BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1689—1694 (1966)

Theoretical Studies of the Use of the Double Extrapolation Method to Determine the Forward Scattering of Light by Spherical Colloidal Particles

By Masayuki NAKAGAKI

Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto

(Received December 16, 1965)

An application of the double extrapolation method (the Zimm-plot method) for the reduced intensity of light scattered by colloidal dispersions, instead of polymer solutions, is discussed theoretically on the basis of the Mie theory. The correction factor, F, required to recalculate the experimental value of the molecular weight, M_R, to the true value, M ($M=FM_R$), is equal to unity in the case of the Rayleigh scattering ($\alpha\to 0$) and the Rayleigh-Gans-Debye (R-G-D) scattering ($|m-1|\to 0$, where m is the relative refractive index of the sphere to the medium). Usually, however, the value of F is not equal to unity, but is found to be given by an empirical equation, $F=1-0.155\,Q+bQ^{1.5}$, where Q is a quantity proportional to the reduced specific scattering intensity at $\theta\to 0$. For the determination of the radius of gyration from the "initial slope," the R-G-D equation is applicable even in cases where $|m-1|$ is not small. In order to determine the true molecular weight from the molecular weight, M_τ, obtained from the specific turbidity at the infinite dilution, the factor Φ is needed ($M=\Phi M_\tau$). The factor Φ is considered to be a product; that is, $\Phi=F\,\varphi$, where the factor φ seems to be independent of the m value. The empirical equation obtained was $\varphi=1+0.537\,\alpha^{2.08}$

In the studies of the light scattering of polymer solutions, a double extrapolation method, the so-called Zimm-plot method, is used extensively in order to determine the molecular weight, the radius of gyration, and so forth, according to the Debye theory. The method gives the molecular weight from the scattered light intensity doubly extrapolated to the forward direction ($\theta\to 0$) and to an infinite dilution ($c\to 0$). However, the application of the double extrapolation method to colloidal dispersions is justified only when the light scattering of the systems can be treated according to either the Rayleigh theory ($\alpha\to 0$) or the Rayleigh-Gans-Debye (to be abbreviated as R-G-D) theory ($|m-1|\to 0$). The method must not be applied, without corrections, to the colloidal systems for which neither $\alpha\to 0$ nor $|m-1|\to 0$ holds.

In the present paper,[1] the values of the correction factors to be used for colorless colloidal spheres are calculated according to the Mie theory, since the author believes that the application of the double extrapolation method in the studies of colloidal dispersions is useful because, first, the use of the scattered light intensity in the forward direction ($\theta\to 0$) has the theoretical advantage that maxima and minima on the curve of the scattered light intensity vs. the particle radius occur less frequently in the forward direction than in any other direction,[2] and because, second, it is convenient to use the experimental technique which is used so extensively in the studies of the polymer solutions.

Double Extrapolation Method.—The double extrapolation method is usually based on the following equation, derived by Debye[3] and modified by Zimm[4]:

$$Kc/R_u(\theta) = 1/MP(x) + 2A_2c \tag{1}$$

where c is the concentration; $P(x)$ is the interference factor; M is the molecular weight of the polymer

1) Presented at the 18 th Annual Meeting of the Chemical Society of Japan, Kansai University, Osaka, April, 1965.

2) W. Heller, M. Nakagaki and M. L. Wallach, *J. Chem. Phys.*, **30**, 444 (1959).
3) P. Debye, *J. Appl. Phys.*, **15**, 338 (1944).
4) B. H. Zimm, *J. Chem. Phys.*, **16**, 1093 (1948).

or the colloid particle; A_2 is the second virial coefficient, and $R_u(\theta)$ is the reduced scattering intensity for unpolarized incident light;

$$R_u(\theta) = (r^2 I_u/I_0)/(1+\cos^2\theta) \quad (2)$$

and K is a constant defined by:

$$K = (2\pi^2/\boldsymbol{N_A}\lambda^4\mu_1^2)(\mathrm{d}\mu_{12}/\mathrm{d}c)^2 \quad (3)$$

