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From (13) it follows that a necessary and sufficient condition under which the curvature at every point and element of hypersurface of our space be independent of the orientation is that

$$(14) \quad R_{hijl} = -K(g_{hk}g_{jl} - g_{hl}g_{jk}).$$

If we differentiate covariantly the equation (14) with  $i$  and put in the second relation of (4), and multiply by  $g^{hk}$  and  $g^{jl}$ , and contract the same indexes, we have the relation

$$(15) \quad K_{|i} = K_{,i} + k_{||}^a \Gamma_{aoi}^* = 0.$$

Similarly, differentiate with  $u_i$ , and put in (5), we have

$$K^{||l} (g_{ih}g_{jk} + g_{ik}g_{jh}) + 2R_{ija(h} A_{k)}^{al} = 0.$$

If the above equation be multiplied by  $l^i$  and  $i$  be contracted, from the second condition of (1) we have

$$(16) \quad K^{||l} = (L/\sqrt{g}) \partial K / \partial u_l = 0.$$

From (15) and (16) we have finally  $K = const.$  Thus we have the

*Theorem. The theorem of Schur in the Riemannian geometry holds good again in the special Cartan space in which the fundamental conditions (1) are given.*

(October, 1951)

#### REFERENCES

- [1] EISENHART, L. P. : Riemannian geometry, Princeton University press (1926)
- [2] BERWALD, L. : Über die  $n$ -dimensionalen Cartansche Räume und eine Normalform der zweiten Variation eines  $(n-1)$ -fachen Oberflächenintegrals (§ 22), Acta mathematica 71 (1939).

## On the Molecular Weight of Liquid Polymers.

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清水 清 : 液体重合体の分子量に就て

§ 1 Sound velocity in liquid became useful for the investigation of molecular structure after the discovery by M. R. Rao<sup>1)</sup> of the empirical constant (called the molar sound velocity)

$$R = M \frac{v^3}{d} \quad (1)$$

where  $M$ ,  $v$ , and  $d$  are the molecular weight, sound velocity, and density.

Further, R.T. Lagemann and W.S. Dunbar<sup>2)</sup>

showed that, within a homologous series of liquid polymers, linear relationships exist between any two molar constants. An example of such a relationship is the one involving molar refraction  $N$  and molar sound velocity  $R$

$$R = AN + B \quad (2)$$

where  $A$  and  $B$  are, respectively, the slope and intercept.

Recently, A. Weissler, S. W. Fitzgerald,

and I. Resnick<sup>3)</sup> found a new method for determining number average molecular weight of liquid polymers from Eqs. (1) and (2). Namely, by testing the validity of the relation for several polyethylene glycols (Table I and II), they found that, for the low molecular-weight liquid polymer, the molecular weight is an explicit function

$$M = \frac{Bd}{v^{\frac{1}{3}} - A\left(\frac{n^2-1}{n^2+2}\right)} \quad (3)$$

of the sound velocity  $v$ , density  $d$ , refractive index  $n$ , and the two empirical constants  $A$  and  $B$ .

The molecular weights calculated by this method have accuracy of about 2 parts per hundred for the lower polyethylene glycols (Table III). The essential relation for calculating molecular weights by their method is an empirical linear correlation between molar sound velocity and molar refraction.

§ 2 It occurred to the writer that there is no necessity for making the sound-velocity measurements since the molecular weights are easily calculable from molar refractions. Calculation of molecular weights from molar refractions is based on the well accepted concept of group additivity and the additional step of an empirical correlation between molar velocity and molar refraction is eliminated. Since the molar refraction method is physically analogous to a chemical end-group determination, the resulting molecular weight, in the case of a heterogeneous polymer, will evidently be a number average.

I calculate the molecular weights of polyethylene glycols from the density and refractive index data reported by Weissler, Fitzgerald, and Resnick.

In the system of polyethylene glycols, treated by the above authors, the average empirical

molar refraction increment for each  $-\text{CH}_2--\text{CH}_2-\text{O}-$  structural unit, based on the first five pure members of the series, is 44.05. From the general formula  $\text{HO}-(\text{CH}_2-\text{CH}_2-\text{O}-)_n-\text{H}$ , the molecular weight,  $M$ , of any member may be written

$$M = 44.05z + 62.27 \quad (4)$$

where

$z$  = number of  $-\text{CH}_2-\text{CH}_2-\text{O}-$  units in compound,  
62.27 = molecular weight of ethylene glycol,  
and 44.05 = molecular weight of  $-\text{CH}_2-\text{CH}_2-\text{O}-$  unit.

