THE EFFECTS OF SHAPE ON THE INTERACTION OF COLLOIDAL PARTICLES

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Introduction. The shapes of colloidal particles are often reasonably compact, so that no diameter greatly exceeds the cube root of the volume of the particle. On the other hand, we know many colloids whose particles are greatly extended into sheets (bentonite), rods (tobacco virus), or flexible chains (myosin, various linear polymers).

In some instances, at least, solutions of such highly anisometric particles are known to exhibit remarkably great deviations from Raoult's law, even to the extent that an anisotropic phase may separate from a solution in which the particles themselves occupy but one or two per cent of the total volume (tobacco virus, bentonite). We shall show in what follows how such results may arise from electrostatic repulsion between highly anisometric particles.

Most colloids in aqueous solution owe their stability more or less to electric charges, so that each particle will repel others before they come into actual contact, and effectively claim for itself a greater volume than what it actually occupies. Thus, we can understand that colloids in general are apt to exhibit considerable deviations from Raoult's law and that crystalline phases retaining a fair proportion of solvent may separate from concentrated solutions. However, if we tentatively increase the known size of the particles by the known range of the electric forces and multiply the resulting volume by four in order to compute the effective van der Waal's co-volume, we have not nearly enough to explain why a solution of 2 per cent tobacco virus in 0.005 normal $NaCl$ forms two phases.

General Kinetic Theory and Conventions. Some care is needed when we apply the general principles of statistical thermodynamics to solutions of colloidal particles. On one hand, any force acting on a particle of whatever size is important as soon as the work of the force is comparable to kT. On the other hand, the presence of one colloidal particle will usually affect the free energy of dilution of the electrolyte present by a large multiple of kT. This difficulty must be circumvented by all theories and experiments pertaining to the distribution of colloidal particles. One suitable piece of experimental apparatus is an osmometer whose membrane is impermeable to the colloidal particles, but permeable to all small molecules and ions of the electrolytic solvent. The osmotic pressure measured across such a membrane will be exactly proportional to the number of particles if the solution behaves like an ideal gas. The analogy can be extended to real gases and real solutions, whereby the gas pressure still corresponds to osmotic pressure.

The imperfection of an ideal gas can be computed when we know the forces between the molecules for every configuration. For that purpose, we have to evaluate the integral

$$B(T) = \int e^{-u/kT}\, d\tau/N! \tag{1}$$

where u stands for the potential of the forces and $d\tau$ denotes a volume element in configuration-space. The free energy of the gas in terms of this integral is

$$F(N, V, T) = N\mu_0(T) - kT \log B(N, V, T) \tag{2}$$

where the additional function $\mu_0(T)$ depends only on the temperature and does not enter into the computation of the pressure,

$$P = -(\partial F/\partial V)_{N,T} = kT(\partial \log B/\partial V). \tag{3}$$

The osmotic properties of a colloidal solution can be computed by a similar procedure. What we need to know initially is the *potential*

$$w((q_1), (q_2), \ldots (q_N))$$

of the *average forces* which act between the particles in a configuration described by the sets of coordinates $(q_1), (q_2), \ldots (q_{N_p})$ of particles $1, 2, \ldots N_p$. In general, it is necessary to specify the orientations of the particles as well as the positions of their centers, and the work against the corresponding torques must be included in w.

With

$$B_p(N_p, V, T) = \int e^{-w/kT}\, d\tau/N_p\,! \tag{4}$$

we have then

$$F\text{ (solution)} - F\text{ (solvent)}$$

$$= N_p\, \mu_p^{o}\ (T, \text{solvent}) - kT \log B_p\left(N_p, V, T\right). \tag{5}$$

Here, the difference between "solution" and "solvent" means that the former contains colloidal particles, and we compare solutions of different colloid concentrations $c = (N_p/V)$ always in "dialytic" equilibrium across an osmometer membrane with a "solvent" of constant composition. The proportions of ions and molecules present between the particles in the colloidal solution may differ from those in the "solvent" as we have defined it. This complication can hardly be avoided if we want simple relations and *precise interpretation of practicable experiments.*

With these conventions the analog of EQUATION 3,

$$P = kT(\partial \log B_p/\partial V), \tag{6}$$

is valid for the osmotic pressure and

$$\mu_P = \mu_P^0 - kT(\partial \log B_p/\partial N_p) \tag{7}$$

for the chemical potential of the colloidal particles.

Moreover, the conditions for coexistence of two phases are simply

$$P = P' \tag{8a}$$

$$\mu_p = \mu_p' \tag{8b}$$

The assumed dialytic equilibrium takes care of all small molecules and ions.

Electric Forces. According to theories developed by Helmholtz, Lamb, and Smoluchowski, the speed of migration of a colloid in an electric field is quantitatively related to the potential difference between the first mobile layer of liquid in contact with the particle and the bulk of the solution. It is customary to specify the electric charges of particles indirectly in terms of this so-called ζ-potential. The theory is still somewhat incomplete as regards cases where the thickness of the electric double layer is of the same order of magnitude as the dimensions of the particle; a factor variable between the limits of unity and 3/2 then enters into the interpretation.

With slight approximations, the general kinetic theory for the distribution of ions near charged particles leads to the well-known Poisson-Boltzmann differential equation for the electric potential

$$\nabla^2\psi \equiv \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = -\frac{4\pi}{D}\sum_j n_j e_j e^{-e_j\psi/kT} \tag{9}$$

where $e_1, e_2, \cdots$ denote the charges of ions present in concentrations n_1, $n_2, \cdots$ (in the solution or, rather, in a "solvent" maintained in dialytic equilibrium), and D denotes the dielectric constant. Whenever the condition $|e_j\psi| << kT$ is satisfied for all kinds of ions present, EQUATION 9 may be replaced by

$$\nabla^2\psi = \kappa^2\psi$$

$$\kappa^2 = (4\pi/DkT)\sum_j n_j e_j^2. \tag{10}$$

The normal gradient of ψ at the surface of the particle is related to the charge density on the particle. We have to expect an implicit boundary condition determined by the adsorption and surface ionization in equilibrium with ions present at the surface in local concentrations $n_1 \exp(-e_1\zeta/kT)$, $n_2\exp(-e_2\zeta/kT)$, etc. Since the kinetics of the surface ionization is rarely known, the relation

$$\psi = \zeta = \text{constant}; \qquad \text{(at surface)} \tag{11}$$

has often been assumed, regardless of modifying factors, although systematic variations of ζ with electrolyte concentration, etc., should be expected and have been demonstrated in some cases. We shall not pursue these questions, because the expected variations of ζ will have but little effect on the forces between the particles.

In one-dimensional cases, $\psi = \psi(x)$, EQUATION 9 is generally soluble by quadratures. However, even the simplest case of a binary electrolyte between parallel plates, both maintained at the potential ζ, leads to elliptic integrals (Langmuir, 1938), and the resulting exact formula for the force is fairly involved (Verwey and Overbeek, 1948). Their approximation

$$K(x) = 16\,n\,kT(\tanh(e_1\zeta/4kT))^2\,e^{-\kappa x} \qquad (12)$$

for the force per unit area between two parallel plates separated by a distance x is valid for not too small distances and will suffice as a basis for discussion. We note that the force decreases exponentially and that the screening constant κ, given by EQUATION 10, depends only on the ionic strength of the solvent. Moreover, for any fixed distance d between the plates, the force approaches a finite limit with increasing particle potential ζ. These two features are general.

We may use the result of EQUATION 12 to estimate the force between two infinite cylinders of the same diameter d crossing at an angle γ in such a manner that the mantles are separated by a distance x_0 between the points of closest approach.

We choose Cartesian coordinates in a plane parallel to the axes of both cylinders and identify points on the cylinder mantles by the coordinates (y, z) of their projections upon that plane. Then, the distance between points on the two cylinder mantles with the same (y, z) coordinates will be:

$$x(y, z) = x_0 + d - (\tfrac{1}{4}d^2 - y^2)^{1/2} - [\tfrac{1}{4}d^2 - (y\cos\gamma - z\sin\gamma)^2]^{1/2}.$$

If we allow the approximation

$$x(y, z) \sim x_0 + (y^2/d) + ((y\cos\gamma - z\sin\gamma)^2/d),$$

and compute the local force density $K(x)$ according to EQUATION 12, an elementary integration yields for the total force

$$\text{Average Force} = (\pi d/\kappa\sin\gamma)K(x_0) \qquad (13)$$

and we obtain for the potential w of the average force

$$w/kT = (d/q\sin\gamma)[\tanh(e_1\zeta/4kT)]^2 e^{-\kappa x_0} \qquad (14)$$

where we use the abbreviation

$$q = e_1^2/2\,DkT = z_1^2 \times 3.56 \times 10^{-8}\text{ cm.} \qquad (15)$$

and $e_1 = -e_2$ denote the charges, $z_1 = -z_2$ the valences of the ions in the solvent; the numerical value refers to water at 25°C.

As an example, we may consider two perpendicular cylindrical particles of $d = 150$ A. U., $\zeta = 0.15$ volt, in a 0.005 mol NaCl solution, whereby $1/\kappa = 43$ A. U. We find

$$w/kT = 34.5\, e^{-\kappa x_0} \tag{16}$$

which equals $e^{-C} = 0.561$ at a distance $x_0 = \delta = 4.12/\kappa = 184$ A. U.

Here, we have neglected the divergence of the electric force-lines, which must be quite appreciable because δ is by no means small, compared to d. We apply a correction of the right order of magnitude if we multiply w by the factor $d/(d + x_0)$; according to the corrected formula we then find $w = 0.561\, kT$ at a distance of about 151 A.U.

It will be evident that over a considerable range of particle diameters and orientations and over a wide range of concentrations of electrolyte, the effective range of the electrostatic repulsion will be a modest multiple of the screening distance $1/\kappa$. While exact computations are not available, there can be little doubt about the orders of magnitude involved.

One further observation is in order: unless the electric double layers of three particles overlap *in the same region*, the repulsive forces are additive. When $\kappa d >> 1$, the exceptional configurations are just about impossible; but even under much less stringent conditions very few of them can occur. On the strength of these estimates, we shall treat the electrostatic repulsion as an additive *short range effect.* For very low concentrations of ions such that κd is small, our procedure may be unreliable. On the other hand, we shall make no allowance for differential van der Waal's attraction. This omission would tend to become particularly serious for high concentrations of ions and low ζ-potentials, under conditions approaching those which lead to flocculation of the particles.

Imperfect Gas Theory. We proceed to evaluate the configuration integral of Equation 4 according to the general method developed by Mayer and Mayer. Assuming additive forces:

$$w = w_N((q_1), \cdots (q_N)) = \sum_{i<j} w_{ij}\,; \tag{17}$$

$$w_{ij} = w_2((q_i), (q_j))$$

we put

$$\Phi_{ij} = \Phi_{ij}((q_i), (q_j)) = e^{-w_{ij}/kT} - 1. \tag{18}$$

In order to avoid confusion with a distribution-function f, we write Φ_{ij} for the functions which Mayer and Mayer denote by f_{ij}. Their notation sometimes implies the hypothesis that w_{ij}, and with it Φ_{ij}, depends only on the distance between two particles. Their specialization is not essential and their method is valid, with obvious pertinent modifications, for the more general case with which we have to deal.

