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The Determination of Refractive Indices of Colloidal Particles by Means of a New Mixture Rule or from Measurements of Light Scattering

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A new theoretical mixture rule is developed for determining the refractive index of colloidal particles from differential refractometric measurements. The new rule gives better results for colloidal solutions than the mixture rules of Newton, Lorenz-Lorentz, or Wiener if the difference between the refractive indices of the colloidal particles and of the medium is small. If the difference is large, but not in excess of 0.7, the refractive index of the particles can still be obtained with an accuracy in the third or fourth decimal by using an empirical correction equation. If colloidal solutions are very opaque, the refractive index of the particles can be calculated from light scattering. Application of the respective equation requires that the refractive index of the medium and the size of the particles are known. The gravimetric and volumetric measurements involved in the determination of density of colloidal particles can be replaced in part or entirely by measurements of light scattering and refractivity.

I. A NEW MIXTURE RULE FOR DETERMINING THE REFRACTIVE INDEX OF COLLOIDAL CRYSTALS OR MOLECULES

A. The Classical Mixture Rules

A SERIES of mixture rules has been proposed for determining the refractive index of a dispersed substance, n_p, indirectly, from measurements of the refractive index of the total dispersed system, n_t, and of the refractive index of the medium of dispersion, n_m. Except for a few rules of minor significance, they are:

Newton, theoretical:

$$n_t^2=\varphi_m n_m^2+\varphi_p n_p^2, \tag{1}$$

Lorenz-Lorentz, theoretical:

$$\frac{n_t^2-1}{n_t^2+2}=\varphi_m\frac{n_m^2-1}{n_m^2+2}+\varphi_p\frac{n_p^2-1}{n_p^2+2}, \tag{2}$$

Wiener, theoretical:

$$\frac{n_t^2-n_m^2}{n_t^2+u}=\varphi_p\frac{n_p^2-n_m^2}{n_p^2+u}, \tag{3}$$

Lichtenecker, empirical:

$$\log n_t=\varphi_m \log n_m+\varphi_p \log n_p, \tag{4}$$

Avogadro-Biot-Beer-Landolt-Christiansen-Wintgen, empirical:

$$n_t=\varphi_m n_m+\varphi_p n_p. \tag{5}$$

φ_m and φ_p are the respective volume fractions. The term u in Eq. (3) is a function of the shape of the particles. $u=2n_m^2$, if the particles are spherical. Equation (3) is then identical with Eq. (2).

A large series of experiments by various authors has shown that the "refractive increment" $(n_t-n_m)/c$—in which c is the weight concentration of the particles—is practically independent of c in dilute colloidal solutions. *A priori*, the empirical Eq. (5) appears therefore to be most suited for colloidal systems. All equations are tested in Table I in which n_p is calculated for colloidal sulphur.[1]

In addition to being empirical, Eq. (5) has a second disadvantage, which is shared also by the other mixture rules: both n_t and n_m must be known. If they are determined in two separate experiments, small temperature differences will play a role, because they affect the values of n_t, n_m, and φ.

TABLE I. Refractive indices of S at room temperature.

Experimental values (Mean) (From *International Critical Tables*)	Values calculated for infinite dilution from mixture rules (Assumed density: 2.000)				
	Eq. (1)	Eqs. (2, 3)	Eq. (4)	Eq. (5)	Eq. (9)
2.085	1.885	2.267	2.184	2.008	1.992

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[1] Since sulphur is only slightly lyophilic, the medium of dispersion should have little effect upon n_p, i.e., it should be expected that $n_{p\,\mathrm{exp}}=n_{p\,\mathrm{calc}}$.

It appeared desirable, therefore, to develop a new mixture rule which has a theoretical foundation and which allows the direct use of differential refractometric data.

B. The New Mixture Rule

A mixture rule which meets the two requirements can be derived easily on the basis of the two principal theories developed on light-scattering. There is, on the one hand, the well-known theory of Rayleigh[2] and Mie,[3] in which light scattering is considered as an effect due to material units. As a consequence, n_p enters into the equations developed, in addition to n_m. On the other hand, there is the theory of Smoluchowski[4] and Einstein[5] in which light scattering is considered as an effect due to fluctuations, fluctuations in density in liquids and fluctuations in concentration in liquid mixtures. More complete equations for liquid mixtures and solutions have been derived by Raman[6] who takes into account in these systems both fluctuations in density and in concentration. Light scattering due to fluctuations in density is negligible compared to light scattering due to fluctuations in concentration, if the solutions are colloidal. This special case has been considered recently by Debye.[7] In the equation at which Debye arrives, the refractive index of the particles obviously does not enter, but n_t enters in addition to n_m.

