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Determination of Molecular Shape by Osmotic Measurement

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The second coefficient A_2 of osmotic pressure π of high-polymer solutions is calculated in the case of the rigid ovaloid. A_2 is a function of the molecular shape and thus we can determine the shape of high polymers.

1. PRINCIPLE OF CALCULATION

RECENTLY Zimm¹ has calculated the second coefficient A_2 in the expansion of osmotic pressure π of high-polymer solutions:

$$\frac{\pi}{RTC} = \frac{1}{M_2} + A_2 C + A_3 C^2 + \dots, \quad (1)$$

and lately Kotani² has calculated the same quantity in the case of rigid ellipsoid of revolution in an approximate manner and has shown that the numerical factor f in the expression,

$$A_2 = (4N_0 v / M_2^2) f, \quad (2)$$

becomes larger than 1 when the solute molecules deviate from spherical shape. In this equation N_0 is Avogadro's number, v the volume of a solute molecule and M_2 is the molecular weight of a polymer. In this paper, we shall show that more general expression for A_2 can be given, which is rigorous in the case of the rigid ovaloid.

The integral for f is to be extended over all the positions of a molecule, say B , relative to another molecule A , in which A and B commute with each other. Such motions of B constitute a subset I in the group of motions G and the determination of f reduces to search for the volume of I . In order that the results do not depend on the choice of the standard position of B we are required to seek the Haar's measure $m(I)$ of I in G . This is obtained by integrating the characteristic function $f(x)$:

$$f(x) = \begin{cases} 1; & x \in I, \\ 0; & x \notin I, \end{cases} \quad (3)$$

of I over whole G . This integration can be performed as:

$$m(I) = \int_{G/g} d\bar{x} \int_g f(x\xi) d\xi, \quad (4)$$

$$f = (1/8v)m(I),$$

where ξ is the element of translation group g which is the normal subgroup of G and \bar{x} is the element of G/g which is isomorphic to the three-dimensional rotation group in the case of rigid body model. The meaning of this integration is that we at first integrate $f(x)$ over the translation group, and then integrate the result over the group G/g , because the result of the former integration is a function of \bar{x} only:

$$\int_g f(x\xi) d\xi = \int_g f(xa\eta) da\eta = \int_g f(xa\eta) d\eta = f(\bar{x}), \quad (5)$$

(aeg)

if we remember $d\xi$ is the left invariant measure of g . Also, because $d\bar{x}$ is the left invariant measure of G/g ,

$$\int_{G/g} f(\bar{x}) d\bar{x} = \int_{G/g} \bar{f}(\bar{b}\bar{x}) d(\bar{b}\bar{x}) = \int_{G/g} f(\bar{y}) d\bar{y}, \quad (6)$$

$b \in G; \quad \bar{b} \in G/g.$

Hence,

$$m(bI) = \int_{G/g} d\bar{x} \int_g f(bx\xi) d\xi \quad (7)$$

$$= \int_{G/g} d\bar{x} f(\bar{b}\bar{x}) = \int f(\bar{x}) d\bar{x},$$

or

$$m(bI) = m(I), \quad (8)$$

which shows that $m(I)$ given by Eq. (3) does not depend on the standard position of B .

The infinitesimal Haar's measure of translation group g is nothing but the ordinal volume element in three dimensional Euclidian space and that of the rotation group G/g is given by

$$\frac{1}{8\pi^2} \sin\theta d\theta d\varphi d\tau = \frac{1}{8\pi^2} d\omega d\tau, \quad (9)$$

if we express its elements by

$$\begin{pmatrix} \sin\varphi \sin\tau + \cos\theta \cos\varphi \cos\tau, & -\cos\varphi \sin\tau + \cos\theta \sin\varphi \cos\tau, & -\cos\tau \sin\theta \\ -\sin\varphi \cos\tau + \cos\theta \cos\varphi \sin\tau, & \cos\varphi \cos\tau + \cos\theta \sin\varphi \sin\tau, & -\sin\theta \sin\tau \\ \sin\theta \cos\varphi, & \sin\theta \sin\varphi, & \cos\theta \end{pmatrix}. \quad (10)$$

¹ B. H. Zimm, J. Chem. Phys. 14, 164 (1946).