Here $(r^2 I_u/I_0)$ is the Rayleigh ratio, r is the photometric distance; I_0 is the intensity of the incident light; I_u is the intensity of the scattered light at the scattering angle, θ; $\boldsymbol{N_A}$ is the Avogadro number; μ_{12} is the refractive index of the solution or dispersion, and λ is the wavelength of light in the medium, which is related to the wavelength in the vacuum, λ_0, and the refractive index of the medium, μ_1, according to the relation:

$$\lambda = \lambda_0/\mu_1 \quad (4)$$

In the double extrapolation method named the Zimm-plot method, the value of $Kc/R_u(\theta)$ is taken on the ordinate and the value of $\sin^2(\theta/2)+kc$ is taken on the abscissa, where k is an arbitrary constant. The data are extrapolated to an infinite dilution, and a curve for $c\to 0$ is drawn. This curve corresponds to the equation:

$$Kc/R_u(\theta) = 1/MP(x) \quad (5)$$

where x is defined by the equations:

$$x = 2\alpha\sin(\theta/2) \quad (6)$$

and

$$\alpha = 2\pi a/\lambda \quad (7)$$

Here, a is the radius of a spherical colloidal particle. A further extrapolation to $\theta\to 0$ yields an apparent value of molecular weight, M_R, according to the equation:

$$Kc/R_u(0) = 1/M_R \quad (8)$$

The value of M_R is, in general, not equal to the molecular weight, M. The factor F is, therefore, required in order to obtain the value of M from the value of M_R:

$$M = F\cdot M_R \quad (9)$$

If Eq. 5 is used,

$$F = 1/P(0) = MKc/R_u(0) \quad (10)$$

where $P(0)$ is the value of $P(x)$ at $x\to 0$ or $\theta\to 0$.

Theoretical Value of the Factor F.—The reduced scattering intensity for unpolarized incident light is given theoretically by the following equation:

$$R_u(\theta) = (\lambda^2/8\pi^2)Ni_T(\theta)/(1+\cos^2\theta) \quad (11)$$

where N is the number of particles per unit of volume and where:

$$i_T(\theta) = 2i_u(\theta) = 2(4\pi^2/\lambda^2)(r^2 I_u/I_0)/N \quad (12)$$

The numerical value of $i_T(\theta)$ calculated according to the Mie theory[5] has been given by Pangonis and Heller[6] for colorless spherical particles. In order to calculate the value of K according to Eq. 3, the value of $(\mathrm{d}\mu_{12}/\mathrm{d}c)$ is required. The latter can be expressed by the equation:

$$\mathrm{d}\mu_{12}/\mathrm{d}c = (m'-1)\mu_1/\rho_2 \quad (13)$$

where ρ_2 is the density of the particles and m' is the apparent relative refractive index. The theoretical values of m' calculated for colorless spherical particles according to the Mie theory have been given by Nakagaki and Heller.[7] Using these values, together with the equations:

$$c = (\lambda^3/6\pi^2)\rho_2 N\alpha^3 \quad (14)$$

$$M = (\lambda^3/6\pi^2)\rho_2 N_A\alpha^3 \quad (15)$$

Eq. 10 can be rewritten as:

$$F = (8/9)(m'-1)^2\alpha^6/i_T(0) \quad (16)$$

In the case of the Rayleigh scattering,

$$F = 1 \quad (\alpha\to 0) \quad (17a)$$

is obtained from Eq. 16, because

$$i_T(0) = 2i_u(0) = 2[(m^2-1)/(m^2+2)]^2\alpha^6 \quad (17b)$$

and[7]

$$m'-1 = (3/2)(m^2-1)/(m^2+2) \quad (17c)$$

where m is the relative refractive index of the sphere to the medium.

In the case of the R-G-D scattering, the intensity of the scattered light is equal to the Rayleigh value multiplied by $P(x)$, where:

$$P(x) = 9(\sin x - x\cos x)^2/x^6 \quad \text{(R-G-D)} \quad (18)$$

Since $P(0)=1$, the value of F given by Eq. 10 is:

$$F = 1 \quad (|m-1|\to 0) \quad (19)$$

Therefore, the apparent molecular weight, M_R, obtained by the double extrapolation method[8] is equal to the true molecular weight, M, if either $\alpha\to 0$ or $|m-1|\to 0$ holds.