A mixture rule can therefore be obtained by combining the equation of Rayleigh and the equation of Debye. This can be achieved by a simple transformation of the former equation. The classical formulation of the Rayleigh equation is

$$R=\frac{24\pi^3}{\lambda^4}\left(\frac{a^2-1}{a^2+2}\right)^2 \nu v^2 I_0, \tag{6}$$

where R is the Tyndall radiation, I_0 the intensity of the incident primary beam, $a=n_p/n_m$, ν the number of the light scattering particles per cm^3, v the volume of these particles, and λ the wave-length in the medium. The quantities R and I_0 which are inconvenient for the present purpose can be replaced by considering rather the decrease in intensity of the primary beam during its passage through the light scattering system. Since the light intensity can be defined as the energy incident upon the unit surface area per unit time, the absolute loss in intensity (I_0-I) has the dimension erg$\times$cm$^{-3}\times$sec.$^{-1}=$g$\times$cm^{-1} $\times$sec.$^{-3}$. Since the light radiation has the dimension, erg$\times$sec.$^{-1}$, it follows that the Tyndall radiation, which is proportional to the volume illuminated, has also the dimension g$\times$cm^{-1} $\times$sec.$^{-3}$. Consequently, the absolute loss in intensity $(I_0-I)=R$ (whenever the decrease in intensity of the primary beam is due exclusively to coherent light scattering), and the fractional decrease in intensity over unit distance:

$$\tau=\frac{I_0-I}{I_0}=\frac{24\pi^3}{\lambda^4}\left(\frac{a^2-1}{a^2+2}\right)^2 \nu v^2. \tag{6a}$$

After substituting the wave-length in vacuum, λ_0, for λ and after replacing the ratio, a, by differences of the refractive indices involved, the transformed equation:

$$\tau=\frac{24\pi^3}{\lambda_0^4}\,\frac{n_m^4(n_p^2-n_m^2)^2}{(n_p^2+2n_m^2)^2}\,\varphi v, \tag{6b}$$

is obtained, which is suitable for the present purpose. Debye's equation, on the other hand, is:

$$\tau=\frac{32\pi^3}{3\lambda_0^4}\,n_m^2(n_t-n_m)^2\frac{1}{\nu}. \tag{7}$$

Upon combining (6b) and (7) the mixture rule

$$n_{p(8)}{}^2=\frac{n_m^3+2bn_m^2(n_t-n_m)}{n_m-b(n_t-n_m)} \tag{8}$$

is obtained where

$$b=2/3\varphi.$$

Compared to Eq. (5), the measurement of n_t is replaced by a differential measurement (n_t-n_m) under elimination of temperature errors. The advantage of the differential measurement may be expected to be particularly pronounced in very dilute solutions where (n_t-n_m) is very small. Such solutions are not likely to give reliable results unless differential measurements are carried out.

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[2] Lord Rayleigh, Phil. Mag. **41**, 107, 274, 447 (1871); **44**, 28 (1897); **47**, 375 (1899).

[3] G. Mie, Ann. d. Physik **25**, 377 (1908); P. Debye, Thesis, Munich (1908).

[4] M. v. Smoluchowski, Ann. d. Physik **25**, 205 (1908).

[5] A. Einstein, Ann. d. Physik **33**, 1275 (1910).

[6] C. V. Raman and K. R. Ramanathan, Phil. Mag. **45**, 213 (1923); see also R. Gans, Zeits. f. Physik **17**, 371 (1923).

[7] P. Debye, J. App. Phys. **15**, 338 (1944).

TABLE II. Magnitude of error in calculations of refractive indices from Eq. (8).