² M. Kotani read 1947 in the meeting of the Physical Society of Japan.

2. RIGID OVALOID

Let us consider two ovaloids A and B , A being fixed in space and B moves around it. $\tilde{f}(\bar{x})$ is nothing but the volume of C which is described by a point O' fixed in B when B moves around A keeping its orientation and always in touch with A . It is easily shown that C is another ovaloid.

Next, let us consider a common contact plane of A and B and draw perpendiculars from a point O of A and O' of B to the plane and designate respective lengths by $H(\theta, \varphi)$ and $K(\bar{x}; \theta, \varphi)$. Here (θ, φ) represents the direction of the perpendicular and \bar{x} the rotation θ_1, φ_1 and τ_1 of B . Again we define the linear differential expression with respect to H or K of regular functions on the unit sphere:

$$(H, K) = \left(\frac{\partial^2 H}{\partial \theta^2} + H \right) \left(\frac{1}{\sin^2 \theta} \frac{\partial^2 K}{\partial \varphi^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial K}{\partial \theta} + K \right) - 2 \frac{\partial}{\partial \theta} \left(\frac{1}{\sin \theta} \frac{\partial H}{\partial \varphi} \right) \cdot \frac{\partial}{\partial \theta} \left(\frac{1}{\sin \theta} \frac{\partial K}{\partial \varphi} \right) + \left(\frac{1}{\sin^2 \theta} \frac{\partial^2 H}{\partial \varphi^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial H}{\partial \theta} + H \right) \left(\frac{\partial^2 K}{\partial \theta^2} + K \right). \quad (11)$$

Then the volume of C that is $\tilde{f}(\bar{x})$ is given by

$$\tilde{f}(\bar{x}) = \frac{1}{6} \int (H + K(\bar{x}))(H + K(\bar{x}), H + K(\bar{x})) d\omega. \quad (12)$$

This comes from the fact that on the one hand (H, H) is twice times the product of principal radii of the ovaloid corresponding to (θ, φ) :

$$(H, H) = 2R_1 R_2, \quad (13)$$

and on the other the volume of an ovaloid is expressed as:

$$v = \frac{1}{3} \int H R_1 R_2 d\omega, \quad (14)$$

where $d\omega$ is the surface element on the unit sphere belonging to the direction (θ, φ) , and the integration extends over whole surface of unit sphere.³ Thus the Haar's measure $m(I)$ of Eq. (3) is expressed:

$$\begin{aligned} m(I) &= \frac{1}{8\pi^2} \int \tilde{f}(\bar{x}) d\omega_1 d\tau_1 \\ &= \frac{1}{48\pi^2} \int d\omega_1 d\tau_1 \int (H + K(\bar{x})) \\ &\quad \times (H + K(\bar{x}), H + K(\bar{x})) d\omega. \quad (15) \end{aligned}$$

To evaluate this we at first show that the above differ-

ential expression (11) is self-adjoint on the whole surface of unit sphere. That is, if $L(\theta, \varphi)$ is another one-valued function on the surface as is $H(\theta, \varphi)$ or $K(\theta, \varphi)$, we demonstrate the equality:

$$\int L(H, K) d\omega - \int H(L, K) d\omega = 0. \quad (16)$$

For convenience we put:

$$L \frac{\partial H}{\partial \theta} - H \frac{\partial L}{\partial \theta} = P; \quad \frac{1}{\sin \theta} \frac{\partial H}{\partial \varphi} L - \frac{1}{\sin \theta} \frac{\partial L}{\partial \varphi} H = Q. \quad (17)$$