The theoretically calculated values of F for general cases ($\alpha\neq 0$ and $m\neq 1$) are shown in Fig. 1, where the quantity, Q, taken on the abscissa is a quantity proportional to the reduced specific scattering, $R_u(\theta)/c$, at $\theta\to 0$; that is:

$$Q = (8\lambda\rho_2/3)R_u(0)/c \quad (20)$$

Here the proportionality factor $(8\lambda\rho_2/3)$ is a constant for a given particle and a given wavelength. Therefore, the value of Q can be obtained

5) G. Mie, *Ann. Phys.*, (4), **25**, 377 (1908).

6) W. J. Pangonis and W. Heller, "Angular Scattering Functions for Spherical Particles," Wayne State University Press, Detroit (1960).

7) M. Nakagaki and W. Heller, *J. Appl. Phys.*, **27**, 975 (1956).

8) In the case of the random coil of high polymer molecules, it may also be concluded that $F=1$ and $M_R=M$, because $P(0)=1$ if the segments are considered to be Rayleigh spheres, where $P(x)=(2/x^4)[\exp(-x^2)-(1-x^2)]$.

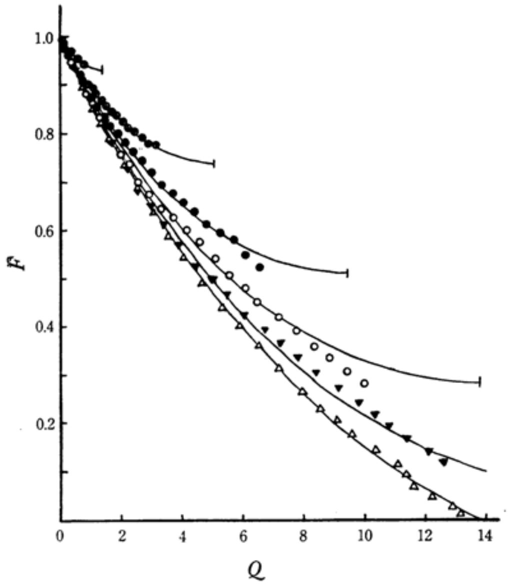

Fig. 1. Relation between F and Q. m=1.05 (⊗), 1.10 (⊕), 1.15 (●), 1.20 (○), 1.25 (▼), and 1.30 (△)

experimentally. On the other hand, the theoretical value of Q is;

$$Q = i_T/\alpha^3 \tag{21}$$

It may be seen from Fig. 1 that an appreciable error will be introduced if the correction factor, F, is not used.

An empirical equation to find the value of F from the experimental value of Q was looked for. The equation obtained is:

$$F = 1 - 0.155\,Q + bQ^{1.5} \tag{22}$$

where;

$$b = 0.0115 + 0.00310(m - 1.01) \tag{23}$$

The solid lines of Fig. 1 show the values obtained from these empirical equations. The equations cannot be used, however, when Q is greater than Q^*;

$$Q^* = 0.01068/b^2 \tag{24}$$

The values of Q^* are shown in Fig. 1 by short vertical lines.

Initial Slope.—The double extrapolation method is used to determine the radius of gyration or the radius of the particles, besides the molecular weight or particle weight. In determining radius, the initial slope of the experimental curves drawn by taking $Kc/\mathrm{R}_u(\theta)$ on the ordinate and $\sin^2(\theta/2)$ on the abscissa is used. It is, therefore, necessary to understand thoroughly what the theory will predict about the shape of the curves for spherical colloidal particles. For this purpose, a quantity, ξ, proportional to the $Kc/R_u(\theta)$ is used:

$$\xi = [Kc/R_u(\theta)]/[Kc/R_u(0)] \tag{25}$$

where $kc/R_u(0)$ is constant for a given colloidal system, as has been discussed above. On the other hand, the theoretical values of ξ can be calculated according to the relationship:

$$\xi = [i_T(0)/i_T(\theta)][(1 + \cos^2\theta)/2] \tag{26}$$

The results of the calculation are shown in Fig. 2 for m=1.20 and in Fig. 3 for m=1.30.