Upon suitable rearrangement of the sum

$$e^{-w/kT} = 1 + \sum_{i>j} \Phi_{ij} + \sum \Phi_{ij} \Phi_{i'j'} + \cdots \tag{19}$$

which now constitutes the integrand of EQUATION 4, Mayer and Mayer obtain an expansion for the integral in terms of the irreducible cluster integrals

$$\beta_1 = \frac{1}{V} \int \Phi_{12}\, d\tau_1\, d\tau_2 \tag{20}$$

$$\beta_2 = \frac{1}{2V} \int \Phi_{12}\, \Phi_{23}\, \Phi_{31}\, d\tau_1\, d\tau_2\, d\tau_3$$

and these furnish the first two correction terms tо the ideal gas laws in the expansion

$$\log B_p = N_p\{1 + \log (V/N_p) + \tfrac{1}{2}\beta_1(N_p/V) + \tfrac{1}{3}\beta_2(N_p/V)^2 + \cdots \}. \tag{21}$$

Similarly, for a solution which contains $N_1, \cdots, N_s, \cdots$ particles, of different types $1, \cdots, s, \cdots$, respectively, we have

$$\log B_p = \sum_s N_s(1 + \log (V/N_s)) + \frac{1}{2V} \sum_{s,s'} \beta_1(s, s')N_s N_{s'}$$
$$+ \frac{1}{3V^2} \sum_{s,s',s''} \beta_2(s, s', s'')N_s N_{s'} N_{s''} + \cdots. \tag{22}$$

The arguments of the cluster integrals indicate that the functions Φ_{12}, $\Phi_{23}, \cdots$ involve the interaction potentials w appropriate to pairs of particles from the sets of types (s, s'), (s, s', s''), etc.

In EQUATION 21, the generalized volume elements $d\tau_j$ are ordinary volume elements whenever the forces are central, so that w_{ij} and with it Φ_{ij} depend only on the distance between the two particles involved; but we shall be very much interested in the mutual orientations of the particles. In dealing with *isotropic* solutions, we have two alternative procedures at our disposal. The first method is to include an averaging over orientations (Ω) in the definitions of volume elements, thus

$$d\tau_j = dV_j\, d\Omega_j \Big/ \int d\Omega_j. \tag{23}$$

With particles of axial symmetry, it is, of course, enough to specify the directions of the symmetry axes, so that, for a cylindrical particle, we may let $d\Omega$ be an element of solid angle including the direction $\mathbf{a}_j$ of the cylinder axis:

$$d\tau_j = dV_j\, d\Omega_j/4\pi. \tag{23a}$$

The second method is more general, in that it applies to anisotropic phases without periodic structure, in other words, liquid crystals of the *nematic* type. For the purpose of computing B_p, we then introduce the artifice that we treat particles of different orientation as particles of different kinds. The distribution of particles among different orientations is determined by the condition that B_p must be a maximum. Incidentally, the convention that the terms $\log (V/N)$ are now formed separately for each "kind" of particles makes due allowance for the entropy of "mixing" (Gibbs Paradox). On the other hand, we must remember that the generalized volume in space and orientation available to a particle of orientation restricted to an element of solid angle $d\Omega$ is only $Vd\Omega$, rather than $4\pi V$ for a particle of unrestricted orientation. Thus, when we divide the total of all directions in space among elements of solid angle $\Delta\Omega_1, \cdots, \Delta\Omega_\nu, \cdots, \Delta\Omega_s$ surrounding the directions $\mathbf{a}_1, \cdots, \mathbf{a}_\nu, \cdots, \mathbf{a}_s$, respectively, these will have populations of particles which we shall denote by

$$\Delta N_\nu = N_p f(\mathbf{a}_\nu)\Delta\Omega_\nu \,;\, \nu = 1, 2, \cdots, s, \tag{24}$$

whereby, of course,

$$\sum_1^s \Delta N_\nu = N_p \sum_\nu f(\mathbf{a}_\nu)\Delta\Omega_\nu = N_p. \tag{24a}$$

With this notation, EQUATION 21 is generalized as follows:

$$\begin{aligned}\log B_p = \sum_\nu \Delta N_\nu(1 + \log (V\Delta\Omega_\nu/4\pi\Delta N_\nu)) \\ + \frac{1}{2V}\sum_{\nu,\nu'} \beta_1(\mathbf{a}_\nu, \mathbf{a}_{\nu'})\Delta N_\nu N_{\nu'} \\ + \frac{1}{3V^2}\sum_{\nu,\nu',\nu''} \beta_2(\mathbf{a}_\nu, \mathbf{a}_{\nu'}, \mathbf{a}_{\nu''})\Delta N_\nu \Delta N_{\nu'} \Delta N_{\nu''} + \cdots.\end{aligned} \tag{25}$$

Here, the cluster integrals of EQUATION 20 are computed for fixed orientations $\mathbf{a}_1, \mathbf{a}_2$, viz. $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, of the particles involved. Replacing the sums by integrals in terms of the distribution-function $f(\mathbf{a})$, the integral of which is now normalized:

$$\int f(\mathbf{a})\, d\Omega(\mathbf{a}) = 1, \tag{26}$$

we may write EQUATION 23 in the form

$$\begin{aligned}\log B_p = N_p\Big\{1 + \log (V/N_p) - \int f(\mathbf{a}) \log (4\pi f(\mathbf{a}))\, d\Omega(\mathbf{a}) \\ + (N_p/2V) \iint \beta_1(\mathbf{a}, \mathbf{a}')f(\mathbf{a})f(\mathbf{a}')\, d\Omega\, d\Omega' \\ + (N_p^2/3V^2) \iiint \beta_2(\mathbf{a}, \mathbf{a}', \mathbf{a}'')f(\mathbf{a})f(\mathbf{a}')f(\mathbf{a}'')\, d\Omega\, d\Omega'\, d\Omega'' + \cdots\Big\}.\end{aligned} \tag{27}$$

The Cluster Integrals. When the forces are repulsive at all distances, we have $w \geqq 0$ everywhere, whence the functions Φ_{ij}, defined by EQUATION 19, satisfy the inequalities

$$-1 \leqq \Phi_{ij} \leqq 0 \tag{28}$$

everywhere. In this case, the first two cluster integrals β_1 and β_2, defined by EQUATION 21, are necessarily negative, because the integrands are formed from one and three negative factors, respectively. The former has a particularly simple geometrical meaning in the ideal case of "hard" particles, which repel each other at contact but do not interact otherwise. In this case, we have

$$\begin{aligned} &w_{ij} = +\infty; \quad \Phi_{ij} = -1; \quad \text{(particles intersecting)} \\ &w_{ij} = 0; \quad \Phi_{ij} = 0; \text{otherwise} \end{aligned}$$

and $(-\beta_1)$ then equals the volume which is denied to particle j by the condition that it must not intersect particle i. For a pair of spheres of radius r, the excluded volume is obviously a sphere of radius $2r$. This leads to the familiar result first derived by Boltzmann, that the van der Waal's "covolume" (per particle) equals four times the volume of one spherical particle

$$b = -\tfrac{1}{2}\beta_1 = 4(4\pi r^3/3) = 4v_p$$

The analogous problem for two cylinders of lengths of l_1, l_2 and diameters d_1, d_2 is solved in the Appendix; we reproduce here the result (from A 11)

$$\begin{aligned} -\beta_1(\gamma) &= (\pi/4)d_1\, d_2(d_1 + d_2) \sin \gamma \\ &+ (\pi/4)(l_1\, d_1^2 + l_2\, d_2^2) + (\pi/4)(l_1\, d_2^2 + l_2\, d_1^2) \mid \cos \gamma \mid \\ &+ (l_1 + l_2)d_1\, d_2 E(\sin \gamma) + l_1 l_2(d_1 + d_2) \sin \gamma, \end{aligned} \tag{30}$$

where $E(\sin\gamma)$ denotes the complete elliptic integral of the second kind

$$E\,(\sin \gamma) = \int_0^{\pi/2} (1 - \sin^2 \gamma \sin^2 \phi)^{1/2}\, d\phi. \tag{30a}$$

For special orientations or dimensions, the formula simplifies more or less. The following cases are instructive:

$$\gamma = 0: \quad -\beta_1 = (\pi/4)(l_1 + l_2)(d_1 + d_2)^2 \tag{31a}$$

$$\gamma = 0: \quad l_1 = l_2 = l; \quad d_1 = d_2 = d: \quad 8(\pi/4)l\, d^2 \tag{b}$$

$$\gamma = \pi/2: \; l_1 l_2(d_1 + d_2) + (l_1 + l_2 + d_1 + d_2)d_1\, d_2 + (\pi/4)\,(l_1\, d_1^2 + l_2\, d_2^2)$$

$$l_1 = l_2; \quad d_1 = d_2: \tag{c}$$

$$(2\, l^2 d + (\pi/2)d^3) \sin \gamma + \{(\pi/2)(1 + \mid \cos \gamma \mid) + 2\, E(\sin \gamma)\} l\, d^2, \tag{d}$$

$$l_1 = l_2 = 0: \quad (\pi/4)d_1\, d_2(d_1 + d_2) \sin \gamma \tag{e}$$

$$l_1 = d_2 = 0: \quad (\pi/4)l_2\, d_1^2 \mid \cos \gamma \mid \tag{f}$$

$$l_2 = d_2 = 0: \quad (\pi/4)l_1\, d_1^2 \tag{g}$$

$$l_1 \gg d_1 + d_2 \ll l_2: \quad l_1 l_2(d_1 + d_2) \sin \gamma. \tag{h}$$

Case (b) yields 8 times the volume of one particle, as for spheres. This is generally true for centrosymmetrical convex particles in parallel orientation. Most of the others explain themselves. We call attention to the idealized cases (e) and (f), where the particles have a mutual covolume although neither has any volume, and to the case (h), which shows that the ratio (covolume/volume) for long needles is (length/diameter) rather than (4/1).

The theory of isotropic solutions involves a simple average of EQUATION 30 over all directions in space:

$$
\begin{aligned}
&-\bar{\beta}_1(l_1\,,\, d_1;\, l_2,\, d_2)\\
&= 2b = -\int \beta_1(\gamma_{12})\, d\Omega_2/4\pi\\
&= -\frac{1}{2}\int \beta_1(\gamma)\,\sin\gamma\, d\gamma\\
&= (\pi/4)^2 d_1\, d_2(d_1 + d_2) + (\pi/4)(l_1\, d_1^2 + l_2\, d_2^2)\\
&+ (\pi/8)(l_1\, d_2^2 + l_2\, d_1^2) + (\pi^2/8)(l_1 + l_2) d_1\, d_2\\
&+ (\pi/4) l_1 l_2 (d_1 + d_2). \qquad (32)
\end{aligned}
$$

For details of the integration, we again refer to the Appendix (A 14). For particles of equal diameters $d_1 = d_2 = d$, EQUATION 32 simplifies

$$
\begin{aligned}
-\bar{\beta}_1(l_1\,;\, l_2) &= 2b_{12} = \tfrac{1}{2}\,\pi d\{l_1 l_2 + \tfrac{1}{4}(\pi + 3)(l_1 + l_2)\, d + \tfrac{1}{4}\pi\, d^2\} \qquad (33)\\
&= 1.5708\, d(l_1 l_2 + 1.5354(l_1 + l_2)\, d + 0.7854\, d^2),
\end{aligned}
$$

and, when the lengths as well as the diameters are equal, it simplifies still a little further

$$
-\,\bar{\beta}_1 = \tfrac{1}{2}\pi d(l^2 + \tfrac{1}{2}(\pi + 3) l\, d + \tfrac{1}{4}\pi\, d^2). \qquad (34)
$$

It is interesting to examine the ratio of covolume to volume as a function of the ratio (l/d) according to EQUATION 34. The ratio

$$
-\bar{\beta}_1/2(\pi/4)\, d^2 l = b/(\pi/4)\, d^2 l = b/v_p
$$

becomes in various limiting cases

$$
\begin{aligned}
&b/v_p \sim l/d;\ (l \gg d)\\
&b/v_p = \text{minimum} = \pi^{1/2} + \tfrac{1}{2}(\pi + 3) = 4.843; \qquad (l = (\pi/4)^{1/2}\, d)\\
&b/v_p \sim (\pi/4)\, d/l; \qquad (l \ll d).
\end{aligned}
$$

When the dimensions are about equal the ratio is not much more than 4, but for highly anisometric particles, whether needles or pancakes, (b/v_p) is about equal to the ratio of the long to the short dimension.