Similarly, the molar refraction, on the basis of additivity of groups, may be expressed

$$N = 10.97z + 14.47 \quad (5)$$

where 14.47 = molar refraction of ethylene glycol.

On the other hand, I have

$$N = r(44.05z + 62.07) \quad (6)$$

where  $r = (n^2 - 1/n^2 + 2)$  = specific refractivity of compound. From Eqs. (5) and (6), I have

$$r(44.05z + 62.07) = 10.97z + 14.47 \quad (7)$$

Eq. (7) is easily solved for  $z$ , and substitution of  $z$  in Eq. (4) gives the molecular weight

$$\begin{aligned} M &= \frac{43.5}{10.97 - 44.05r} \\ &= \frac{43.5}{10.97 - 44.05\left(\frac{n^2-1}{n^2+2}\right)\frac{1}{d}} \quad (8) \end{aligned}$$

From the refractive index and density data reported by Weissler, Fitzgerald, and Resnick, the molecular weights given in Table IV are calculated.

§ 3 The agreement between theoretical molecular weight and molecular weight calculated from the experimental specific refractivities is actually better than that obtained by the molar velocity method.

Since the molar refraction method depends essentially on differences between the molar refractivity of the chain and end-groups, it is

evidently only applicable to compounds of relatively low degree of polymerization. This same limitation, however, applies to the molar velocity method.

For low molecular weight liquid polymers the

molar refraction method is very useful and convenient as the necessary density and refractive index measurements are easily made to high degree of accuracy.

Table I. Physical properties of polyethylene glycols at 30°C.

Glycol	Theoretical Mole. wt.	Density g/cc	Sound velocity m/s	Refractive index n
Ethylene	62.1	1.1068	1642.9	1.4295
Diethylene	106.1	1.1094	1567.7	1.4438
Triethylene	150.1	1.1158	1593.3	1.4531
Tetraethylene	194.2	1.1159	1580.1	1.4567
Pentaethylene	238.2	1.1165	1580.0	1.4593
Poly 200	200±10	1.1168	1592.2	1.4572
Poly 300	300±15	1.1176	1578.0	1.4618
Poly 400	400±20	1.1182	1576.0	1.4636
Poly 600	600±30	1.1183	1570.2	1.4653

Table II. Molar constant of polyethlen glycols.

Glycol	Molar sound velocity R	Molar refraction N
Ethylene	661.7	14.47
Diethylene	1111.2	25.40
Triethylene	1571.6	36.37
Tetraethylene	2027.1	47.36
Pentaethylene	2485.1	58.36
Poly 200	2091	48.79
Poly 300	3125	73.71
Poly 400	4163	98.63
Poly 600	6236	148.40

Table III. Determination of molecular weight by sound velocity.

$$M = \frac{Bd}{v^{\frac{1}{3}} - A \left( \frac{n^2 - 1}{n^2 + 1} \right)}$$

Glycol	Mole. wt. by sound velocity	Deviation from theoretical Mole. wt.
Ethylene	59.9	-3.5%
Diethylene	111.5	5.5
Triethylene	147.3	-1.9
Tetraethylene	195.7	0.8
Pentaethylene	237.7	-0.2

Glycol	Mole. wt. by Sound velocity	Deviation from theoretical Mole. wt.
Poly 200	186.2	-2.0%
Poly 300	302.7	0.0
Poly 400	381.8	0.0
Poly 600	546.9	-4.0
Ave.		2.0%

Table IV. Determination of molecular weight by specific refractivity.

$$M = \frac{43.5}{10.97 - 41.05 \left( \frac{n^2 - 1}{n^2 + 2} \right) \frac{1}{d}}$$

Glycol	Mole. wt. by specific refractivity	Deviation from theoretical Mole. wt.
Ethylene	62.2	0.2%
Diethylene	102.1	-3.8
Triethylene	145.9	-2.8
Tetraethylene	193.3	-0.5
Pentaethylene	244.3	2.6
Poly 200	194.3	0.0
Poly 300	312.9	0.0
Poly 400	405.5	0.0
Poly 600	380.0	0.0
Ave.		1.1%

## References

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## AIRY の虹の理論に関する諸考察

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Takashi SAWADA : Some Considerations on AIRY'S Theory of Rainbow.