According to Eq. 5, it is obvious that the following equation holds:

$$\xi = P(0)/P(x) = 1/FP(x) \tag{27}$$

Therefore, in the case of the Rayleigh scattering, ξ=1, and in the case of the R–G–D scattering:

$$\xi = 1/P(x) = x^6/9(\sin x - x\cos x)^2 \tag{28}$$

In Figs. 2 and 3, the R-G-D values, too, are shown by the solid curves; the broken lines show the initial slope, and the dotted lines show the range of deviation from the R-G-D values. From these figures, it was concluded that the initial slope is

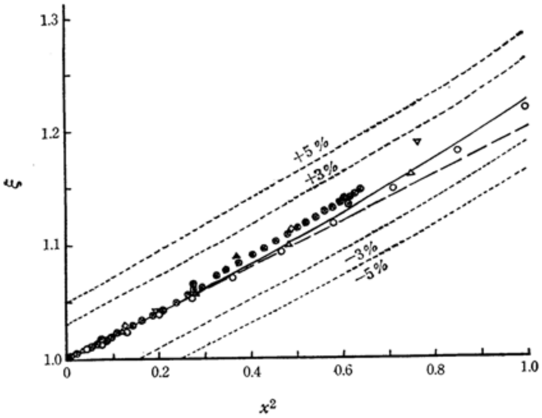

Fig. 2. Relation between ξ and x^2 for m=1.20. α=0.4 (⊗), 1.0 (○), 2.0 (△), 3.0 (⊙), 4.0 (◇), 5.0 (▽), 6.0 (⊕), and 7.0 (▲).

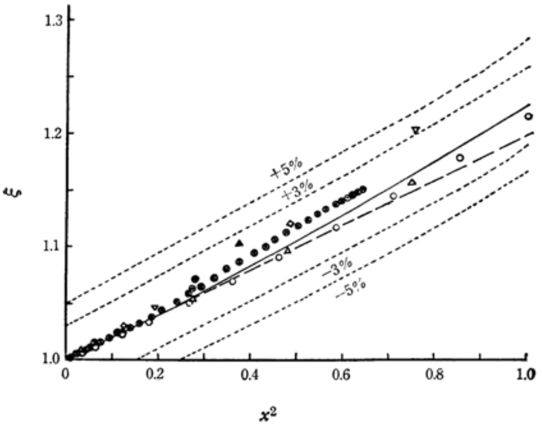

Fig. 3. Relation between ξ and x^2 for m=1.30. α=0.4 (⊗), 1.0 (○), 2.0 (△), 3.0 (⊙), 4.0 (◇), 5.0 (▽), 6.0 (⊕), and 7.0 (▲)

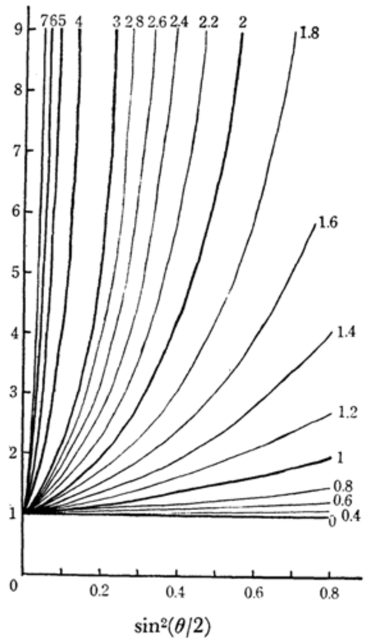

Fig. 4. Relation between ξ and $\sin^2(\theta/2)$ for various α-values.

approximated well enough by the R-G-D equation, irrespective of the values of m and α, if, at least, $m \leq 1.30$, $\alpha \leq 7.0$, and $x \leq 1.0$.

From the experimental point of view, however, it may be worthwhile to point out that the quantity to be taken on the abscissa is not x^2 but $\sin^2(\theta/2)$. This means that the scattering angle to make the value of x small enough is very small when the particle size or α is large, as may readily be understood from Eq. 6. The relation between ξ and $\sin^2(\theta/2)$, instead of x^2, is shown in Fig. 4 for the R-G-D scattering and for various α values. It may be seen that measurements in the range of very small θ values are required for the determination of the "initial" slope when α is large. The measurement of the scattering at such a small angle will be possible after the development of an apparatus which can provide a very narrow incident beam.

Extrapolated Values of Specific Turbidity. —In the studies of polymer solutions, Eq. 1 for the reduced scattering intensity, $R_u(\theta)$, is used exclusively. In the studies of colloidal dispersion, however, the turbidity, τ, may be used instead of the reduced scattering intensity, because the turbidity of the colloidal dispersions is not so small as that of polymer solutions, even in a fairly dilute concentration range.