While the evaluation of the first cluster integral β_1 defined by EQUATION 20 proved perfectly feasible, the integral β_2 depends on three directions, and to compute it exactly would be an extremely tedious task at best. For that reason we shall be content to estimate the order of magnitude of β_2.

The value for spheres of equal diameters was computed by Boltzmann; in that case, one finds

$$-\beta_2 = (15/64)\beta_1^2.$$

This result gives us the right order of magnitude of the ratio (β_2/β_1) for isometric particles in general. Where anisometric particles are concerned, we must distinguish between slender rods and thin plates. For the latter case, a little experimentation with various orientations will show that in most cases where two plates intersect each other, the volume within which a third plate of comparable diameter will intersect the other two simultaneously will be a sizable fraction of the volume within which it will intersect a given one of the others. Accordingly, barring special orientations, we have the result

$$\beta_2/\beta_1 = O(-\beta_1); \text{ (spheres, cubes, plates).} \tag{35}$$

For the slender rods, we obtain the same result only if the three rods are nearly coplanar, whereby the admissible deviation in angle is of the order (d/l). Otherwise, it is easily seen that if we look at a pair of interesting rods along the direction of a third, the projection of their intersection upon the plane normal to the axis of the third rod will be (at most):

$$d_1d_2/\sin\phi_3,$$

where ϕ_3 is the angle between the projections of two rods, alias the angle between the planes containing the pairs of directions $(\mathbf{a}_1, \mathbf{a}_3)$ and $(\mathbf{a}_2, \mathbf{a}_3)$, respectively. Or, considering the spherical triangle whose corners have the directions $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, ϕ_3 is the angle at the third corner. If we denote the three sides of this triangle (angles between the directions pairwise) by γ_{12}, γ_{23} and γ_{31}, we arrive at the following estimate for the second cluster integral:

$$-\beta_2 = (d_1 + d_2)(d_2 + d_3)(d_3 + d_1)\{O(l^2d) + l_1l_2l_3(\sin\gamma_{12}/\sin\phi_3)\}; \quad (\phi_3 > d/l). \tag{36}$$

By the theorem of sine proportions, valid for spherical triangles, the quotient of the two sines is a symmetrical function of the three directions. The angle ϕ_3 vanishes (or equals π) whenever the three directions $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ are coplanar, whereby $\mathbf{a}_1$ and $\mathbf{a}_2$ are normally not parallel. For such directions, the estimate (36) becomes infinite; as we have mentioned above, the estimate (35) is then valid instead.

In computing the average of β_2 over all combinations of directions $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ we find that the combinations of directions which are coplanar within an angle $\pm\phi_m$ do form a fraction of the order ϕ_m of the total. Thus, when we integrate EQUATION 36 over all other orientations the average of the sine ratio will be of the order

$$-\log \phi_m + \text{const.}$$

When we put $\phi_m = d/l$ and substitute the estimate (35) for coplanar orientation, the added term does not change the order of magnitude, and we still obtain

$$-\bar{\beta}_2 = O(d^3l^3(\log (l/d) + \text{const})). \tag{37}$$

No concerted effort has been made to render this estimate more definite. As it is, the result

$$\bar{\beta}_2/(\bar{\beta}_1)^2 = O((d/l) \log (l/d)) \tag{38}$$

will offer some justification for the procedure which we shall, perforce, adopt in the following, where order corrections which depend on β_2 and higher cluster integrals will be neglected altogether. If we talk about "concentrated" solutions whenever $\beta_1 N/V$ is of the order unity or greater, then we may hope that our results will describe fairly concentrated *isotropic* solutions of rod-shaped particles reasonably well. The results for anisotropic solutions will be somewhat doubtful in all cases, and more so the more concentrated the solutions. Where plate-like particles are concerned, our approximations will introduce more serious errors, and we can hardly hope for more than that our result will describe concentrated solutions of such particles qualitatively rather than quantitatively.

We shall inquire, next, about the effects due to the finite range of the electrostatic repulsion between the particles.

We have mentioned before that the force (per unit area) between two parallel plates varies exponentially with the distance, and that the law of force for a different geometry is only modified by the effects due to divergence of the electric force-lines. The data needed for an exact prediction of the forces are not available, and even if we had them it would be a difficult and laborious task to compute the forces. But fortunately the resulting uncertainty will not, as a rule, count for much in the computation of the cluster integrals. Only the cases where very few cations or very few anions are present (or very few of either sign) might well require careful separate analysis. The most important modification of our previous results (EQUATIONS 30 and 31 a–h) will occur for long rods (EQUATION 31 h), in which case the effect of the electrostatic repulsion will be equivalent to an increase of the effective *diameter*. A similar increase of the effective *length* will cause a relatively insignificant increase of the covolume, unless the concentration of electrolyte is so low that κl is of the order unity, in which case, the problem of the repulsive forces must be reconsidered as a whole.

For the law of force between two cylindrical particles of the same diameter $d_1 = d_2 = d$, whose mantles are separated by a distance x, we now assume

$$w/kT = A(\gamma)e^{-\kappa x} \tag{39}$$

(of EQUATION 14 and pertinent discussion). More precisely, we assume that w has the value given by EQUATION 39 whenever the two cylinders cross, in the sense that the projections of their axes upon the plane parallel to both intersect. Such configurations yield the leading term

$$(d_1 + d_2)l_1l_2 \sin \gamma = 2dl_1l_2 \sin \gamma$$

of the excluded volume for long cylinders (the central parallelopiped of the solid figure illustrated in FIGURE 7, and compare EQUATION 30). The first cluster integral β_1 is defined by EQUATIONS 18 and 20. Assuming $w = w(x)$ as given by EQUATION 39 for all "crossed" configurations, the part of β_1 due to such configurations is simply

$$\beta_1 \text{ (crossing)} = 2l_1 l_2 \left\{ -d + \int_0^\infty (e^{-w(x)/kT} - 1)\, dx \right\} \sin \gamma. \tag{40}$$

The consequent correction to the effective diameter, assuming EQUATION 39, is accordingly

$$\begin{aligned} \int_0^\infty (1 - e^{-Ae^{-\kappa x}})\, dx &= \int_0^A (1 - e^{-u})\, du/\kappa u \\ &= \kappa^{-1}\left(\log A + C + \int_A^\infty e^{-u}\, du/u\right). \end{aligned} \tag{41}$$

Here C denotes Euler's constant

$$\int_0^1 (1 - e^{-u}) \frac{du}{u} - \int_1^\infty e^{-u} \frac{du}{u} = C = -\Gamma'(1) = 0.5772 \cdots. \tag{41a}$$

For reasonably large values of A the exponential integral in EQUATION 41 may be neglected, and we get simply

$$\begin{aligned} -\beta_1(\text{crossing}) &= 2l_1l_2\, d_{\text{eff}}(\gamma) \sin \gamma \\ &= 2l_1l_2\{d + \kappa^{-1}(C + \log A(\gamma))\} \sin \gamma. \end{aligned} \tag{42}$$

Thus, the effective diameter equals the actual diameter increased by the distance δ at which the condition

$$w(\delta) = kTe^{-C} = 0.561\, kT \tag{43}$$

is satisfied.

In deriving this important rule, we have made certain physical assumptions and mathematical approximations; but, as long as κd is reasonably small (less than unity), the errors thus incurred ought to be very modest and EQUATION 42 should describe a good estimate. Moreover, the result is rather insensitive to modifications of the geometry, so that the required modifications of the first four terms of EQUATION 30 may be estimated in a similar manner. We shall be content to observe that the increments of the effective lengths and diameters are of the same order of magnitude for all terms. This observation together with EQUATIONS A 14 and A 15 should be helpful in case an estimate of the end-corrections for long rods (which we shall neglect in the following) should be desired.

In EQUATION 42 we have indicated that the force constant A is expected to vary with the angle of intersection γ. A precise specification of that variation is contained in our EQUATION 13, and, in spite of the several approximations involved in the derivation, the relation

$$A(\gamma) = A(\pi/2)/\sin\gamma \tag{44}$$

ought to be very nearly true, with the one exception that, for small angles $\gamma < d/l_{12}$ the factor $1/\sin\gamma$ must be replaced by a smaller number of the order l_{12}/d, where l_{12} denotes the length of the overlap between the two cylinders.

If we disregard the exception just mentioned and neglect terms which represent end-wise approach of the particles, (corresponding to the first four terms in EQUATION 30), we may write EQUATION 42 in the form

$$\begin{aligned} -\beta_1(\gamma) = 2l_1l_2\{[d + \kappa^{-1}C + \kappa^{-1}\log A(\pi/2)]\sin\gamma \\ - \kappa^{-1}(\sin\gamma)\log(\sin\gamma)\}. \end{aligned} \tag{45}$$

The average of the excluded volume over all orientations equals

$$\begin{aligned} -\bar{\beta}_1 = 2b_{12} = -\int \beta_1(\gamma)\,d\Omega/4\pi = -\frac{1}{\pi}\int_0^\pi \beta_1(\gamma)\sin\gamma\,d\gamma \\ = (\pi/2)l_1l_2(d + \bar{\delta}), \end{aligned} \tag{46}$$

with

$$\bar{\delta} = \kappa^{-1}[C + \log A(\pi/2) + \log 2 - \tfrac{1}{2}] = \kappa^{-1}[0.7704 + \log A(\pi/2)]. \tag{47}$$

The integral

$$\int_0^\pi \log(\sin\gamma)\sin^2\gamma\,d\gamma,$$

which enters into the computation, might seem difficult, but it is easily computed from the Fourier series

$$-\log|2\sin\gamma| = \cos 2\gamma + \tfrac{1}{2}\cos 4\gamma + \tfrac{1}{3}\cos 6\gamma + \cdots.$$

Concerning the absolute value of the force-constant A, we refer back to EQUATION 14 with attendant discussion and references.

Our results (33) and (46) for straight rods should apply without change to bent rods and *flexible chains* as long as they are not so tightly coiled that multiple contacts between pairs of different chains will be common. The statistics of such multiple contacts has not been investigated. In addition, it stands to reason that, when the particles are so slender as to be very flexible, the effective range of the electrostatic repulsion will constitute the main part of their effective diameters.