$n_{p(8)}-n_m$	$n_{p(8)}$ if $n_m=1.333000$	Errors occur in the
0.00235–0.00775	1.33535–1.34075	6th decimal
0.00775–0.0245	1.34075–1.3575	5th decimal
0.0245 –0.082	1.3575 –1.415	4th decimal
0.082 –0.225	1.415 –1.588	3rd decimal
0.225 –0.750	1.588 –2.083	2nd decimal
0.750 –2.18	2.083 –3.51	1st decimal

C. The Limits of Validity of the New Mixture Rule

The theory of Rayleigh-Mie has been verified repeatedly,[8] i.e., particle sizes determined on the basis of the equation developed by Mie, of which the Rayleigh Eq. (6) is a special case, were found to be in quantitative agreement with the actual particle sizes. Similarly, the equation of Debye has been verified.[9] There can therefore be no doubt that the new mixture rule is valid for systems which satisfy the assumptions involved in the two theories on light scattering: Eq. (6) is based on the assumption that the difference (n_p-n_m) is very small; Eq. (7) is based on the assumption that fluctuations in density are negligible compared to fluctuations in concentration. Equation (8) should, therefore, be valid, if (n_p-n_m) is very small and if the dispersed particles (crystals or molecules) are large enough to scatter considerably more light than the molecules of the medium. The former condition can be fulfilled by choosing the right medium. The latter condition is fulfilled in colloidal solutions. It is not fulfilled in liquid mixtures nor in solutions of small molecules or ions.

Both Eqs. (6) and (7) presuppose that the dispersed systems are dilute and that the light scattering particles are small as compared to the wave-length used, that they are spherical and isotropic. However, identical correction factors would have to be introduced into either equation in order to make them applicable to systems of moderate concentration and to large or non-spherical or intrinsically anisotropic particles. Consequently, these partly unknown correction factors are cancelled out in the combination of Eqs. (6) and (7) to Eq. (8). No influence of the size or shape of colloidal particles upon $n_{p(8)}$ should therefore be expected unless the refractive index actually varies with the size and shape of the particles, an experimentally unknown effect which might be found, however, in a spectral region near an absorption band.[10] Neither should the colloid concentration have any effect on $n_{p(8)}$ as long as the concentration is small enough so as not to affect the refractive indices themselves. The probable error involved in calculations of $n_{p(8)}$ and as due to the finite value of (n_p-n_m) is compiled in Table II. (The error is obtained by a procedure discussed below.) The error occurs in the fifth or fourth decimal, if $(n_{p(8)}-n_m)$ has a value not in excess of 0.025 and 0.082, respectively.

D. Another Formulation of the New Mixture Rule

Upon reviewing the present paper, Professor Debye drew the author's attention to another simple possibility of deriving the result expressed by Eq. (8). The same result can be obtained by calculating (Clausius-Mosotti) what the dielectric constant is of a medium in which a sufficiently small number of spheres of different dielectric constant is dispersed.

According to Debye, the result expressed by the new mixture rule can be formulated as follows:

$$\alpha=\Delta/(1+\tfrac{1}{3}\Delta), \tag{8a}$$

or

$$\Delta=\alpha/(1-\tfrac{1}{3}\alpha). \tag{8b}$$

The quantity

$$\Delta=\frac{n_p^2-n_m^2}{n_m^2},$$

and the quantity

$$\alpha=2\frac{(n_t-n_m)/n_m}{\varphi}.$$

It is assumed, as in the case of Eqs. (6) and (7) that the dielectric constant $\epsilon=n^2$. Equations (8a) and (8b) check, of course, with Eq. (8).

E. Application of the New Mixture Rule Outside of the (n_p-n_m) Range of Satisfactory Validity

It is sometimes not possible to select the medium in which (n_p-n_m) is sufficiently small in

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[8] E.g., Niels Pihlblad, Thesis; Uppsala (1918).

[9] W. Heller and H. B. Klevens, Phys. Rev. **67**, 61 (1945).

[10] W. Heller, Comptes rendus **205**, 971 (1937).

Table III. Refractive indices in hydrosols.

