiting value of χ, as G increases, does not appear always to approach zero, Cerf (15, 16) developed Haller's idea that, for deformable particles, the optical ellipsoid may not coincide with the deformation ellipsoid. He assumed that each molecule acquires a static and a dynamic anistropy. The former, caused by deformation due to the external flow gradient of value G, gives a static birefringence Δn_s and would, if it existed alone, give values of χ which decrease from 45° to zero as G increases. The dynamic anisotropy arises because of the velocity of deformation or existence of an internal flow gradient G' of value $2\eta_o G/(2\eta_o + \eta_i)$. Under the influence of this gradient the molecule, which is regarded as behaving as a pure liquid, gives a dynamic birefringence Δn_d and an extinction angle of 45°. The resultant birefringence Δn, and extinction angle χ, are given by

$$\Delta n^2 = \Delta n_s^2 + \Delta n_d^2 = (cPG)^2 \tag{193}$$

$$\chi = \frac{1}{2}\tan^{-1}\left(\frac{\Delta n_d}{\Delta n_s}\right) \tag{194}$$

where $\Delta n_s = cP_sG$ and $\Delta n_d = cP_dG'$. Elimination of Δn_s gives the limiting value χ_o of the extinction angle, i.e.,

$$\chi_o = \frac{1}{2}\sin^{-1}\frac{P_dG'}{PG} \tag{195}$$

In these equations, c is the volume concentration, and P_s, P_d, and P are constants. According to Cerf, values of the ratio P_d/P and of η_i can be obtained from experimental observations, and hence χ_o may be found.

The theories of W. Kuhn and H. Kuhn for the elastic dumbbell and of Cerf for the elastic sphere may be compared briefly (10, 11, 19, 122). For small gradients, according to Kuhn, the birefringence is due to the orientation of a molecular cluster, nonsymmetrical in shape and optically anisotropic, whereas Cerf thinks the birefringence to be a result of deformation. Thus equations 143 and 185 show that, for small gradients, a graph of Δn against G will take the same general form for both theories, but according to equations 155, 189, and 190 graphs of $T\tan(\chi G)_o$ against η_o show considerable differences (figure 22). The two theories, therefore, agree at least qualitatively in the behavior of Δn but differ in their predictions with regard to χ. The elastic sphere theory is, however, restricted to spherelike clusters, provided their fluctuations in shape are small.

Cerf in 1955 (20, 23) modified his theory for chain molecules by using a model suggested by Rouse (117), in which the molecule is subdivided into N_m subchains each just of sufficient length A_m so that at equilibrium the separation of the molecule ends obeys a Gaussian probability distribution. The configuration of a molecule is described by a set of N_m vectors, each of which specifies the configuration of a subchain and corresponds to its end-to-end separation. The frictional forces which arise in flow are localized at the junctions between two chains. Cerf takes the molecule as free draining and neglects the fluctuations in shape due to thermal agitation. Into this model he introduces an internal viscosity defined (21) by the equation $\mathcal{R} = \eta_i(v_A - v_B)$, where v_A and v_B are the velocities of the ends A and B of a subchain and $\mathcal{R}$ is the force at B (or A) opposing the motion of A (or B). This concept of η_i is analogous to the shape resistance of W. Kuhn and H. Kuhn. The theory did not agree with the experimental results of Leray (83) and Čopič (26). A modification was made (23) by associating a coefficient of internal friction to each of the principal modes of motion of the chain molecule, instead of using a single coefficient so that η_i is only a constant for a series of homologous polymers. The final deductions (24), which then agree with the work of Leray and the later results of Čopič, are as follows:

If $\eta_o \gg \eta_i$, deformation occurs and, in the absence of hydrodynamic interactive forces between different subchains,

$$T \tan (\chi G)_o = 0.2 \frac{M}{R} [\eta]\eta_o + \frac{0.0062}{k} \eta_i \overline{h^2} \tag{196}$$

in which $\overline{h^2}$ is the mean square of the distance between the ends of the molecule. When hydrodynamic interactions are strong, the figures 0.2 and 0.0062 are replaced by 0.09 and 0.0045, respectively. Equation 196 has the same form as equation 189.