We shall deal summarily with the case of thin, plate-shaped particles. According to EQUATION 30, the mutual excluded volume for a pair of such particles is practically independent of their thickness, barring only nearly parallel orientations of the particles. Then, if only

$$\kappa d \gg 1, \tag{48}$$

which condition excludes very low concentrations of electrolyte at the most, an increase of the effective diameter by a distance δ, determined according to EQUATION 43, will make very little difference. For the case of very low electrolyte concentration, the question of the forces would seem to require a more careful analysis than we have available at present.

Thermodynamic Properties of Isotropic Solutions. We shall be generally content with the first order corrections to the laws of ideal solutions. Accordingly, we abbreviate the expansion (21) as follows

$$\begin{aligned} \log B_p &= N_p(1 + \log (V/N_p) + \tfrac{1}{2}\beta_1(N_p/V)) \\ &= N_p(1 + \log (V/N_p) - b(N_p/V)), \end{aligned} \tag{48}$$

whereby, for a monodisperse solution of rod-shaped particles of length l and diameter d according to EQUATION 46

$$b = (\pi/4)l^2(d + \bar{\delta}), \tag{49}$$

including a correction δ for the "padding" due to an ionic double layer. For a solution of plate-shaped particles EQUATION 48 is also valid over a more limited range of concentrations with the different value

$$b = (\pi/4)^2\, d^3 \tag{50}$$

for the covolume, as given by EQUATION 34 when specialized to the case $l = 0$.

The variation of the free energy with the particle concentration can be obtained by substituting the result (48) in EQUATION 5. We are particularly interested in the derived quantities. We obtain from EQUATIONS 6 and 7, respectively,

$$P = kT\{(N_p/V) + b(N_p/V)^2\} \tag{51}$$

for the osmotic pressure and

$$\mu_p = \mu_p^0 + kT\{\log (N_p/V) + 2b(N_p/V)\} \tag{52}$$

for the chemical potential. These correspond to well-known formulas in the theory of gases; the salient point of the present theory is that the covolumes may be much greater than the actual volumes of the particles. We also get reasonably simple results for a polydisperse solution which contains rod-shaped particles of various lengths $l_1, \cdots, l_s, \cdots$, but of identical diameters $d_1 = \cdots = d_s = \cdots = d$, and otherwise sufficiently similar, so that the effective diameter for any pair of particles is always $d + \bar{\delta}$. For this purpose, we substitute the covolumes given by EQUATION 46 in the more general formula (22), which yields

$$\begin{aligned} \log B_p &= \sum_s N_s(1 + \log (V/N_s)) - (\pi(d + \bar{\delta})/4V) \sum_{s,s'} N_s N_{s'} l_s l_{s'} \\ &= \sum_s N_s(1 + \log (V/N_s)) - (\pi/4)(d + \bar{\delta})(L^2/V), \end{aligned} \tag{53}$$

for the configuration integral, with the abbreviation

$$L = \sum_s N_s l_s \tag{54}$$

for the *sum of the lengths of all particles present.* The osmotic pressure is accordingly

$$P = kT \left\{ \sum_s (N_s/V) + (\pi/4)(d + \bar{\delta})(L/V)^2 \right\}, \tag{55}$$

and we get

$$\mu_s = \mu_s^0 + kT \log (N_s/V) + 2kT(\pi/4)(d + \bar{\delta})(L/V)l_s \tag{56}$$

for the chemical potential of the particles of length l_s.

The corresponding formulas for a polydisperse solution of circular plate-shaped particles are almost equally simple. We specialize EQUATION 32 to the case $l_1 = l_2 = 0$:

$$-\bar{\beta}_1(0, d_1; 0, d_2) = 2b = (\pi/4)^2 d_1 d_2 (d_1 + d_2);$$

then, with the abbreviations

$$\begin{aligned} D &= \sum N_s d_s \\ A &= (\pi/4) \sum N_s d_s^2 \end{aligned} \tag{57}$$

for the sums of all the diameters viz. areas of all particles present, we obtain

$$\log B_p = \sum_s N_s(1 + \log (V/N_s)) - (\pi/4)(DA/V) \tag{58}$$

$$P = kT \left\{ \sum_s (N_s/V) + (\pi/4)(DA/V^2) \right\} \tag{59}$$

$$\mu_s = \mu_s^0 + kT \log (N_s/V) + kT[Ad_s + D(\pi/4)\, d_s^2](\pi/4V). \tag{60}$$

These results for plates might well have qualitative rather than quantitative significance. While certain colloids (bentonite) are known to consist of sheet-like particles, it is not known whether the outlines of the sheets are regular curves or polygons that might be reasonably approximated by circular disks. Nevertheless, it seems worth pointing out, that for a given total area of the particles, both terms in the formula (59) for the osmotic pressure do increase as the degree of dispersion increases. (When all particles are cut into quarters the sum of the diameters is doubled and the total number of particles is increased by a factor of four.)

Returning to our result (55) for the osmotic pressure of *rod-shaped* particles, we note that the absolute value of the second term, which represents the deviation from the value appropriate to ideal solutions, is quite *independent of the subdivision into individual lengths.* (On the other hand, a lengthwise splitting of the particles, if possible, will increase both terms in EQUATION 55.) On this basis, we should be prepared to find that the osmotic pressures of *flexible* chain-like particles in concentrated solutions may be practically independent of the subdivision of the chains. For rigid rod-shaped particles, we do not anticipate this phenomenon (in the isotropic phase, anyway), because, as we shall show next, such solutions will form an anisotropic phase as soon as the ratio (total covolume/volume) exceeds a certain critical value.

Anisotropic Solutions. We shall investigate the possibility that a solution of rod-shaped particles may form a nematic *liquid crystal* in which the distribution of orientations of the particles is anisotropic, while the distribution of the particles in space is homogeneous, and does not exhibit the periodic variation of density which characterizes solid crystals (periodicity in three dimensions) and *smectic* liquid crystals (periodicity in one dimension). We shall show that the concentration of particles need not be so very large (in terms of actual volume occupied) before the isotropic solution becomes unstable, relative to an anisotropic phase of the nematic type. Whether the latter will be stable, relative to other types of anisotropic phases, is a question which involves much more difficult computations, and we shall not try to settle it.

We introduce a distribution-function $f(\mathbf{a})$ for the directions $\mathbf{a}$ of the axes of the cylindrical particles, normalized according to EQUATION 26. When we neglect the terms which depend on β_2 and higher cluster integrals in the expansion given by EQUATION 27, we arrive at the following formula for the configuration-integral

$$\log B_p = N_p\{1 + \log (V/N_p)\} - \int f(\mathbf{a}) \log 4\pi f(\mathbf{a})\, d\Omega(\mathbf{a}) \\ + (N_p/2V) \int \beta_1 (\cos^{-1} (\mathbf{a}\cdot\mathbf{a}'))f(\mathbf{a})f(\mathbf{a}')\, d\Omega\, d\Omega'. \tag{61}$$

The function $f(\mathbf{a})$ is implicitly determined by the condition

$$B_p = \text{maximum}, \tag{62}$$

(subject to the restriction (26)).

We shall introduce convenient abbreviations for the two functionals which enter into EQUATION 61:

$$\sigma(f) = \int f(\mathbf{a}) \log 4\pi f(\mathbf{a})\, d\Omega(\mathbf{a}), \tag{63}$$

$$-2b\rho(f) = \bar{\beta}_1 \rho(f) = \int \beta_1 (\cos^{-1} (\mathbf{a}\cdot\mathbf{a}'))f(\mathbf{a})f(\mathbf{a}')\, d\Omega\, d\Omega'; \tag{64}$$

where, in conformity with EQUATION 46, we understand:

$$-2b = \bar{\beta}_1 = \int_0^{\pi/2} \beta_1(\gamma) \sin \gamma\, d\gamma. \tag{64a}$$

In addition, we shall denote the concentration of particles by

$$c = (N_p/V). \tag{65}$$

In this shorthand, the condition (62) becomes

$$\sigma(f) + bc\rho(f) = \text{minimum}, \tag{66}$$

wherein f is subject to the restriction

$$\int f\, d\Omega = 1. \tag{26}$$

The value of the minimum required by the condition (66) determines the free energy of the system according to EQUATIONS 5 and 61:

$$\begin{aligned} F(\text{solution}) - F(\text{solvent}) &= N_p\mu_p^0 - kT \log B_p \\ &= N_p\mu_p^0 + N_p kT\{\log c - 1 + \sigma(f) + bc\rho(f)\}. \end{aligned} \tag{67}$$

We may apply Lagrange's method to the problem (66), thus

$$\delta\sigma(f) + bc\delta\rho(f) - \lambda\delta \int f\, d\Omega = 0. \tag{68}$$

The usual manipulations lead to the non-linear integral equation

$$\log (4\pi f(\mathbf{a})) = \lambda - 1 + c \int \beta_1(\mathbf{a}, \mathbf{a}')f(\mathbf{a}')\, d\Omega'. \tag{69}$$

EQUATION 69 is satisfied by every function which renders the functional of the problem (66) stationary; the true solution of (66) is included among these. The constant function

$$f = f_0 = 1/4\pi, \tag{70a}$$

which describes the isotropic distribution, is always a solution of EQUATION 69, with

$$\sigma(f_0) = 0; \qquad \rho(f_0) = 1; \qquad \lambda = 1 + 2bc \tag{70b}$$

On the other hand, in order to show that for sufficiently large values of c the solution (70) will not be the true solution of the problem (66), we only have to find some function f_1 such that $\sigma(f_1)$ is finite and $\rho(f_1) < 1$; then, when we take c large enough, the inequality

$$\sigma(f_1) + bc\rho(f_1) < \sigma(f_0) + bc\rho(f_0) = bc$$

can certainly be satisfied.

According to our previous considerations, the function $-\beta_1(\gamma)$ is an increasing function of $(\sin \gamma)$, so that a trial function f_1 with the required properties can be constructed very simply as follows: We choose an angle γ_1 such that

$$-\beta_1(\gamma) < -\bar{\beta}_1; \qquad \gamma < 2\gamma_1,$$

a preferred direction $\mathbf{a}_0$ and the following trial function

$$f_1(\mathbf{a}) = 0; \qquad |(\mathbf{a}_0 \cdot \mathbf{a})| < \cos \gamma_1$$

$$f_1(a) = 1/4\pi(1 - \cos \gamma_1); \qquad \cos \gamma_1 < |(\mathbf{a}_0 \cdot \mathbf{a})| < 1.$$

Some of the unwanted solutions of EQUATION 69—possibly all of them—may by interpreted as solutions of a modified variation problem:

$$\left.\begin{aligned} \int f\, d\Omega &= 1 \\ \sigma(f) &= \sigma_1 \geqq 0 \end{aligned}\right\} \text{prescribed}$$

$$\rho(f) = \text{minimum} = \rho_m(\sigma_1). \tag{71}$$

This leads again to EQUATION 68 with the difference that c is interpreted as a Lagrange multiplier on par with λ.

The second restriction in the problem (71) is in effect no different than the inequality

$$\sigma(f) \lesseqgtr \sigma_1, \tag{71a}$$

because the function $\beta(\gamma)$ in EQUATION 64 is continuous (less would suffice). In consequence, if we know one function $f(\mathbf{a})$, which realizes a certain value of ρ, we can always find another which realizes very nearly the same value of ρ, but gives us a *greater* value of σ. All we have to do is introduce a very rapid local fluctuation of $f(\mathbf{a})$. This reasoning leads to the inequality

$$(\rho_m(\sigma_2) - \rho_m(\sigma_1))/(\sigma_2 - \sigma_1) \leqq 0; \tag{71b}$$

in words: the minimum of ρ is a never-increasing function of σ.