Dispersed substance	$\varphi \times 10^2$	n_t	n_m	$n_{p(8)}$	$n_{p(9)}$	$n_{p(5)}$	$(n_{p(8)}-n_{p(5)}) \times 10^3$	$(n_{p(9)}-n_{p(5)}) \times 10^3$
SiO_2	3.075	1.33705	1.3325	1.4837	1.4805	1.4803	3.4	0.2
SiO_2	0.5815	1.33353	1.3325	1.5144	1.5097	1.5099	4.5	−0.2
Egg albumin	3.10	1.33946	1.3325	1.5651	1.5571	1.5571	8.0	0.0
Gelatin	3.10	1.34110	1.3332	1.5988	1.5882	1.5881	10.7	0.1
Hg-sulfosalicylic acid	2.323	1.34388	1.3330	1.8457	1.8014	1.8015	44.2	−0.1
AlOOH	1.047	1.33789	1.3325	1.9035	1.8472	1.8471	56.4	0.1
ThO_2	1.609	1.34302	1.3325	2.0893	1.9834	1.9863	103.0	−2.9
S	3.805	1.35917	1.33408	2.0985	1.9901	1.9934	105.1	−3.3
S	0.395	1.33592	1.33329	2.1070	1.9956	2.0000	107.0	−4.4
TiO_2	0.373	1.33657	1.3325	2.8599	2.3518	2.4236	436.5	−71.8
TiO_2	7.577	1.41991	1.3325	3.0080	2.3878	2.4861	521.9	−98.3

Table IV. Refractive indices at various sol concentrations. I. SiO_2—sol.

$\varphi \times 10^2$	n_t	n_m	$n_{p(8)}$	$n_{p(9)}$	$n_{p(5)}$	$(n_{p(8)}-n_{p(5)}) \times 10^3$	$(n_{p(9)}-n_{p(5)}) \times 10^3$
0.5815	1.33353	1.3325	1.5144	1.5097	1.5099	4.5	−0.2
0.8626	1.33394	1.3325	1.5037	1.4995	1.4990	4.7	0.5
1.0213	1.33421	1.3325	1.5042	1.5000	1.5000	4.2	0.0
1.3155	1.33469	1.3325	1.5032	1.4991	1.4990	4.2	0.1
1.6076	1.33514	1.3325	1.5008	1.4968	1.4966	4.2	0.2
1.9460	1.33561	1.3325	1.4962	1.4924	1.4923	3.9	0.1
2.5815	1.33634	1.3325	1.4846	1.4813	1.4813	3.3	0.0
3.0751	1.33705	1.3325	1.4837	1.4805	1.4803	3.4	0.2

Table V. Refractive indices at various sol concentrations. II. S—sol.

g S/100 cc	n_t	n_m	$n_{p(8)}$	$n_{p(9)}$	$n_{p(5)}$	$(n_{p(8)}-n_{p(5)}) \times 10^3$	$(n_{p(9)}-n_{p(5)}) \times 10^3$
0.79	1.33592	1.33329	2.1070	1.9956	2.0000	107.0	−4.4
1.59	1.33871	1.33338	2.1136	2.0001	2.0038	109.8	−3.7
2.72	1.34256	1.33347	2.1108	1.9982	2.0022	108.6	−4.0
3.81	1.34612	1.33364	2.0921	1.9856	1.9890	103.1	−3.4
4.23	1.34755	1.33370	2.0918	1.9854	1.9887	103.1	−3.3
4.76	1.34933	1.33375	2.0915	1.9852	1.9882	103.3	−3.0
5.44	1.35171	1.33384	2.0949	1.9875	1.9908	104.1	−3.3
6.34	1.35473	1.33394	2.0933	1.9865	1.9899	103.4	−3.4
7.61	1.35917	1.33408	2.0985	1.9901	1.9934	105.1	−3.3

Table VI. Refractive indices in methyl-ethylketon-sols.

Dispersed substance	$\varphi \times 10^2$	n_t	n_m	$n_{p(8)}$	$n_{p(9)}$	$n_{p(5)}$	$(n_{p(8)}-n_{p(5)}) \times 10^3$	$(n_{p(9)}-n_{p(5)}) \times 10^3$
Acetylcellulose	1.047	1.37899	1.3778	1.4933	1.4914	1.4919	1.4	−0.5
Acetylcellulose	7.277	1.38711	1.3778	1.5080	1.5056	1.5057	2.3	−0.1
Nitrocellulose	2.746	1.37841	1.3741	1.5346	1.5309	1.5310	3.6	−0.1

order to make the probable error negligible. This is particularly true in the case of colloids which are stable only in one medium, e.g., in an aqueous medium. A selection of the medium is excluded also in those cases where the value of n_p shall be used for obtaining information on the approximate degree of solvation (hydration) of the particles in a particular medium. The probable error will then often not be negligible. For example, if water is the medium, the error will most often be in the fourth or third decimal if the dispersed substance is a liquid or a solid respectively.