If $\eta_0 \ll \eta_i$, the effect is one of orientation and then for negligible hydrodynamical forces

$$T \tan (\chi G)_o = 0.9 \frac{M}{R} [\eta]\eta_o \tag{197}$$

which may be compared with equation 190. For strong forces 0.9 is replaced by 0.705. The specific Maxwell constant, with and without interactions, is given by equation 153, but with the factor $24\pi/43$ replaced by $4\pi/5$.

L. THEORY OF ZIMM

Zimm (169) used the method of Kirkwood and Riseman to account for hydrodynamic interactions in chain molecules but, like Cerf, used a model similar to that suggested by Rouse. In a very complete mathematical study a generalized diffusion equation was deduced, giving the distribution function F of the molecules. This equation has the same form as the equation of Kirkwood (58). By a suitable mathematical transformation an exact solution was obtained and then expressions for the intrinsic viscosity, χ, and Δn were deduced. The final general expressions are

$$[\eta] = \frac{N_A A_m{}^2 \lambda_o}{6M\eta_o} \sum_{k=1}^{N_m} \frac{1}{\lambda_k} \tag{198}$$

$$G \tan 2\chi = \sum_{k=1}^{N_m} \tau_k \bigg/ \left(\sum_{k=1}^{N_m} \tau_k{}^2 \right) \tag{199}$$

$$\Delta n = \Pi c G \eta_o \frac{N_m \overline{A_m{}^2}}{MRT} \left(1 + \frac{1}{4} \tan^2 2\chi \right)^{1/2} \tag{200}$$

where Π is an optical factor, λ_o is a frictional constant as introduced by Kramers, $\overline{A_m{}^2}$ is the mean of the squares of the lengths of the subchains, λ_k is a parameter which takes different values according to the degree of "draining" of the molecule, τ_k is the relaxation time of the configuration of the k^{th} chain, and the other symbols are as before.

If it is assumed that N_m is very large, then

$$\frac{\cot 2\chi}{\eta_o G} = \frac{1}{\alpha} \frac{M}{RT} [\eta] \tag{201}$$

so that

$$T \tan (\chi G)_o = \frac{1}{2\alpha} \frac{M}{R} [\eta] \eta_o \tag{202}$$

where, for free-draining molecules,

$$[\eta] = N_A N_m^2 \overline{A_m^2} \lambda_k / 36 M \eta_o$$

and $\alpha = 2.5$, and for nondraining molecules

$$[\eta] = 0.47 N_A^{3/2} N_m \overline{A_m^2} / M \quad \text{and} \quad \alpha = 4.88$$

Zimm, like Kirkwood, has disregarded molecular interactions so that the results are applicable only to dilute solutions and, unlike the treatment of Cerf, the effect of internal viscosities has been neglected.

M. THEORY OF LODGE

Lodge (84) gives a theory for polymer solutions which have concentrations of the order of 0.1 per cent to a few per cent and which are subjected to small flow gradients. Particular attention is given therefore to the effects of molecular interactions. Unlike Peterlin (102), who assumed that equations derived from a dilute solution theory could be used by replacing the solvent viscosity coefficient by a larger "effective" viscosity, Lodge assumed that the chain molecules were entangled with each other, forming a loose network structure extending throughout the solution. Not all the chain molecules need be joined to the structure at a given instant. The structure is essentially the model used for the statistical theory of rubberlike elasticity (35, 154). Green and Tobolsky (42) extended this last-mentioned theory for application to solid polymers to allow, during deformation, for the breaking and re-forming of the network chains, and Lodge uses their extension to calculate the optical effects exhibited by a polymer solution in flow. He considers that the molecular interactions between the molecules are sufficiently localized and long-lived to be treated as junctions in a deforming network and that the stress, apart from an additive isotropic component, arises entirely from entropy changes consequent upon the deformation of the network. Some parts of the network will be older than others and will be more deformed. It is further considered that a network element of given age gives its own contribution to the total stress, independent of the rest of the network, of an amount given by the statistical theory of rubberlike elasticity. The total stress is the sum of these contributions. The birefringence is assumed to be due to orientation by network deformation of optically anisotropic chain links. Hydrodynamic flow forces are neglected, as are contributions from orientation of free chains by solvent flow and from solvent and form double refraction.