One way to solve the problem (66), at least in principle, is to solve the more general problem (71) first for all values of σ. For greater flexibility, we may describe the resulting relation between ρ_m and σ in parameter form

$$\sigma = \sigma(\alpha); \qquad \rho_m = \rho(\alpha); \tag{72a}$$

then the solution of EQUATION 66 must satisfy the condition

$$\sigma'(\alpha) + bc\rho'(\alpha) = 0, \tag{72b}$$

and, in order that the state thus described be stable

$$\sigma''(\alpha) + bc\rho''(\alpha) > 0. \tag{72c}$$

According to these results, if the function

$$(-d\rho_m/d\sigma) = -\rho_m'(\sigma) \tag{73}$$

is a steadily decreasing function of σ, then the transition from the isotropic to the anisotropic phase will be continuous and take place at the concentration given by the condition

$$1 + bc(d\rho_m/d\sigma)_{\sigma=0} = 0. \tag{74}$$

On the other hand, if the function (73) increases for small values of σ, reaches a maximum (as it must because $\rho > 0$), and decreases thereafter, then the isotropic solution will become unstable towards finite disturbances at some concentration lower than that required by EQUATION 74. In this case, the anisotropic phase will always possess a finite degree of anisotropy. Moreover, there will be a pair of concentrations for which the two phases can coexist; a solution of concentration intermediate between these will separate into two phases.

It is possible to show by rather general qualitative reasoning that the second alternative—a discontinuous transition—must be realized when an anisotropic solution is formed. We may as well assume that the anisotropic phase has cylindrical symmetry around some preferred direction $\mathbf{a}_0$; this restriction is unimportant, because it allows the distribution-function to contain spherical harmonics of all (even) orders. The odd orders are excluded if we assume that the solution is not polar in the crystallographic sense (seignette-electric):

$$f(\mathbf{a}) = f(-\mathbf{a}).$$

Under these assumptions, $f(\mathbf{a})$ may be developed in a series of even Legendre polynomials

$$4\pi f(\mathbf{a}) = 1 + 5A_2P_2(\mathbf{a}\cdot\mathbf{a}_0) + 9A_4P_4(\mathbf{a}\cdot\mathbf{a}_0) + \cdots \tag{75}$$

Moreover, since the homogeneous quadratic functional defined by EQUATION 64 is invariant against all rotations of the frame of reference, the Legendre polynomials are its eigenfunctions and an expansion of the type

$$\rho(f) = 1 - B_2A_2^2 - B_4A_4^2 - \cdots \tag{76}$$

is valid. Only even powers of $A_2, A_4, \cdots$, (in fact, only the second powers), occur in EQUATION 76. However, when we substitute the expansion (75) in EQUATION 73, we get

$$\begin{aligned}\sigma(f) = {} & (5/2)A_2^2 + (9/2)A_4^2 + \cdots \\ & - (25/21)A_2^3 - (45/7)A_2^2A_4 - \cdots \\ & + (125/28)A_2^4 + \cdots\end{aligned} \tag{77}$$

Linear terms do not occur in this expansion either, but *every cubic term is present.* The critical condition defined by EQUATION 74 is fulfilled by the smallest value (c_0) of c, which causes any one of the coefficients in the expansion

$$((5/2) - B_2bc)A_2^2 + ((9/2) - B_4bc)A_4^2 + \cdots$$

to vanish. It does not matter which one vanishes first; for the sake of argument let us assume that it is the coefficient of A_2^2. Then, if we take

$$f(\mathbf{a}) = 1 + A_2P_2(\mathbf{a}\cdot\mathbf{a}_0)$$

we have the expansion (convergent for $|A_2| < 1$):

$$\sigma(f) + bc_0\rho(f) = bc_0 - (25/21)A_2^3 + (125/28)A_2^4 + \cdots$$

For finite, not too large, positive values of A_2, the sum of this expansion certainly takes values smaller than bc_0. This means that the isotropic solution becomes unstable towards finite disturbances at some concentration lower than that required by EQUATION 74 for a continuous transition, so that a *discontinuous transition* must take place at some lower concentration.

We shall try next, to get some idea about the distribution of orientations of the particles in the anisotropic solutions, and to estimate the thermodynamic functions for these solutions. The variation problem (66) is best attacked directly: the technique is to construct plausible trial functions with as many variable parameters as one can handle conveniently; the parameters are then adjusted so as to approach the required minimum as closely as possible.

As regards the general nature of the distribution, we note that $-\beta_1(\mathbf{a}, \mathbf{a}')$ has a minimum when the directions $(\mathbf{a}, \mathbf{a}')$ are parallel and a maximum when they are perpendicular. The smallest possible value of $\rho(f)$ is, therefore, attained when all particles have exactly the same orientation; according to our somewhat approximate formula (45), the function $\rho(f)$ then vanishes. For this singular distribution, however, $\sigma(f)$ becomes infinite. As a compromise, we have to expect a distribution which is more or less concentrated around a preferred direction $\mathbf{a}_0$, with this direction as an axis of symmetry. EQUATION 69 indicates, in a general way, how the density will decrease with the angle

$$\Theta = \cos^{-1}(\mathbf{a}\cdot\mathbf{a}_0) \quad ; \qquad (78)$$

for large angles an exponential function of $(\sin\Theta)$ is thus indicated. A trial function of the type

$$\text{constant} \times (\cosh(\alpha\sin\Theta))^{-n} \qquad (79)$$

would therefore seem promising, and tentative computations for $n = 3$ gave encouraging results, but this lead was abandoned on account of the effort involved. The simpler function

$$f(\mathbf{a}) = (\alpha/4\pi \sinh \alpha) \cosh (\alpha(\mathbf{a}\cdot\mathbf{a}_0)) = (\alpha/4\pi \sinh \alpha) \cosh (\alpha \cos \Theta) \quad (80)$$

decreases rather too rapidly for large angles, and it contains but one parameter. It was, nevertheless, adopted as the best tractable function. Even so, according to EQUATION 67, the function to be minimized for the problem (66) is the *free energy* itself, so that our results for this important thermodynamic function ought not to be very much in error.

Further, to simplify the computations, we shall allow the approximate description

$$-\beta_1(\gamma) \sim 2l_1l_2(d + \bar{\delta}) \sin \gamma = (8/\pi)b \sin \gamma \quad (81)$$

of the more complicated function given by EQUATION 45. When EQUATIONS 80 and 81 are substituted in EQUATION 64, the resulting integral can be evaluated in terms of elementary functions, together with a Bessel function of order 2, and imaginary argument. For the definition (B 18) and properties of this function, and for the details of the integration, we refer to the Appendix, Section 2. We quote here the result for a monodisperse solution

$$\rho(\alpha) = 2(\sinh \alpha)^{-2}I_2(2\alpha) \quad (82)$$

(cf. EQUATION B 17). The evaluation of the integral in EQUATION 63 for the function (80) is elementary and yields

$$\sigma(\alpha) = \log(\alpha \coth \alpha) - 1 + (\sinh \alpha)^{-1} \tan^{-1}(\sinh \alpha). \quad (83)$$

The power series

$$4\rho(\alpha) = 4 - (\alpha^4/90) + (2\alpha^6/945) - (71\alpha^8/226800) + \cdots; \quad (|\alpha| < \pi) \quad (84)$$

$$\sigma(\alpha) = (\alpha^4/90) - (2\alpha^6/810) + (108\alpha^8/226800) - \cdots; \quad (|\alpha| < \pi/2),$$

illustrate our consideration of continuous vs. discontinuous transition (when an expansion of the type (75) is constructed for the function (80), the coefficient of P_2 is of the order (α^2)). However, the values of α which correspond to stable anisotropic solutions are far outside the limits of convergence of the series (84). Fortunately, the required values of α are so large that the asymptotic representations

$$\sigma(\alpha) \sim \log \alpha - 1, \quad (85)$$

$$\rho(\alpha) \sim 4(\pi\alpha)^{-1/2}\{1 - 30(32\alpha)^{-1} + 210(32\alpha)^{-2} + 1260(32\alpha)^{-3} + \cdots\}, \quad (86)$$

(cf. B 20), are eminently suitable for computation. The condition (72b) for internal equilibrium becomes, after rearrangement,

$$(\pi\alpha)^{1/2} = 2\mathrm{bc}\{1 - 90(32\alpha)^{-1} + 1050(32\alpha)^{-2} + 8820(32\alpha)^{-3} + \cdots\}. \quad (87)$$

The asymptotic behavior of α for high concentrations is evident from the inverted series

$$\alpha \sim (4/\pi)\,(bc)^2 - (45/8) + O((bc)^{-2}). \tag{88}$$

As a measure of the spread in angle, we may compute the mean square of $\sin(\Theta/2)$, if we understand by Θ, (this time), the angle between the direction $\mathbf{a}$ of a particle and the nearer of the two directions $(+\mathbf{a}_0, -\mathbf{a}_0)$. With this convention, we have

$$\overline{(2\sin(\Theta/2))^2} = (2/\alpha)\coth\alpha \sim 1/\alpha. \tag{89}$$

The standard deviation of the angle Θ is, therefore, about proportional to $\alpha^{-1/2}$ or, if we disregard the higher terms in EQUATION 87, inversely proportional to the concentration:

$$\overline{(2\sin(\Theta/2))^2} \sim (\pi/4)\,(bc)^{-2} \tag{89a}$$

Combination of EQUATIONS 85, 86, and 87 yields for high concentrations

$$bc\rho \sim 2 + 75\pi(8bc)^{-2} + \cdots \tag{90}$$

$$\sigma \sim \log(4/\pi) - 1 + 2\log(bc) - 90\pi(8bc)^{-2} + \cdots. \tag{91}$$

The free energy is given by EQUATION 67; in view of EQUATION 72b we derive therefrom the following simple *general* formula for the *osmotic pressure*

$$P = -(\partial F/\partial V)_{N_p} = kTc(1 + bc\rho). \tag{92}$$

In particular, if we take EQUATION 90 seriously

$$P = kT\,c(3 + 75\pi(8bc)^{-2} + \cdots). \tag{93}$$

On this basis, the osmotic pressure should be just a little greater than three times the ideal pressure.

The simple results (89a) and (93), however, depend on a rather severe over-simplification of the physical picture. The approximation (81) for EQUATION 45 tends to overestimate the deviation of the angles for high concentrations. The several approximations and simplifications which enter into EQUATION 93 would tend to make this an underestimate, possibly a very bad one; it is barely conceivable that our neglect of the attractive van der Waal's (dispersion) forces might in some cases bring about a measure of compensation.

For the lowest concentrations at which the anisotropic solutions can exist, the approximations which lead to EQUATIONS 85 and 86 may still be quite tolerable. In those cases it is best to solve EQUATION 87 numerically, because the expansion is only semi-convergent and the inversion (88) aggravates its tendency to diverge. In constructing tables or graphs there is, of course, no need for the inversion; it is just as well to compute σ, ρ and c all as functions of the parameter α.