Then

$$\begin{aligned} &\{L(H, K) - H(L, K)\} \sin \theta \\ &= \frac{\partial P}{\partial \theta} \left(\frac{1}{\sin \theta} \frac{\partial^2 K}{\partial \varphi^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial K}{\partial \theta} + \sin \theta \cdot K \right) \\ &\quad + \left(\cos \theta \cdot Q - \frac{\partial P}{\partial \varphi} - \sin \theta \frac{\partial Q}{\partial \theta} \right) \cdot \frac{\partial}{\partial \theta} \left(\frac{1}{\sin \theta} \frac{\partial K}{\partial \varphi} \right) \\ &\quad + \left(\frac{\partial Q}{\partial \varphi} + \cos \theta \cdot P \right) \left(\frac{\partial^2 K}{\partial \theta^2} + K \right) \\ &= \frac{\partial}{\partial \theta} \left[\sin \theta \left\{ P \left(\frac{1}{\sin^2 \theta} \frac{\partial^2 K}{\partial \varphi^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial K}{\partial \theta} + K \right) - Q \frac{\partial}{\partial \theta} \left(\frac{1}{\sin \theta} \frac{\partial K}{\partial \varphi} \right) \right\} \right] \\ &\quad - \frac{\partial}{\partial \varphi} \left\{ P \frac{\partial}{\partial \theta} \left(\frac{1}{\sin \theta} \frac{\partial K}{\partial \varphi} \right) - Q \left(\frac{\partial^2 K}{\partial \theta^2} + K \right) \right\}, \end{aligned}$$

from which we can easily arrive at Eq. (16).

Now remembering Eq. (11) is linear with respect to H or K and using Eq. (16), we can rewrite Eq. (15) as follows:

$$\begin{aligned} m(I) &= v_A + v_B \\ &\quad + \frac{1}{16\pi^2} \int H(K(\bar{x}), K(\bar{x})) d\omega d\omega_1 d\tau_1 \\ &\quad + \frac{1}{16\pi^2} \int K(\bar{x})(H, H) d\omega d\omega_1 d\tau_1. \quad (18) \end{aligned}$$

The remaining two integrals in this equation can easily be shown to be separated with respect to $d\omega$, $d\omega_1$ and $d\tau_1$ owing to the self-adjoint character expressed by Eq. (16) and the fact that we can apply the constant rotation \bar{b} to B :

$$\int K(\bar{x}) d\bar{x} = \int K(\bar{b}\bar{x}) d\bar{b}\bar{x} = \int K(\bar{b}\bar{x}) d\bar{x},$$

³ W. Blaschke, Kreis und Kugel, Jber. Deutsch. Math.-Verein. Band 24 (1915).

which rotates B from (θ, φ) to $(0, 0)$, and also the fact that because of Eq. (10) $K(\bar{x}; 0, 0)$ reduces to $K(\theta_1, \varphi_1)$:

$$K(\theta_1, \varphi_1, \tau_1; 0, 0) = K(\theta_1, \varphi_1). \quad (19)$$

On the other hand we utilize the formulas which express the surface F and mean of the mean radius of curvature $M/4\pi$ of ovaloid by the surface integration over unit sphere:

$$\left. \begin{aligned} F &= \int R_1 R_2 d\omega = \frac{1}{2} \int H(R_1 + R_2) d\omega, \\ M &= \int H d\omega = \frac{1}{2} \int (R_1 + R_2) d\omega. \end{aligned} \right\} \quad (20)$$

Then Eq. (18) reduces to

$$\begin{aligned} m(I) &= v_A + v_B + \frac{1}{8\pi} \int H d\omega \int (K, K) d\omega_1 \\ &\quad + \frac{1}{8\pi} \int K d\omega_1 \int (H, H) d\omega \\ &= v_A + v_B + \frac{1}{4\pi} (M_A F_B + M_B F_A). \end{aligned} \quad (21)$$

Therefore we obtain the final expression for f :

$$f = \frac{MF}{16\pi v} + \frac{1}{4}, \quad (22)$$

in the homogeneous case. When the solution is heterogeneous, we are only required to replace the three quantities M , F and v by their number averages.