A survey on the variation of the error with (n_p-n_m) is given in Table III for aqueous colloidal systems. Experimental data on n_p and n_m

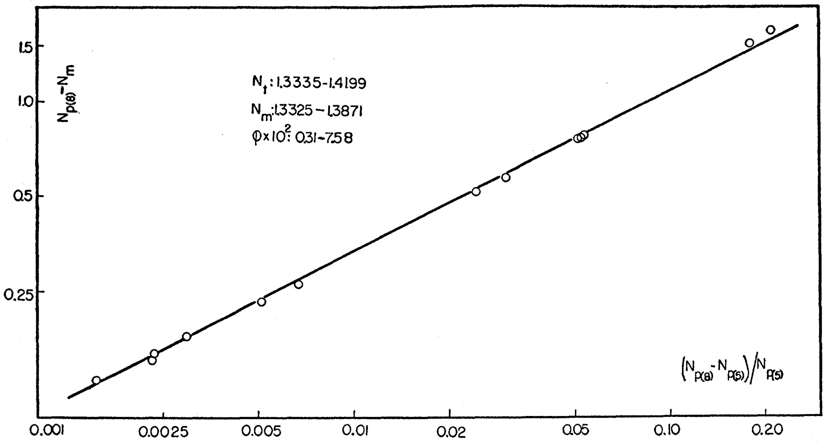

FIG. 1. (Wherever N appears in the figure n should be substituted.)

as obtained by Freundlich and Rogowski[11] and by Odén[12] are used. It is assumed that the n_p-values obtained by means of Eq. (5), $n_{p(5)}$, are correct in a first approximation and that consequently the difference $(n_{p(8)}-n_{p(5)})$ can be taken as an approximate criterion on the error committed in applying Eq. (8) in the case of large (n_p-n_m) values.

An inspection of Table III shows that the log of the fractional discrepancy $(n_{p(8)}-n_{p(5)})/n_{p(5)}$ is a linear function of the log of $(n_{p(8)}-n_m)$. This relationship is plotted in Fig. 1 which contains data of the Tables IV and V. From Fig. 1 the empirical function

$$n_{p(9)}=\frac{n_{p(8)}}{0.093(n_{p(8)}-n_m)^{1.99}+1} \tag{9}$$

is obtained. The use of this correction equation reduces the discrepancy considerably if $(n_{p(8)}-n_m)$ assumes large values. For small $(n_{p(8)}-n_m)$ values, on the other hand, the use of the correction equation is not advisable.

F. Influence of the Colloid Concentration

The influence of the colloid concentration is tested in Tables IV and V, the latter referring to a case where $(n_{p(8)}-n_m)$ is far too large to give reliable results by means of Eq. (8) alone. In either of the two systems, the calculated n_p increases somewhat with decreasing colloid concentration. The increase is the same whether Eq. (8) or the equation combination (9) or Eq. (5) are used. It is therefore advisable to calculate n_p for infinite dilution. Differential measurements of (n_t-n_m) as directly used in Eq. (8) are the only procedure which will allow one to obtain the most accurate n_p for $\varphi\to0$.

G. The Influence of the Absolute n_m-Values

Careful refractometric measurements on nonaqueous colloidal solutions are scarce. A few data of Freundlich and Rogowski are used in Table VI. The comparison of these data with those of Table III seems to indicate that the absolute value of n_m has no influence upon the validity of Eq. (8). No influence was to be expected.

II. DETERMINATION OF REFRACTIVE INDICES FROM "ABSORPTION" MEASUREMENTS

Equation (6b) can be transformed to

$$n_p^2=n_m^2\frac{n_m^2+2f}{n_m^2-f}, \tag{10}$$

where

$$f=\frac{\lambda_0^2}{2}\left(\frac{\tau}{6\pi^3v\varphi}\right)^{\frac{1}{2}}=\frac{\lambda_0^2p}{2m}\left(\frac{\tau}{6\pi^3\nu}\right)^{\frac{1}{2}}=\frac{\lambda_0^2p}{2}\left(\frac{\tau}{6\pi^3mc}\right)^{\frac{1}{2}}$$

(m: the mass of a particle, p its density, c the concentration, in g cm^{-3}). Since

$$I/I_0=\tau-1,$$

the refractive index n_p can be determined from

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[11] H. Freundlich and F. Rogowski, Kolloid Beih. **37**, 215 (1933).