We still have to compute the conditions for equilibrium of the two liquid phases. The osmotic pressure of the anisotropic solution is given by EQUATION 92. The chemical potential is computed according to the definition (7) by differentiation of EQUATION 67, whence in view of EQUATIONS 65 and 72b:

$$\mu_p = (\partial F/\partial N_p)_V = \mu_p^0 + kT\{\log c + \sigma + 2bc\rho\}. \tag{94}$$

The equilibrium conditions (8) require that the functions given by (92) and (94) be equated with the corresponding functions (51) and (52) for the isotropic phase. The two concentrations c_a and c_i are thus determined by the two equations

$$c_a + bc_a^2\rho = c_i + bc_i^2$$
$$\log c_a + \sigma + 2bc_a\rho = \log c_i + 2bc_i,$$

which we may write in terms of the total covolumes as follows:

$$bc_a(1 + bc_a\rho) = bc_i(1 + bc_i)$$
$$\log(bc_a) + \sigma + 2bc_a\rho = \log(bc_i) + 2bc_i. \tag{95}$$

Here, σ and ρ are functions of (bc_a) described implicitly by EQUATIONS 85, 86, and 87. The following results were obtained by numerical solution of the system of equations:

$$\begin{aligned} \alpha &= 18.584 & bc_i &= 3.3399 \\ \rho &= 0.49740 & bc_a &= 4.4858 \\ \sigma &= 1.9223 & \rho bc_a &= 2.2313 \end{aligned} \tag{96}$$
$$c_a/c_i = 1.343.$$

The standard deviation of sin $(\Theta/2)$ given by EQUATION 89 corresponds to an angle $\Theta = 13.3°$.

It is a matter of interest to see how the expansions (88), (90), and (91) work out in the worst possible case. The values obtained from these formulae, as abbreviated, for the case $bc_a = 4.486$,

$$\alpha = 19.9; \qquad \rho bc_a = 2.184; \qquad \sigma = 2.021,$$

may be compared with the accurately computed values (96).

It would take us too far to develop a theory for the anisotropic phase of a polydisperse solution. The difficulty is that long rods will be more perfectly oriented than short rods, so that one has to compute a whole set of mutually dependent distribution-functions, one for each size of particles. Moreover, each composition of the anisotropic phase presents a separate problem of this type. Nevertheless, the mathematical analysis in the Appendix has been kept as general as was feasible, in order to facilitate computations for polydisperse systems.

It is possible to foresee that when two phases are formed, the longest particles will collect preferentially in the anisotropic phase, and that the total concentrations in each phase will vary with the ratio of the volumes.

Possibly, the best experimental tests of the present theory will consist in measurements of light scattering. As is well known, the light scattering per particle is inversely proportional to (dP/dc). However, when the longest dimensions of the particles are comparable to that of the measuring light, this simple relation applies only to *scattering at small angles.* We have, in effect, shown that the presence of one particle reduces the density of scattering matter up to a distance which equals the length of a presumptive neighbor, so that the *phase relations* of the light waves scattered from *different particles* must be considered in the interpretation of the large angle scattering.

On the basis of our results (92) and (51), the *anisotropic solution* ought to *scatter more light at small angles* than the isotropic phase in equilibrium with it. Predictions for large angles must await a mathematical analysis of the optical problems; the distribution of scattering matter around any one particle obviously depends on the degree of orientation of the particles.

Appendix

The Mutual Excluded Volume of Two Cylinders

We first compute the excluded volume $-\beta_1(0, d_1; 0, d_2)$ for two circular plates of vanishing thickness and diameters $d_1 = 2r_1; d_2 = 2r_2$. Besides, this is one of the interesting limiting cases.

Let the first plate be fixed with its center at the origin and let its normal form an angle γ with the y axis, in the (y, z) plane. We allow the second plate to move, but we keep its orientation constant, so that its normal is always parallel to the y axis. When we require that the two plates must not intersect, what is the volume inaccessible to the center of the second plate?

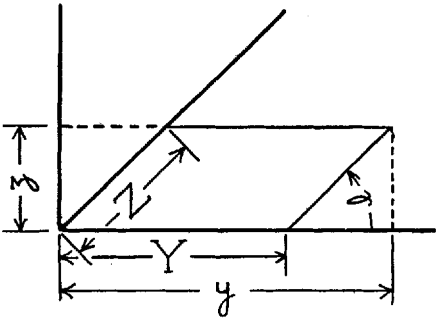

FIGURE 1.

Some of the analysis becomes a little simpler if we replace the coordinates (y, z) by the pair (Y, Z) referred to skew axes parallel to the plates 2, 1 respectively:

$$y = Y + Z\cos\gamma \qquad \text{(A 1)}$$
$$z = Z\sin\gamma$$

Then the intersection of the excluded region with the plane

$$z = Z\sin\gamma = \text{const.}$$

is bounded by the curve formed by the center of circle 2 as this circle rolls on a chord AB of the circle 1 (see FIGURE 2).

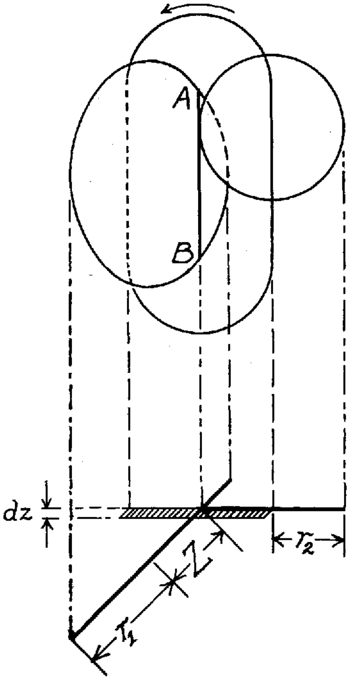

FIGURE 2.

The length of the chord equals

$$2(r_1^2 - Z^2)^{1/2}.$$

The area of the intersection is, evidently,

$$A(Z) = 4(r_1^2 - Z^2)^{1/2} r_2 + \pi r_2^2$$

(rectangle + two half circles), and the excluded volume is, accordingly,

$$\begin{aligned} -\beta_1(0, d_1; 0, d_2) &= \int A(Z)\, dz = \int A(Z)\, dZ \sin\gamma \\ &= 2\pi r_1 r_2 (r_1 + r_2) \sin\gamma \qquad \text{(A 2)} \\ &= (\pi/4)\, d_1\, d_2 (d_1 + d_2) \sin\gamma\,. \end{aligned}$$

The excluded region, illustrated in FIGURE 3, is bounded by four planes and by the fourth degree surface described by the equations

$$(r_1^2 - Z^2)^{1/2} + (r_2^2 - Y^2)^{1/2} = \pm\, x\,. \qquad \text{(A 3)}$$

(Here and in the following we always take positive roots). This surface joins the planes

$$\begin{aligned} Z &= \pm\, r_1 \\ Y &= \pm\, r_2 \qquad \text{(A 4)} \end{aligned}$$

along the circles

$$x^2 + Y^2 = r_2^2$$

$$x^2 + Z^2 = r_1^2,$$

respectively, in such a manner that the normal directions are continuous except at the points

$$x = 0, \qquad Y = r_1, \qquad Z = r_2$$

where two such circles touch one another.

A curve bounding the intersection of the excluded region with a plane $x = \text{const.}$ is described by EQUATION A 3 for $x = \text{const}$, or it consists of segments of curves described thus alternating with segments of the straight lines described by EQUATION A 4, according to the value of x. The cross-section for $x = 0$ is simply the parallelogram given by EQUATION 4. The four possible cases are illustrated in FIGURE 3.

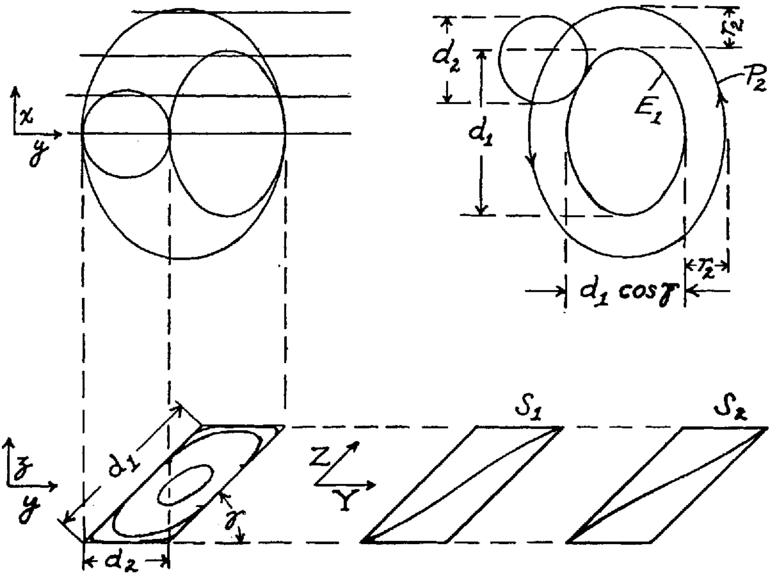

FIGURE 3.

On each curve of this type there is a pair of points for which

$$y = Y + Z\cos\gamma = \text{extremum } (S_2)$$

and another pair for which

$$z' = Y\cos\gamma + Z = \text{extremum } (S_1).$$

The loci of such points are space-curves S_1, S_2 on the surface of the excluded volume; their projections on the (y, z) plane are described by the equations

$$(Z/Y)(r_1^2 - Z^2)^{-1/2}(r_2^2 - Y^2)^{1/2} = \begin{cases} \cos\gamma; & (S_2) \\ 1/\cos\gamma; & (S_1) \end{cases} \qquad \text{(A 5)}$$

The significance of S_2 will be clear from the observation that when the center of plate 2 is on S_2, not only does this plate make rim-to-rim contact with plate 1, but (in addition), a cylinder raised perpendicularly on the rim of plate 2 also just touches the rim of plate 1. Similarly, when the center of plate 2 is on S_1, then the rim of plate 2 just touches a cylinder raised perpendicularly on the rim of plate 1.

The curve S_2 separates the two parts of the surface of the excluded volume which are seen from opposite directions along the normal of plate (2). Its projection P_2 on the (x, y) plane (parallel to plate 2), which delimits the projection of the excluded volume, may be described as the locus of points whose distance from the nearest point of the projection of plate (1) is precisely r_2. The projection of plate (1) on the plane of plate (2) is an ellipse E_1 of semi-axes r_1, $r_1 \cos\gamma$; if a circle of radius r_2 rolls on this ellipse its center traces P_2.

The area $A(P_2)$ can be evaluated by a general method applicable to rolling-figures of continuous tangent. We let R denote the curve described by the center of a circle of radius r as the circle rolls on closed curve C. The algebraic sum of the curvatures of the circle and the curve C must be positive (convex) everywhere on C. The area between C and R is easily found as follows (FIGURE 4):

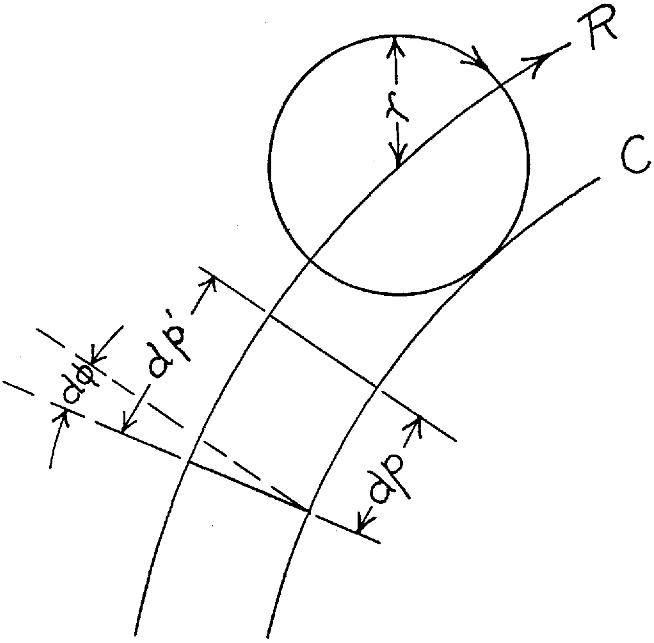

FIGURE 4.