It is well known historically that Debye's fluctuation theory was, at first, applied to the turbidity, τ, resulting in:

$$Hc/\tau = 1/M_\tau + 2A_2c \tag{29}$$

This equation was, then, rewritten to Eq. 1, by replacing the turbidity with the reduced scattering intensity and H with K, where:

$$H = (16\pi/3)K \tag{30}$$

The latter is an equation justifiable only in the case of the Rayleigh scattering ($\alpha \ll 1$).

If the particles are not so small that the Rayleigh theory does not hold, the molecular weight, M_τ, obtained by Eq. 29, or by the equation:

$$M_\tau = (1/H)(\tau/c)_0 \tag{31}$$

is not equal to the true molecular weight, M. Here, $(\tau/c)_0$ is the specifice turbidity at an infinite dilution. A factor Φ, just like the factor F in Eq. 9, is required to obtain M from M_τ:

$$M = \Phi M_\tau \tag{32}$$

The factor Φ may be considered to be a product of the above-mentioned factor, F, and another factor, φ:

$$\Phi = F\varphi \tag{33}$$

where:

$$\varphi = M_R/M_\tau \tag{34}$$

The theoretical expression of φ is given by:

$$\varphi = (16\pi/3)R_u(0)/\tau = (2/3)i_T(0)/\sum \tag{35}$$

where $\sum$ is a quantity related to the turbidity by the equation:

$$\tau = (\lambda^2/2\pi)N\sum \tag{36}$$

Numerical values of the factor φ can be calculated for colorless spherical particles according to Eq. 35 and by using the numerical values of $\sum$ given by Pangonis, Heller and Jacobson,[9] together with the numerical values of $i_T(0)$ already mentioned.[6] The numerical values of Φ, too, can be calculated according to Eq. 33 by using the values of F obtained above. The resulting Φ values are shown in Fig. 5 as a function of Q_τ. Here, the quantity Q_τ is defined as a quantity proportional to the specific turbidity at the infinite dilution $(\tau/c)_0$ by the following equation;

$$Q_\tau = (\lambda\rho_2/3\pi)(\tau/c)_0 \tag{37}$$

and the theoretical values of Q_τ can be obtained according to the following relation:

$$Q_\tau = \sum/\alpha^3 \tag{38}$$

In the case of the Rayleigh scattering ($\alpha \to 0$ or $Q_\tau \to 0$):

$$\varphi = 1, \quad \Phi = 1 \quad (\alpha \to 0) \tag{39a}$$

are obtained from Eq. 35, since the following equation:

$$\sum = (4/3)[(m^2-1)/(m^2+2)]^2\alpha^6 \tag{39b}$$

holds, besides Eqs. 17a and 17b.

9) W. J. Pangonis, W. Heller and A. Jacobson, "Tables of Light Scattering Functions for Spherical Particles," Wayne State University Press, Detroit (1957).

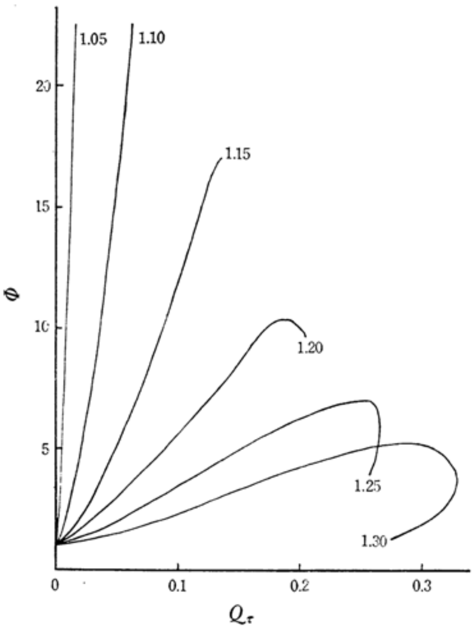

Fig. 5. Relation between Φ and Q_τ for various m-values.