3. SPECIAL FORMS OF f

(1) Ellipsoid of Revolution

First we consider the typical case of ellipsoid of revolution:

$$\left. \begin{aligned} x &= a \sin\theta \cos\varphi, \\ y &= a \sin\theta \sin\varphi, \\ z &= b \cos\theta, \end{aligned} \right\} \quad (23)$$

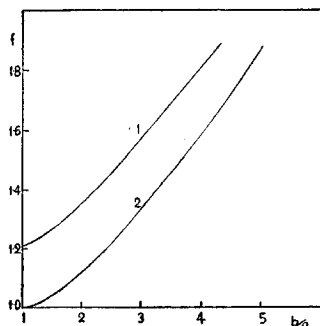


FIG. 1. f as a function of axial ratio. 1: Cylinder; 2: Ellipsoid of revolution. Curve 1 corresponds to the elongated form; the case of flat cylinder is not shown.

In this case $H(\theta, \varphi)$ is independent of H and is given by

$$H = (a^2 \sin^2\theta + b^2 \cos^2\theta)^{1/2}. \quad (24)$$

Thus, if we use the eccentricity:

$$\begin{aligned} \epsilon^2 &= \frac{a^2 - b^2}{a^2}, \quad (a \geq b: \text{oblate}) \\ &= \frac{b^2 - a^2}{b^2}, \quad (a \leq b: \text{prolate}) \end{aligned} \quad (25)$$

Then the mean of the mean radius of curvature $M/4\pi$ and the surface area F are given by

$$M = 2\pi a \left\{ (1 - \epsilon^2)^{1/2} + \frac{\sin^{-1}\epsilon}{\epsilon} \right\}, \quad (\text{oblate}) \quad (26)$$

$$= 2\pi b \left\{ 1 + \frac{1 - \epsilon^2}{2\epsilon} \log \frac{1 + \epsilon}{1 - \epsilon} \right\}; \quad (\text{prolate})$$

$$F = 2\pi a^2 \left\{ 1 + \frac{1 - \epsilon^2}{2\epsilon} \log \frac{1 + \epsilon}{1 - \epsilon} \right\}, \quad (\text{oblate}) \quad (27)$$

$$= 2\pi ab \left\{ (1 - \epsilon^2)^{1/2} + \frac{\sin^{-1}\epsilon}{\epsilon} \right\}. \quad (\text{prolate})$$

Introducing these equations into Eq. (23) we arrive at the same expression for f regardless of both types of ellipsoids:

$$\begin{aligned} f &= \frac{1}{4} + \frac{3}{16} \left(1 + \frac{1}{(1 - \epsilon^2)^{1/2}} \frac{\sin^{-1}\epsilon}{\epsilon} \right) \\ &\quad \times \left(1 + \frac{1 - \epsilon^2}{2\epsilon} \log \frac{1 + \epsilon}{1 - \epsilon} \right). \end{aligned} \quad (28)$$

When $\epsilon \ll 1$ this can be expanded as a power series of ϵ :

$$f = 1 + \frac{\epsilon^4}{15} + \frac{37}{60}\epsilon^6 + \dots \quad (29)$$

Figure 1, curve 2 shows the variation of f with axial ratio a/b . Comparing these theoretical values with the experimental data we can thus determine the axial ratio of solute molecules as ellipsoid of revolution. Actually, f for hemoglobin is 1.27 and for serum albumin 1.6.¹ Accordingly, we obtain $b/a = 2.5$ in the former case and 4 in the latter case. Considering elongated case,⁴ the viscosity value for hemoglobin is 4.6 and for serum albumin is 5.6 whereas the diffusion values are 3.7 and 5.0 respectively.