According to the statistical theory for a solid deformed at a constant temperature T,

$$s_{ij} - s\delta_{ij} = zF_o \, kT \sum_{\alpha=1}^{3} \frac{\delta x_i}{\delta x'_\alpha} \frac{\delta x_j}{\delta x'_\alpha} \qquad (i, j = 1, 2, 3) \tag{203}$$

where s_{ij} are the components of the stress tensor; s is the isotropic stress component; $\delta_{ij} = 1, 0$ according as i, j are equal or unequal; F_o is the concentration of junctions; z is a numerical factor such that zF_o is the concentration of chain segments in the network (usually $z = 2$); x_i, x_i' denote the rectangular Cartesian coördinates of the positions occupied by a particle in the strained and unstrained configurations, respectively. It is then assumed that the network chains, formed by the solution which joined the network in a previous time interval $(t', t' + \mathrm{d}t')$ and are still joined at the current time t, make a stress contribution as if they formed a network chain of a rubberlike solid in which the unstrained and strained configurations are identified with the configurations of the solution at times t' and t, respectively. Then equation 203 may be applied to find the stress tensor with F_o replaced by the number of effective junction points in unit volume which exist in the solution at time t and were formed in the interval $(t', t' + \mathrm{d}t')$. The dissociation of junctions is envisaged as being due only to the thermal motion of solvent and solute molecules, i.e., the flow gradient G is taken to be so low that it has no effect in lowering the mean lifetime of junction points. With these assumptions F_o is taken to be a function of junction age $(t - t')$, temperature T, and polymer concentration c; it is called the "junction age distribution function" and is given by $F_o = F(t - t', T, c)$.

The total stress contributed by the solution network is now

$$\begin{aligned} s_{ij}(x, t) - s(x, t)\delta_{ij} &= zkT \int_{t'=-\infty}^{t} F(t - t', T, c) \sum_{\alpha=1}^{3} \frac{\delta x_j}{\delta x_\alpha'} \, \mathrm{d}t' \\ &= zkT\Sigma \end{aligned} \tag{204}$$

where x is an abbreviation for x_i $(i = 1, 2, 3)$, x_i, x_i' are now interpreted as the coördinates of the positions occupied at times t, t' by a particle of the "solution continuum", and Σ designates the integral.

In calculating the streaming double refraction, Lodge extends the theory of Treloar (155), which is itself a more general treatment of that given by Kuhn and Grun (67), to allow for the creation and dissociation of junctions during deformation. Following the same argument as above, the total optical polarizability of the flowing polymer is given by

$$p_{ij}(x, t) - p(x, t)\delta_{ij} = \tfrac{1}{5}(\alpha_1 - \alpha_2)z\Sigma \tag{205}$$

where p_{ij} are the components of the polarizability tensor, p is the isotropic polarizability component, and α_1 and α_2 are the principal polarizabilities of a chain. Thus from equations 204 and 205

$$p_{ij} - p\delta_{ij} = \frac{1}{5} \frac{(\alpha_1 - \alpha_2)}{kT} (s_{ij} - s\delta_{ij}) \tag{206}$$

For laminar flow at a gradient G with the flow and the gradient in the direction of the x_1 and x_2 axes, respectively,

$$x_1 = x_1' + Gx_2'(t - t'), \qquad x_2 = x_2', \qquad x_3 = x_3' \tag{207}$$

Then, assuming that the Lorentz–Lorenz relationship between polarizability and refractive index is applicable, the tensor components of stress, polarizability, and refractive index, referred to the chosen coördinate system, are obtained from equations 206 and 207; thus

$$\frac{s_{11} - s_{22}}{kT} = \frac{p_{11} - p_{22}}{C} = \frac{n_{11} - n_{22}}{C_o} = zF_2(T, c)G^2 \tag{208}$$

$$\frac{s_{12} - s_{33}}{kT} = \frac{p_{22} - p_{33}}{C} = \frac{n_{22} - n_{33}}{C_o} = 0 \tag{209}$$

$$\frac{s_{21}}{kT} = \frac{p_{21}}{C} = \frac{n_{21}}{C_o} = zF_1(T, c)G \tag{210}$$

$$s_{23} = s_{31} = p_{23} = p_{31} = n_{23} = n_{31} = 0$$

where

$$C = \frac{1}{5}(\alpha_1 - \alpha_2);\ C_o = 2\pi\bar{n}\left(\frac{\bar{n}^2 + 2}{3\bar{n}}\right)^2 C;\ F_\beta(T, c) = \int_{t^1=-\infty}^{t} F(t - t', T, c)(t - t')^\beta \mathrm{d}t' \ (\beta = 1, 2)$$

and $\bar{n}$ is the mean refractive index of the solution.