[12] S. Odén, Zeits. f. physik. Chemie **80**, 735 (1912).

measurements of the apparent (conservative) absorption without any refractometric measurement being necessary, in the case of known n_m, provided only that the particle weight (molecular weight), the density and the concentration of the particles are known. Since data on the two latter quantities must be known also if any of the preceding mixture rules are to be applied, the practical difference of Eq. (10) compared to the earlier ones is that the n_t or (n_t-n_m) measurement is replaced by an absorption measurement. This practical difference defines the cases where the use of Eq. (10) is of particular practical interest (very turbid systems or very opaque particles).

This alternate principle of n_p determinations is restricted, of course, to application under the well-known conditions (particle size, particle shape, colloid concentration, and value of (n_p-n_m)) for which the Rayleigh equation is valid. If all conditions are met except the condition of spherical shape and of isotropy, Eq. (10) may still be applied, however, by introducing the Cabannes factor.[13] This means that τ must be replaced by

$$\tau\frac{1-(7/6)\delta}{1+0.5\delta},$$

where the depolarization factor $\delta=i_{\parallel}/i_{\perp}$ ($i_{\perp}$ is the intensity of the "Rayleigh component" which vibrates perpendicular to the plane of observation and $i_{\parallel}$ is the intensity of the orthogonal component).

APPENDIX—OPTICAL DETERMINATION OF DENSITIES

The density of colloidal particles is generally determined by pyknometric methods or by methods of floating. In some instances, it may be of advantage to substitute optical methods for these methods. There are several possibilities which are implied in equations given in preceding sections of this paper.

The transformation of Eq. (5) leads to

$$\rho_p=\rho_m\frac{w_p}{w_m}\frac{n_p-n_t}{n_t-n_m}=\rho_t\frac{w_p}{w_t}\frac{n_p-n_m}{n_t-n_m}, \qquad (11)$$

where w is the weight in g. The use of this equation differs from the use of the conventional Eq. (12) (case of exclusive pyknometric determinations of ρ_p)

$$\rho_p=\frac{w_p}{w_t/\rho_t-w_m/\rho_m} \qquad (12)$$

by the substitution of two gravimetric-volumetric data, e.g., of w_m and ρ_m by two refractometric data (n_t-n_m) and n_p. Both Eqs. (11) and (12) should be valid on the assumption of additivity and of negligible volume contraction.

More interesting appears the relation

$$\rho_p=\frac{3}{2}c\frac{n_m(n_p^2-n_m^2)}{(n_t-n_m)(n_p^2+2n_m^2)}, \qquad (13)$$

which is obtained by transformation of Eq. (8). This equation makes it possible to determine densities exclusively from refractometric data, provided, of course, that the concentration is known. The application of Eq. (13) is subject to the restrictions imposed on the use of Eq. (8).

If the particle weight (molecular weight) and the light scattering power of the dispersed substance is known, then part of the refractometric data may be replaced by data on turbidity (absorption). This is possible by transforming Eq. (6b) to:

$$\rho_p=\frac{24\pi^3}{\lambda_0^4}\frac{n_m^4(n_p^2-n_m^2)^2}{(n_p^2+2n_m^2)^2}\frac{m}{\tau}\varphi, \qquad (14)$$

or

$$\rho_p=\frac{2}{\lambda_0^2}n_m^2\frac{n_p^2-n_m^2}{n_p^2+2n_m^2}\left(\frac{6\pi^3cm}{\tau}\right)^{\frac{1}{2}}. \qquad (14a)$$

Equations (13) and (14) have the disadvantage of requiring that n_p is known. This will often be a deterrent to using them in the place of Eq. (12).

This disadvantage can be avoided by using rather a transformation of Eq. (7)

$$\rho_p=\frac{3\lambda_0^4}{32\pi^3}\frac{\tau}{n_m^2(n_t-n_m)^2}\frac{c}{v}, \qquad (15)$$

which requires that the volume of the particles (molecules) is known.

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[13] J. Cabannes, Ann. de physique **15**, 5 (1921); *La diffusion moléculaire de la lumière* (Paris, 1929). See also P. Debye, reference 7.