(2) Cylinder

In this case the calculation is comparatively easy. Let us put the contact plane to the given cylinder of

⁴ R. Simha, J. App. Phys. **13**, 147 (1942).

length $2b$ and radius a on the corner of the cylinder, then the perpendicular from the center of the cylinder that is $H(\theta, \varphi)$ is given by

$$H(\theta, \varphi) = b \cos \theta + a \sin \theta. \quad (30)$$

Therefore, we can calculate f as follows (see Fig. 1, curve 1):

$$f = \frac{1}{4} \left\{ 1 + \frac{b}{a} \left(1 + \frac{a}{2b} \right) \left(1 + \frac{a\pi}{2b} \right) \right\}. \quad (31)$$

When $b \gg a$, A_2 thus evaluated reduces to the expression given by Zimm:

$$A_2 = \frac{4\pi N_0 a b^2}{M_2^2} \quad (b \gg a) \quad (32)$$

Attention must be paid to the fact that whereas we have deduced Eq. (22) in the case of smooth ovaloid, circular cylinder considered here is not smooth. But

from the physical point of view, we can consider that Eq. (22) is also true in this case. The above coincidence with the result of Zimm shows also this plausibility. Thus we can calculate the "second virial coefficient" in a wide range of shapes of molecules. At least the principle of calculation explained in Section 1 can be applied if the molecules are not ovaloid-shaped.

Another attention must be drawn to the general character that f is always larger than 1 when the molecules are not spherical. This is easily seen if we rewrite Eq. (22) as

$$f = 1 + \left(\frac{MF}{16\pi v} - \frac{3}{4} \right) \quad (33)$$

the quantity in the bracket is not negative owing to the inequality:

$$M^2 \geq 4\pi F; \quad F^3 \geq 36\pi v^2. \quad (34)$$

Here the equality is established only in the case of sphere.

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The Magnetic Anisotropy of α -NiSO₄·6H₂O between 13 and 295°K. A Torsion Balance for Magnetic Anisotropy Measurements

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The magnetic anisotropy of single crystals of α -NiSO₄·6H₂O has been measured at temperatures between 13 and 295°K. Two crystals of different origin gave concordant results. The difference in magnetic susceptibility between directions parallel and perpendicular to the tetragonal crystallographic axis is given by $\chi_{\parallel} - \chi_{\perp} = 1.37 \times 10^{-5} + 1.502 \times 10^{-2}/T + 1.686/T^2$. The susceptibility difference was independent of field strength up to 10,000 gauss over the temperature range investigated. The results are discussed in connection with the theoretical treatment of the susceptibility of nickel salts by Schlapp and Penney. A torsion balance for the magnetic anisotropy measurements is described.

INTRODUCTION

THE theory of the splitting of the ground states of paramagnetic ions by the electrical fields present in crystalline solids has been developed by Van Vleck and co-workers. In particular, Schlapp and Penney¹ have calculated the case of Ni⁺⁺ ion in a crystalline field of predominantly cubic symmetry with a superimposed smaller field of rhombic symmetry. The ground state which is triply degenerate in the cubic field is split by the combined action of the rhombic field and the spin-orbit coupling. This splitting produces an anisotropy in the magnetic susceptibility.

The anisotropy of NiSO₄·6H₂O has been measured by Krishnan and co-workers² over the temperature

range 90 to 300°K. From these measurements and the theory they deduced a value for the spin-orbit coupling constant in good agreement with that obtained from spectroscopic measurement of gaseous nickel ion. The present paper presents more accurate measurements of the magnetic anisotropy and extends the range of the measurements to liquid hydrogen temperatures. The torsion balance used for this and other crystals is also described.

APPARATUS

Torsion Balance

The magnetic anisotropy was measured with the torsion balance whose construction is shown in Fig. 1. The single crystal sample, T8, which is symmetrically located between the poles of the electromagnet, H, is cemented with thin collodion to a 2-mm diameter quartz rod, T7, which is flared and ground flat on the bottom. The quartz rod is fastened to a 3.2-mm diameter phosphor bronze rod, T6, on which are mounted the

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¹ R. Schlapp and W. G. Penney, Phys. Rev. **42**, 666 (1932).

² (a) Krishnan, Chakravorty, and Banerjee, Trans. Roy. Soc. A232, 107 (1934). (b) K. S. Krishnan and A. Bose, Nature **141**, 329 (1938). (c) Krishnan, Mookherji, and Bose, Trans. Roy. Soc. A238, 125 (1940).