The tensor components in terms of the principal values and principal directions of the refractive index tensor enable the difference in principal values, Δn, and the orientation, χ, for the section by the x_1x_2 plane of the refractive index ellipsoid to be found. Thus

$$\tan 2\chi = \frac{2F_1}{GF_2} = \frac{2s_{21}}{s_{11} - s_{22}} \tag{212}$$

and

$$\frac{\Delta n}{\bar{n}} = 2\pi\left[\frac{\bar{n}^2 + 2}{3\bar{n}}\right]^2 \left[(p_{11} - p_{22})^2 + 4p_{21}^2\right]^{1/2} \tag{213}$$

Since, by definition the viscosity of the solution $\eta = s_{21}/G$ or $zkTF_1$, equation 213 becomes

$$\Delta n = \frac{2C_o\eta G}{kT}\left[1 + \left(\frac{F_2\,G}{2F_1}\right)^2\right]^{1/2} \tag{214}$$

so that

$$\frac{\Delta n}{\bar{n}} = \frac{4\pi}{5}\left[\frac{\bar{n}^2 + 2}{3\bar{n}}\right]^2 \frac{\alpha_1 - \alpha_2}{kT}\,\eta G \operatorname{cosec} 2\chi \tag{215}$$

The quantities Δn and χ are the flow birefringence and the extinction angle for light rays normal to the x_1x_2 plane. When the birefringence of the solvent is negligible and a correction is made for the effect of solvent viscosity η_o, equation 215 may be rewritten as

$$\frac{\Delta n \sin 2\chi}{\bar{n}} = \frac{4\pi}{5}\left[\frac{\bar{n}^2 + 2}{3\bar{n}}\right]^2 \frac{(\alpha_1 - \alpha_2)}{kT}(\eta - \eta_o)G \tag{216}$$

which means that the curves of $\Delta n \sin 2\chi$ plotted against $G(\eta - \eta_o)$ should coincide for all concentrations.

Equation 206 shows that the polarizability (and refractive index) ellipsoid at a point has the same orientation as the stress ellipsoid and that differences in the principal values of polarizability Δp (and refractive index Δn) are proportional to the corresponding differences of principal values of stress Δs; the ellipsoids are not in general similar in shape. Thus by equation 208

$$\frac{\Delta p}{\Delta s}\frac{C_o}{C} = \frac{\Delta n}{\Delta s} = \frac{C_o}{kT} = \frac{2\pi}{5}\frac{\bar{n}}{kT}\left(\frac{\bar{n}^2 + 2}{3\bar{n}}\right)^2(\alpha_1 - \alpha_2) \tag{217}$$

The quantity $\Delta n/\Delta s$ is the "stress optical coefficient."

In connection with the value of χ, Lodge deduces that if the relaxation of stress following a sudden cessation of flow can be described in terms of a single exponential function of time, $e^{-t/\tau}$ say, then χ will remain constant. In this case $\tau F_o = F_1 = F_2/2\tau$, so that from equation 212, $\tan 2\chi = (G\tau)^{-1}$. If the relaxation shows a different behavior with time, then χ will decrease.

Examination of the theory indicates that the assumptions are such as to limit its application to solutions of long flexible molecules with strong mutual interactions, concentrated enough to possess a network structure, yet not so concentrated that the mean length between successive junctions is too small for the Gaussian approximation, assumed in the statistical theory of rubberlike solids, to be valid. Moreover, the concentration must be low enough for a chain on leaving the network to be able to retract fully before joining the network again. The gradient G must be small compared to the reciprocal of period τ, or the macroconstellation changing time τ' of Kuhn, to ensure that the network deformation can be treated as a quasi-static process. The fact that η is independent of G is explained by this limitation of G.

VIII. Conclusions

The following comments may be made on the theories given in this review.