Consider the area contained between two normals of directions φ, $\varphi + d\varphi$, the segments $dp(C)$ of the perimeter of C, and the segment

$$dp'(R) = dp(C) + r d\varphi$$

of the perimeter of R. The area of the trapezium thus formed equals

$$\tfrac{1}{2}r(dp + dp') = r dp + \tfrac{1}{2}r^2 d\varphi .$$

Integrating around C we find simply

$$A(R) - A(C) = \int r\, dp(C) + \tfrac{1}{2}r^2 \int d\varphi = rp(C) + \pi r^2 \qquad \text{(A 6)}$$

where $p(C)$ denotes the circumference of C, and $A(C)$ its area. For the ellipse E_1 described above we have

$$A(E_1) = \pi r_1^2 \,|\cos\gamma\,| \tag{A 7}$$

$$p(E_1) = 4r_1\,E(\sin\gamma) = 4r_1\int_0^{\pi/2}(1-\sin^2\gamma\,\sin^2\varphi)^{1/2}\,d\varphi$$

where the customary notation $E(\sin\gamma)$ is used for a complete elliptic integral of the second kind. We substitute these results in (A 6) along with $r = r_2$ and obtain for the projection P_2:

$$A(P_2) = \pi r_1^2\,|\cos\gamma\,| + 4r_1 r_2 E(\sin\gamma) + \pi r_2^2 \tag{A 8}$$

Similarly, of course,

$$A(P_1) = \pi r_1^2 + 4r_1 r_2 E(\sin\gamma) + \pi r_2^2\,|\cos\gamma\,|\,. \tag{A 9}$$

Actually, the profile areas (A 8) and (A 9) are the only properties of S_1 and S_2 which will enter into our final result for the excluded volume of two cylinders, but some additional analysis has been included as an aid to visualization.

So far, we have considered the thin plates of diameters d_1, d_2. Now, let us replace the second by a cylinder of length l_2, diameter d_2. Our solution for the case $l_2 = 0$ has an important connection with the more general problem: As we consider the two halves of the surface illustrated in FIGURE 3 separated by the curve S_1, the front half is the locus for the center of the rear end of cylinder (2) at closest approach to plate 1, and the rear half of the surface is the locus for the front end-center of the cylinder for the opposite type of end-wise contact. The corresponding loci for the center of cylinder (2) are displaced by distances $\pm\,\frac{1}{2}l_2$ in the direction of the cylinder axis. If the two end surfaces formed by these loci are joined rim to rim by a cylindrical mantle parallel to the axis of cylinder (2), then that mantle is the locus for the center of (2) when this cylinder makes lateral contact with the rim of plate (1).

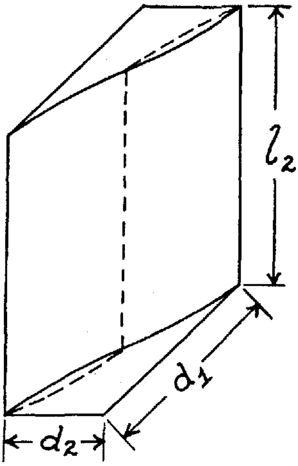

FIGURE 5.

The excluded volume for this case is the same as for $l_1 = l_2 = 0$, plus that of a cylinder of length l_2 and orthogonal section P_2:

$$-\beta_1(0,\,d_1\,,\,l_2\,,\,d_2) = -\beta_1(0,\,d_1\,,\,0,\,d_2) + l_2\,A(P_2). \tag{A 10}$$

The end-faces of the inserted cylindrical piece are parallel, so that the computation of the volume is not affected by their complicated shape.

The final generalization to the case $l_1 > 0$ proceeds in a similar manner: The body illustrated by FIGURE 5 is cut as indicated by the dotted line. The cut, most simply taken perpendicularly to the plane of the projection, follows the separated halves of the curve S_1 and the median plane of the cylinder inserted in the previous step. A second cylindrical

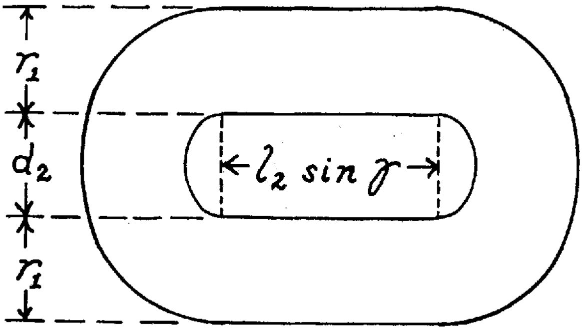

FIGURE 6.

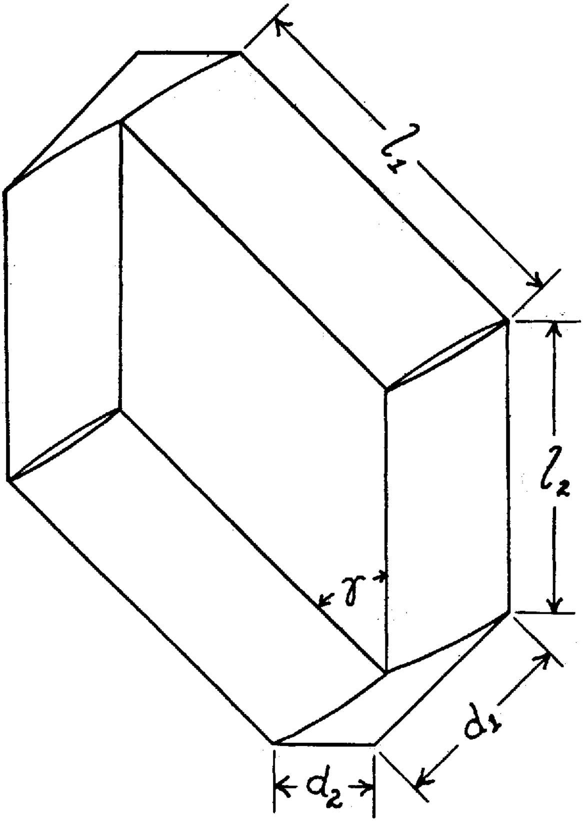

FIGURE 7

piece of length l_2 parallel to the normal of the plate (1) and cross-section, as indicated by FIGURE 6, is inserted. This time the added volume is

$$l_1 A(P_1) + 2\, l_1 l_2 (r_1 + r_2) \sin\gamma,$$

and the volume of the resulting domain, illustrated in FIGURE 7, equals

$$\begin{aligned} -\beta_1(l_1, d_1; l_2, d_2; \gamma) &= (\pi/4)d_1\, d_2(d_1 + d_2)\sin\gamma \\ &+ l_2\{(\pi/4)d_2^2 + d_1\, d_2 E(\sin\gamma) + (\pi/4)d_1^2\,|\cos\gamma|\} \\ &+ l_1\{(\pi/4)d_1^2 + d_1 d_2 E(\sin\gamma) + (\pi/4)d_2^2\,|\cos\gamma|\} + l_1 l_2(d_1 + d_2)\sin\gamma. \end{aligned} \tag{A 11}$$

The integrations involved in the computation of the average

$$\int \beta_1(\gamma)\, d\Omega/4\pi = \tfrac{1}{2}\int_0^{\pi} \beta_1(\gamma)\sin\gamma\, d\gamma$$

should be obvious for all terms except those which involve the elliptic integral $E(\sin\gamma)$. These too, reduce to a very simple form by a suitable substitution. By the definition of the complete elliptic integral we have

$$4E(\sin\gamma) = 4\int_0^{\pi 2/} (1 - \sin^2\gamma\sin^2\psi)^{1/2}\, d\psi = \int_0^{2\pi} (1 - \sin^2\gamma\sin^2\psi)^{1/2}\, d\psi$$

Hence

$$4\int_0^{\pi} E(\sin\gamma)\sin\gamma\, d\gamma = \int_0^{\pi}\sin\gamma\, d\gamma\int_0^{2\pi} d\psi(1 - \sin^2\gamma\sin^2\psi)^{1/2} \tag{A 12}$$

By the substitution

$$\sin\gamma\sin\varphi = \cos\vartheta$$

$$\cos\gamma = \sin\vartheta\sin\varphi,$$

(which may be interpreted as a change of polar coordinates in space), the integral (A 12) becomes

$$4\int_0^{\pi} E(\sin\gamma)\sin\gamma\, d\gamma = \int_0^{\pi}\sin\vartheta\, d\vartheta\int_0^{2\pi} d\varphi\sin\vartheta = \pi^2 \tag{A 13}$$

With the aid of this result and obvious elementary integrations we find from EQUATION A 11:

$$\begin{aligned} -\int \beta_1(l_1, d_1; l_2, d_2; \gamma)\, d\Omega/4\pi &= (\pi/4)^2\, d_1\, d_2(d_1 + d_2) \\ &+ (\pi/4)\,(l_1 d_1^2 + l_2 d_2^2) + (\pi/8)\,(l_1 d_2^2 + l_2 d_1^2) \\ &+ (\pi^2/8)(l_1 + l_2)\, d_1\, d_2 + (\pi/4)\, l_1\, l_2\,(d_1 + d_2) \end{aligned} \tag{A 14}$$

For a pair of cylinders of lengths l_1, l_2, capped by hemispheres of diameters d_1, d_2, the computation of the mutual excluded volume is quite analogous to the preceding. Several details are much simpler. For the case $l_1 = l_2 = 0$, the result (A 2) is replaced by the volume of a sphere of diameter $d_1 + d_2 = 2d$. The profiles(P_1, P_2) are replaced by circles of radius d (compare A 8, A 9). The assembled final result for capped cylinders is

$$-\beta_1(\gamma) = (4\pi/3)d^3 + \pi d^2(l_1 + l_2) + 2dl_1 l_2\sin\gamma. \tag{A 15}$$

Here, the averaging over directions involves only the simple integral

$$\int \sin\gamma\, d\Omega/4\pi = \pi/4. \tag{A 16}$$

The Mean Covolume for Anisotropic Solutions

We shall show how the multiple integral

$$\bar{\beta}_{1\rho}(f_1, f_2) = \int f_1(\mathbf{a}_1)f_2(\mathbf{a}_2)\beta_1\,(\cos^{-1}(\mathbf{a}_1\cdot\mathbf{a}_2))\, d\Omega(\mathbf{a}_1)\, d\Omega(\mathbf{a}_2), \tag{B 1}$$

where $\mathbf{a}_1$, $\mathbf{a}_2$ denote variable unit vectors which specify the orientations of particles, can be reduced to a single integral when the distribution-functions are of the special type

$$f_s(\mathbf{a}) = (\alpha_s/4\pi \sinh \alpha_s) \cosh \alpha_s(\mathbf{a} \cdot \mathbf{a}_0), \tag{B 2}$$

symmetrical about the discretion $\mathbf{a}_0$ (axis of the liquid crystal). Concerning β_1 we assume only

$$\beta_1(\gamma) = \beta_1(\pi - \gamma) = F(\sin\gamma) \tag{B 3}$$

at this stage, although in the end we shall introduce the approximation

$$\beta_1(\gamma) = \beta_1(\pi/2)\sin \gamma, \tag{B 4}$$

derived in the text.