## 1. は し が き

わが國の氣象光学の書物中、AIRY の料論をもつとも詳細に論じたものは藤原咲平氏の「氣象光学」<sup>1)</sup>である。外國の文献では PERNTER と EXNER の共著の "Meteorologische Optik" がある。これは氣象光学に関する世界的な標準書である。HUMPHREYS の "Physics of the Air" の中にも相当詳しくかいてあるが、内容は PERNTER のものと殆ど同一である。所が藤原氏の計算の方法は PERNTER や HUMPHREYS のものと余程異つており、これは従來の方法を藤原氏が改良したものである。然し最後にえられた波面の方程式は AIRY のえたものと一致しない。そこで筆者は藤原氏の計算を検べた所、途中で明かな間違ひのある事を見出した。その箇所を訂正すると結局、従來と全く同一の式がえらるゝ事を知つた。よつて本論文では藤原氏の計算の方法を紹介しながら、間違ひの箇所を指摘することにした。

次に問題にした点は、AIRY は水滴中で反射屈折したのち出てきた光波の波面が三次曲面となることを証明したのであるが、この波面は光の進行と共に複雑な變化を示す筈である。ところが AIRY の波面方程式の中には、このような變化に対応する因子が全然ふくまれていない。即ちどこまで進行しても波面の形は變らず、單に平行移動するようなものである。そこで筆者は何故このような不都合を生じたかを明かにし、水滴を遠くはなれた点における波面方程式を論じた。

## 2. 藤原氏の方法と修正

藤原氏の方法を紹介するに當り、「氣象光学」との対照を明にするため、記号はすべて同書と同一にする。第 1 図で AB は入射光の波面、AB 面より水滴に到達するまでの時間を  $t_1$ 、その距離を  $S_1$ 、水滴中を通過する時間

を  $t_2$ 、その距離を  $S_2$ 、水滴をはなれたのち、ある一つの波面 A'B' に到達する迄の時間を  $t_3$ 、その距離を  $S_3$  とする。空氣中および水中の光の速度を夫々  $c_1, c_2$  とすると

$$t_1 + t_2 + t_3 = \frac{S_1}{c_1} + \frac{S_2}{c_2} + \frac{S_3}{c_1} = A \quad (1)$$

A'B' 上では A は到る所一定である。水滴の半径を  $a$ 、入射角を  $i$ 、屈折角を  $r$ 、全反射の回数を  $k$  とし  $p = k+1$  とおくと

$$\left. \begin{aligned} S_1 &= a - a \cos i \\ S_2 &= 2pa \cos i \end{aligned} \right\} \quad (2)$$

$$\therefore S_3 = Ac_1 - a + a \cos i - 2pan \cos r \quad (3)$$

但し  $n = c_1/c_2$ 

$Ac_1 - a \equiv B$  とおくと

$$S_3 = B + a \cos i - 2pan \cos r. \quad (4)$$

水滴の中心 O を原点とし、DESCARTES の理論から計算できる出射光の最小偏角の方向を  $y'$  とする。すると A'E' 上の点の座標は

$$\left. \begin{aligned} x' &= a \sin \theta - S_3 \sin d \\ y' &= a \cos \theta - S_3 \cos d \end{aligned} \right\} \quad (5)$$

但し  $d = D - D_m$ 、 $D_m =$  最小偏角、 $D =$  いま考へている点に進んできた出射光の方向。また  $\theta = i - d$ 。

入射角を  $i$ 、屈折角を  $r$ 、最小偏角の場合に夫々  $i_m, r_m$  とする。

$$i - i_m \equiv I, \quad r - r_m \equiv R \quad (6)$$

とおく。以上の関係を (5) に入れると

$$\left. \begin{aligned} x' &= a \sin i_m \cos I \cos d + a \cos i_m \sin I \cos d \\ &\quad - a \cos i_m \cos I \sin d + a \sin i_m \sin I \sin d \\ &\quad - S_3 \sin d; \\ y' &= a \cos i_m \cos I \cos d - a \sin i_m \sin I \cos d \end{aligned} \right\}$$