A. LIQUIDS

The theory of Raman and Krishnan is subject to two major criticisms. Firstly, although streaming double refraction is analogous to electric and magnetic double refraction, the behavior of the molecules is different. Thus in electric and magnetic fields the molecules try to reach a position of minimum potential energy, whereas in a flow field they rotate irregularly to give a nonuniform time of stay of the molecular axis in various directions in space. This latter fact, which is a consequence of thermal agitation, was not considered by Raman and Krishnan, for they considered the thermal agitation to affect only the degree of orientation. Secondly, the theory contains an assumption which does not allow it more than a limited application. The Boltzmann distribution function holds only for an undisturbed statistical equilibrium which is not fulfilled when the molecules are subject to flow unless the flow is such as to cause only an infinitesimally small disturbance of the equilibrium. This will be so for small gradients with large molecules and high gradients with small molecules. For these cases the theory predicts the observed value of 45° for χ and the correct order of magnitude for Δn; for other cases any agreement would appear fortuitous.

The theory of Peterlin and Stuart appears more promising but as yet little is known concerning the extent of, or the energy relationships involved in, the "near-order" conditions. Also, the polarizability of the individual molecules is dependent on the type and arrangement of the neighboring molecules and this dependency is insufficiently known.

B. DILUTE SOLUTIONS OF RIGID PARTICLES

Kuhn, Haller, and Boeder correctly recognize that the particle orientation is kinematic, but their theories suffer from an inadequate treatment of the motion of the particles in flow. Further, in developing the optical considerations an isotropic internal field due to the incident light vector is wrongly assumed. Sadron's attempt to remedy this by applying the Lorentz consideration to an ellipsoid-shaped volume of dimensions equal to that of the particle is difficult to justify. The theory of Bjornstahl and Snellman, which is an extension of that of Peterlin and Stuart, appears rigorous and complete.

C. SOLUTIONS OF FLEXIBLE PARTICLES

For chain particles, where frictional forces on chain segments which have dimensions of the same order as solvent molecules have to be considered, troubles arise in the application of the hydrodynamical equations of continuous media. This fact, coupled with the difficulty of choosing a suitable model, means that such theories as those of Kuhn and Hermans can only lead to approximate solutions. Also in Kuhn's theory, for example, it is assumed that a molecule in flow retains on the average its rotation symmetry about the line joining its end points, but there is no basis for this assumption, because in reality the flow stream acts on all the fiber elements in the chain. Further, it is not rigorously shown that the forces tending to restore the molecular shape remain unchanged in the flow field. Neither Kuhn, Hermans, nor Peterlin has considered the anisotropy of the internal field or the effect of the solvent on the optical anisotropy, and only Kuhn has dealt with the possible effects of branched molecules. The necklace model of Kramers is possibly a better model than the elastic dumbbell, but the attempt by Kramers to introduce chain interaction is incomplete in that only the effects of two neighboring links are taken into account. The solution of the hydrodynamic problem by Zimm appears exact. Since the only approximation used in the mathematics is the use of the Kirkwood–Riseman interaction tensor, any deficiency in this theory must be due either to (*a*) the inadequacy of the Kirkwood–Riseman approximation, (*b*) the incorrect assumption of a perfect Gaussian distribution function for the individual chain segments, or (*c*) a defect in the model. With regard to (*a*) the results are only applicable to dilute solutions, and the model is defective in that there is no provision for the internal viscosity or stiffness of the molecule.

The theories of Čopič and Tsvetkov, despite the simplicity of the models employed and the approximations used, enable many results which cannot be reconciled with theories based on equation 141 to be explained. Thus for a substance for which the form and intrinsic anisotropics θ_f and θ_i are positive and negative, respectively, Δn may, according to equation 169, change its sign from positive to negative as G increases. This is particularly so if $n - n_o$ is small, as for polystyrene in dioxane (148). Furthermore, since θ_f is proportional to the square of $n - n_o$, a parabolic curve of Δn against n_o with a minimum at $n - n_o$ is understandable (119, 129, 141, 143, 151, 152). Although both theories give almost identical results at small gradients, probably because then a randomly coiled linear macromolecule has the form of a not too elongated ellipsoid, the model of Čopič is more realistic and appears better for high gradients, since the form factor changes in the way imagined. Tsvetskov requires the axial ratio of the ellipsoid to alter to produce the necessary change in form factor.