Consider the integral

$$J = \int \cosh\,(\alpha_1(\mathbf{a}_1 \cdot \mathbf{a}_0) + \alpha_2(\mathbf{a}_2 \cdot \mathbf{a}_0))\, F(\sin\gamma)\, d\Omega_1\, d\Omega_2\,;$$

$$\cos \gamma = (\mathbf{a}_1 \cdot \mathbf{a}_2). \tag{B 5}$$

The value of this integral is not affected by the substitution

$$\mathbf{a}_2 \rightarrow -\mathbf{a}_2$$

which changes the first factor of the integrand into

$$\cosh\,(\alpha_1(\mathbf{a}_1 \cdot \mathbf{a}_0) - \alpha_2(\mathbf{a}_2 \cdot \mathbf{a}_0)).$$

The arithmetic mean of the two integrals involves the factor

$$\cosh\,(\alpha_1(\mathbf{a}_1 \cdot \mathbf{a}_0))\cosh\,(\alpha_2(\mathbf{a}_2 \cdot \mathbf{a}_0))$$

instead, and by comparison with EQUATIONS. B 1, B 2, we readily verify the identity

$$J = (4\pi)^2\,(\sinh \alpha_1 \sinh \alpha_2/\alpha_1\alpha_2)\bar{\beta}_1\rho(f_1\,, f_2). \tag{B 6}$$

We proceed to evaluate J.

For the direction $\mathbf{a}_1$, we next introduce polar coordinates $(\Theta_1\,, \phi_1)$ referred to $\mathbf{a}_0$, but the direction $\mathbf{a}_2$ we shall specify in terms of polar coordinates (γ, ϕ) referred to the direction $\mathbf{a}_1$, such that $\phi = 0$ for $\mathbf{a}_2 = \mathbf{a}_0$. Then

$$(\mathbf{a}_0 \cdot \mathbf{a}_1) = \cos \Theta_1$$

$$(\mathbf{a}_0 \cdot \mathbf{a}_2) = \cos \Theta_2 = \cos \Theta_1 \cos \gamma + \sin \Theta_1 \sin \gamma \cos \phi \tag{B 7}$$

$$d\Omega_1 = \sin \Theta_1\, d\,\Theta_1\, d\,\phi_1$$

$$d\Omega_2 = \sin \gamma\, d\gamma\, d\phi.$$

Since the integrand does not depend on ϕ_1, we integrate at once over this variable and get

$$J = 2\pi \int \cosh\,(\alpha_1 \cosh \Theta_1 + \alpha_2 \cos \Theta_2) F(\sin \gamma)\, \sin \Theta_1\, d\Theta_1 \sin \gamma\, d\gamma\, d\phi\,. \tag{B 8}$$

The limits of the variables are

$$0 < \Theta_1 < \pi; \qquad 0 < \gamma < \pi; \qquad 0 < \phi < 2\pi.$$

Now we replace the two variables Θ_1 and ϕ by the following substitution:

$$\cos \Theta_1 = \sin \chi \cos\,(\psi + \eta(\gamma)) \tag{B 9}$$

$$\sin \Theta_1 \cos \phi = \sin \chi \sin(\psi + \eta\,(\gamma))$$

$$\tan \eta(\gamma) = \alpha_2 \sin \gamma/(\alpha_1 + \alpha_2 \cos \gamma)$$

$$\partial(\Theta_1\,, \phi)/\partial(\chi, \psi) = \sin \chi/\sin \Theta_1$$

whereby the integral takes the form

$$J = 2\pi \int \cosh\left([\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos\gamma]^{1/2} \sin\chi \cos\psi\right) F(\sin\gamma) \sin\gamma \, d\gamma \sin\chi \, d\chi \, d\psi, \tag{B 10}$$

the integral to be taken between the limits

$$0 < \gamma < \pi; \qquad 0 < \chi < \pi; \qquad 0 < \psi < 2\pi. \tag{B 10a}$$

After a final substitution

$$\begin{aligned} \sin\chi \cos\psi &= \cos\mu \\ \cos\chi &= \sin\mu \cos\xi \\ \partial(\chi, \psi)/\partial(\mu, \xi) &= \sin\mu/\sin\chi, \end{aligned} \tag{B 11}$$

we can integrate over μ and ξ under the integral sign as follows

$$\begin{aligned} &\int_{\mu=0}^{\pi} \sin\mu \, d\mu \int_{\xi=0}^{2\pi} \cosh\left([\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos\gamma]^{1/2} \cos\mu\right) d\xi \\ &= 4\pi[\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cosh\gamma]^{-1/2} \sinh\left([\alpha_1^2 + \alpha_2 + 2\alpha_1\alpha_2 \cos\gamma]^{1/2}\right) \\ &= (-4\pi/\alpha_1\alpha_2 \sin\gamma) \frac{\partial}{\partial\gamma} \cosh\left([\alpha_1^2 + \alpha_2^2 + 2\,\alpha_1\alpha_2 \cos\gamma]^{1/2}\right). \end{aligned}$$

The result

$$J = (-8\pi^2/\alpha_1\alpha_2) \int_{\gamma=0}^{\pi} \frac{\partial}{\sin\gamma\,\partial\gamma} \{\cosh\left([\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos\gamma]^{1/2}\right)\} F(\sin\gamma) \sin\gamma \, d\gamma \tag{B 12}$$

may be integrated by parts and we finally obtain

$$\begin{aligned} J = {} & (8\pi^2/\alpha_1\alpha_2) \{2 \sinh\alpha_1 \sinh\alpha_2 F(0) \\ & + \int_{\gamma=0}^{\pi} \cosh\left([\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos\gamma]^{1/2}\right) dF(\sin\gamma)\} \end{aligned} \tag{B 13}$$

or in view of (B 6)

$$\begin{aligned} & 2 \sinh\alpha_1 \sinh\alpha_2 \{\beta_1 \rho(f_1, f_2) - \beta_1(0)\} \\ & = \int_{\gamma=0}^{\pi} \cosh\left([\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos\gamma]^{1/2}\right) d\,\beta_1(\gamma). \end{aligned} \tag{B 14}$$

For identical particles, $\alpha_1 = \alpha_2 = \alpha$,
we have

$$(\alpha^2 + \alpha^2 + 2\alpha^2 \cos\gamma)^{1/2} = 2\alpha \cos \tfrac{1}{2}\gamma. \tag{B 15}$$

Moreover, if we adopt the approximation

$$F(\sin\gamma) = \beta_1(\gamma) = \beta_1(\pi/2)\sin\gamma = -(8/\pi)b \sin\gamma \tag{B 16}$$

(see text), the integral (B 14) can be expressed in terms of a Bessel function as follows

$$\begin{aligned} 2(\sinh\alpha)^2 \beta_1 \rho(f) &= \int_{\gamma=0}^{\pi} \cosh(2\alpha \cos\tfrac{1}{2}\gamma) \beta_1(\pi/2) \cos\gamma \, d\gamma \\ &= \pi\beta_1(\pi/2) I_2(2\alpha) = -8b\, I_2(2\alpha) \end{aligned} \tag{B 17}$$

with the standard notation

$$I_2(2\alpha) = -J_2(2i\alpha) = \sum_{n=0}^{\infty} (\alpha^{n+2}/n!(n+2)!) \tag{B 18}$$

for the Bessel function of order 2. The integral (B 17) is but a variant of the standard integral definition of the Bessel function

$$\pi I_2(2\alpha) = \int_{x=0}^{x=\pi} \cosh(2\alpha\cos x)\cos(2x)\,dx,$$

the last step being justified by the observation that the integrand remains unchanged when the argument x is replaced by $\pi - x$.

In all cases encountered in the present work, the argument of the Bessel function will be either zero (isotropic solution) or else so large that a few terms of the asymptotic expansion

$$2I_2(2\alpha) \sim (\pi\alpha)^{-1/2}e^{2\alpha}\left\{1 - \frac{3\cdot 5}{1!\,16\alpha} + \frac{1\cdot 3\cdot 5\cdot 7}{2!\,(16\alpha)^2} - \frac{(-1)\cdot 1\cdot 3\cdot 5\cdot 7\cdot 9}{3!\,(16\alpha)^3} + \cdots\right\} \qquad \text{(B 19)}$$

will suffice for computation. The corresponding formula for the mean effective excluded volume is

$$-\bar{\beta}_1\rho(f) \sim 8b(\pi\alpha)^{-1/2}\left\{1 - \frac{30}{32\alpha} + \frac{210}{(32\alpha)^2} + \frac{1260}{(32\alpha)^3} + \cdots\right\}. \qquad \text{(B 20)}$$

In the general case $\alpha_1 \neq \alpha_2$, even though we adopt the approximation (B 16), the integral of (B 14) can no longer be expressed in terms of simple known functions. An asymptotic expansion analogous to (B 20) has been obtained by the usual procedure: A new variable t is introduced by the substitution

$$\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2\cos\gamma = (\alpha_1 + \alpha_2 - t)^2; \qquad \text{(B 21)}$$

the hyperbolic function is approximated by an exponential and the factor

$$dF(\sin\gamma)/dt = \cos\gamma\,(d\gamma/dt)$$

by an abbreviated power series in t; finally the range of integration over t is extended to the interval $(0, \infty)$. The following generalization of (B 20) results

$$-\bar{\beta}_1\rho(f_1, f_2) \sim 8b_{12}(\alpha_1 + \alpha_2)^{1/2}(2\pi\alpha_1\alpha_2)^{-1/2}\left\{1 - \frac{3}{8}\left(\frac{1}{\alpha_1} + \frac{1}{\alpha_2} + \frac{1}{\alpha_1 + \alpha_2}\right) + \frac{15}{128}\left[\frac{8}{\alpha_1\alpha_2} - \left(\frac{1}{\alpha_1} + \frac{1}{\alpha_2} + \frac{1}{\alpha_1 + \alpha_2}\right)^2\right] + \cdots\right\}. \qquad \text{(B 22)}$$

By this general technique, it is also possible to deal with the more accurate description of the covolume function given by EQUATION 45 in the text. Some terms involving the factor $\log t$ then occur after the substitution (B 21); but the integrals which correspond to these terms are easily evaluated:

$$\int_0^\infty e^{-t}t^n(\log t)\,dt = \frac{\partial}{\partial n}\int_0^\infty e^{-t}t^n\,dt = \Gamma'(n+1).$$

For the present work, however, it did not seem worth while to complete this computation.

Bibliography

DERJAGUIN, B. 1940. On the repulsive forces between charged colloid particles and on the theory of slow coagulation and stability of lyophobic sols. Trans. Faraday Soc. **36:** 203.

LANGMUIR, I. 1938. The role of attractive and repulsive forces in the formation of tactoids, thixotropic gels, protein crystals and coacervates. J. Chem. Phys. **6:** 873.

ONSAGER, L. 1942. Anisotropic solutions of colloids. Phys. Rev. **62:** 558.

VERWEY, E. J. W., & J. TH. G. OVERBEEK. 1948. *Theory of the Stability of Lyophobic Colloids.* Elsevier Publishing Co. Amsterdam & New York.