On the other hand, a theoretical equation corresponding to Eq. 5 is also known:

$$Hc/\tau = 1/M\Pi \quad (c \to 0) \tag{40}$$

where Π is given by an integral containing $P(x)$:

$$\Pi = (3/4)\int_0^\pi [(1+\cos^2\theta)/2]P(x)\sin\theta\, d\theta \tag{41}$$

By reference to Eq. 32, it is obvious that:

$$\Pi = 1/\Phi \tag{42}$$

In the case of the Rayleigh scattering, Eq. 39a may be concluded from Eqs. 41 and 42, because $P(x)=1$ in this case.

In the case of the R-G-D scattering ($|m-1| \to 0$), Eq. 41 was solved, together with $P(x)$ of Eq. 18. The result:

$$\begin{aligned}\Pi = (27/64\alpha^4)\{&-7(1-\cos 4\alpha)/8\alpha^2 \\ &-(\sin 4\alpha)/2\alpha+5+4\alpha^2 \\ &+[(1/\alpha^2)-4][\gamma+\ln 4\alpha-\mathrm{Ci}(4\alpha)]\}\end{aligned} \tag{43}$$

was already known, and its numerical values, too, had been given.[10,11] Therefore, according to Eqs. 19 and 43, it may be concluded that:

$$\Phi = \varphi = 1/\Pi \quad (|m-1| \to 0) \tag{44}$$

When Eq. 44 is drawn on Fig. 5, the curve coincides with the ordinate, because $Q_\tau \to 0$ if $|m-1| \to 0$.

Usually the relation between Φ and Q_τ is expressed by the rather complicated curves shown in Fig. 5. The complication arises because the Φ quantity is a product of F and φ. Since F has already been discussed it is important now to study how simple the relations between φ vs. m and α will be. As the result of the numerical calculations, it is found that the value of φ scarcely depends at all on the m-value, at least in the range of $m \leq 1.30$ and $\alpha = 0.4$—7.0. This empirical conclusion is important, because it also states that the ratio between the reduced scattering intensity in the forward direction ($\theta \to 0$) and the turbidity is independent of the m-value (cf. Eq. 35), and that the forward scattering is, therefore, more important than the scattering at $\theta = 90°$, although the latter has been used extensively in various experimental works.

Since the independence of φ from m holds even when $|m-1| \to 0$, the relation between φ and α should be given by:

$$\varphi = 1/\Pi \tag{45}$$

For Π, Eq. 43 is used as a fairly good approximation for various m values (at least for $m \leq 1.30$, and very probably for higher m-values also), although this statement has not yet been justified theoretically. Equation 43 is, however, rather complicated. It is, therefore, of some interest to find a simple empirical relation between φ and α. According to Fig. 6, the following one seems to be acceptable:

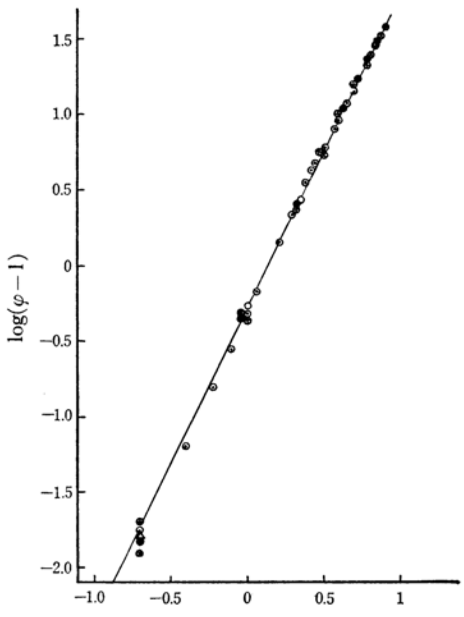

Fig. 6. Relation between $\log(\varphi-1)$ and $\log\alpha$. $m=1.05$ (⊗), 1.10 (⊕), 1.15 (●), 1.20 (○), 1.25 (▼), and 1.30 (△).

10) Lord Rayleigh, *Proc. Roy. Soc.*, **A84**, 25 (1911); **A90**, 219 (1914).
11) R. M. Tabibian, W. Heller and J. N. Epel, *J. Colloid Sci.*, **11**, 195 (1956); M. Nakagaki, *Kagaku no Ryoiki*, **12**, 287 (1958).

$$\varphi = 1 + 0.537\,\alpha^{2.08} \tag{46}$$

The independence of φ from m is a natural consequence if the relation between ξ and x^2 is independent of m, as has been stated above, although the latter statement might not hold for larger x-values.