The elastic sphere theory of Cerf predicts that Δn should rise linearly with G and does not account for departures from this. It is, however, limited to small gradients. The restriction of small fluctuations in shape ($\delta_o < 0.2$) implies that the deformability must be small and that the molecular weights must be large (ca. 2×10^6 for polystyrene), although it may apply for lower values if η_o is not too small. The parameters Y and η_i, which characterize the sphere, have only a phenomenological value in describing the properties of a chain molecule and it is difficult to see how they may be interpreted in terms of molecular structure. Cerf's theory, using the Rouse model, predicts the same behavior for χ as that with the spherical model and gives the same results for Δn as Kuhn's theory using the elastic dumbbell. The model is more realistic than that of the sphere and the parameters have more significance.

D. CONCENTRATED SOLUTIONS OF MACROMOLECULES

Peterlin's theory can at best be expected to give only a rough agreement with experiment. One major reason for this is that it infers that the shape of the coiled molecule in a concentrated solution does not differ essentially from the shape of the molecule in a very dilute solution where no interaction occurs. This is unlikely. Lodge's theory, if correct, would mean that the basic assumption of stress double refraction in solids, i.e., the proportionality of Δn and the difference of the principal stresses (equation 217), is equally valid for streaming double refraction in macromolecular solutions. Allowance should be made, however, for the possible contributions from form double refraction. For a comparison with experiment, data are needed at velocity gradients low enough for the viscosity to be constant and in a concentration range in which the stress relaxation periods are substantially independent of concentration. Unfortunately the experiments of Philippoff (111, 112) do not entirely satisfy these conditions, although they indicate that the graph of $\Delta n \sin 2\chi$ against $G(\eta - \eta_o)$ is linear as Lodge's theory suggests.

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IX. APPENDICES

APPENDIX 1. ROTARY DIFFUSION CONSTANTS

Elongated (prolate) ellipsoid of revolution (Perrin (96)):

Rotation of a_1 axis about a_2 or a_3 ($r > 1$)

$$D = \frac{kT}{\eta_o V} \frac{r^2}{4(r^4 - 1)} \left[\frac{2r^2 - 1}{r(r^2 - 1)} \ln \{r + (r^2 - 1)^{1/2}\} - 1 \right]$$

$$= \frac{kT}{\eta_o \mathrm{V}} f_1(r)$$

If $r \gg 1$,

$$D \simeq \frac{3kT}{16\pi\eta_o a_1^3} [2 \ln 2r - 1]$$

Flattened (oblate) ellipsoid of revolution (Perrin (96)):

Rotation of a_1 axis about a_2 ($r < 1$)

$$D = \frac{kT}{\eta_o V} \frac{r^2}{4(1 - r^4)} \left\{ \frac{1 - 2r^2}{r(1 - r^2)^{1/2}} \tan^{-1} \frac{(1 - r^2)^{1/2}}{r} + 1 \right\}$$

$$= \frac{kT}{\eta_o V} f_2(r)$$

If $r \ll 1$,

$$D \simeq \frac{3kT}{32\eta_o a_2^3}$$

Cylindrical rod ($a_1 \gg a_2$): rotation about transverse axis (Burgers (7)):

$$D = \frac{3kT}{8\pi\eta_o a_1^3} [\ln 2r - 0.8]$$

Coil (Kuhn (80):

$$D = \frac{9kT}{\eta_o A_m^3 N_m^2} \left[-0.08 + 0.052 \left(\frac{bZ}{A_m}\right)^{1/2} + 0.12 \ln \left(\frac{A_m}{d_h}\right) \right]$$

The notation is as in Section II. Alternative forms for ellipsoids are given by Gans (39); they give numerical values almost identical with those of Perrin.

APPENDIX 2. SHAPE FACTORS FOR ELLIPSOIDS OF REVOLUTION (116)

Elongated ellipsoids ($r > 1$):

$$L_1 = \frac{4\pi}{3} (1 - 2l); \quad L_2 = \frac{4\pi}{3} (1 + l) = L_3$$

where

$$l = \frac{1}{4(r^2 - 1)} \left[2r^2 + 4 - \frac{3r}{(r^2 - 1)^{1/2}} \ln \frac{r + (r^2 - 1)^{1/2}}{r - (r^2 - 1)^{1/2}} \right]$$

Alternatively,

$$L_1 = 4\pi \frac{(1 - e^2)}{e^2} \left[\frac{1}{2e} \ln \frac{1 + e}{1 - e} - 1 \right]; \quad L_1 + 2L_2 = 4\pi$$

For $r \gg 1$,

$$L_1 \simeq \frac{4\pi}{T^2} \ln (2r - 1); \quad L_2 \simeq 2\pi$$

Flattened ellipsoids ($r < 1$):

$$L_1 = \frac{4\pi}{3} (1 - 2l); \quad L_2 = \frac{4\pi}{2} (1 + l) = L_3$$

where

$$l = \frac{1}{2(1 - r^2)} \left[\frac{3r}{(1 - r^2)^{1/2}} \tan^{-1} \frac{(1 - r^2)^{1/2}}{r} - r^2 - 2 \right]$$

Alternatively,

$$L_1 = \frac{4\pi}{e^2} \left[1 - \frac{(1 - e^2)^{1/2}}{e} \sin^{-1} e \right]; \quad L_1 + 2L_2 = 4\pi$$

For $r \ll 1$,

$$L_1 \simeq 4\pi - 2\pi^2(1 - e^2)^{1/2}; \quad L_2 \simeq \pi^2(1 - e^2)^{1/2}$$

In these expressions, $e = (a_1^2 - a_2^2)^{1/2}/a_1$, $r = a_1/a_2$. The field shape factors L_ξ and L_η are also given by the above equations, but with l and e replaced by values l_f and e_f, respectively, which depend on particle shape and concentration. In Sadron's notation $e_\xi = -2l$ and $e_\eta = l$.

APPENDIX 3. LIMITING EQUATIONS FOR THE DISTRIBUTION FUNCTION (SOLUTION OF EQUATION 66 WITH $|b| \leqslant 1$)

(a) $\sigma \leqslant 6$.

$$F = 1 + \frac{b\sigma}{2} \left[\frac{3 \sin^2 \theta}{(36 + \sigma^2)} (6 \sin 2\phi - \sigma \cos 2\phi) \right] + \left(\frac{b\sigma}{2}\right)^2 \left[\frac{1}{4(36 + \sigma^2)} \left\{ \left(9 \cos^4 \theta - 18 \cos^2 \theta + \frac{21}{5} \right) + ((\sigma^2 - 60) \cos 4\phi - 16\sigma \sin 4\phi) \frac{15 \sin^4 \theta}{(\sigma^2 + 100)} \right\} \right]$$

(b) $\sigma \leqslant 1.5$:

$$F = 1 + \frac{b\sigma}{4} \sin^2 \theta \sin 2\phi + \left(\frac{b\sigma}{8}\right)^2 \left[\sin^4 \theta (1 - \cos 4\phi) - \frac{8}{15} \left(\frac{5}{b} \sin^2 \theta \cos 2\phi + 1 \right) \right]$$

Maximum when $\theta = 90°$ and $\phi \geqslant 45°$; minimum when $\theta = 90°$ and $\phi \geqslant 135°$.

(c) $\sigma \to 0$:

$$F_{\sigma \to 0} = 1 + \frac{b\sigma}{4} \sin^2 \theta \sin 2\phi$$

Maximum at $\theta = 90°$, $\phi = 45°$; minimum at $\theta = 90°$, $\phi = 135°$.

(*d*) $\sigma \rightarrow \infty$:

$$F_{\sigma\to\infty} = 1 - \frac{3}{2} b \cos 2\phi \sin^2 \theta + b^2 \left[\frac{3}{80} (15 \cos^4 \theta - 30 \cos^2 \theta + 7) + \frac{15}{16} \cos 4\phi \sin^4 \theta \right] - b^3 \left[\frac{\cos 2\phi \sin^2 \theta}{320} (105 \cos^4 \theta - 450 \cos^2 \theta + 201) + \frac{35}{64} \cos 6\phi \sin^6 \theta \right]$$

In this case a maximum occurs at $\theta = 90°$, $\phi < 90°$.

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