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Gouy Interferometry: Properties of Multicomponent System Omega Graphs

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Gouy Interferometry: Properties of Multicomponent System Omega (Ω) Graphs[1]

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Abstract We consider the properties of Ω graphs (Ω vs $f(z)$) obtained from Gouy interferometry on multicomponent systems with constant diffusion coefficients. We show that they must have (a) either a maximum or else a minimum between $f(z)=0$ and $f(z)=1$ and (b) an inflection point between the $f(z)$ value at the extremum and $f(z)=1$. Consequently, an Ω graph cannot have both positive *and* negative Ω values.

Keywords: Diffusion●Gouy interferometry●omega graphs●Rayleigh interferometry●multicomponent systems

1. Introduction

Optical methods are the most precise methods of obtaining diffusion coefficients in liquid mixtures **[1]**. Of these, Gouy and Rayleigh interferometry with "free diffusion" boundaries have been developed the most. In the past, groups at Lawrence Livermore National Laboratory, Texas Christian University, and the University of Naples have reached a precision of 0.05 to 0.1 % for binary systems. Ternary and quaternary system diffusion coefficients can also be obtained but with lesser precision. The experimental techniques for such measurements, including illustrations of the optical arrangements and typical interference patterns, have been detailed in references **[1,2]**.

The most precise optical interferometer, the Gosting Diffusiometer **[3]**, now at Texas Christian University, has both Gouy and Rayleigh optics. When it was at Lawrence Livermore National Laboratory from 1981 to 1991, comparisons showed essentially the same diffusion coefficients were obtained from using both methods after alternately applying both optical systems to each experiment **[2,4,5]**.

At present, the University of Naples group is using Gouy interferometry, and the Texas Christian University group is using Rayleigh interferometry. Since the 1990s, both groups have automated their data collection, which has significantly improved the precision and statistics.

The Gouy method was the first precision optical method developed for binary systems **[6]**. Its first application to 3-component systems was by Fujita and Gosting **[7,8]**. Fujita and Gosting **[8]** extracted the ternary diffusion coefficients D_{ij} from the fringe pattern data of several experiments, using from each experiment the quantity D_A and a quantity Q_0 that is the integral of the Ω graph. The quantity Ω was originally defined by Gosting and collaborators **[7-9]**, and the Ω graph is a plot of Ω versus $f(z)$, both defined below. Experimental examples of the Ω graph can be seen in early papers **[7,9-11]**. Unfortunately, the FG method, while excellent for ternary systems, is not suited to 4 or more component systems **[12]**.

During our ternary Gouy measurements at LLNL in Livermore, the appearance of Ω graphs came into question. Gosting and Fujita **[13]** had shown earlier that all Ω values should be 0 for a *binary* system without a concentration dependence of the diffusion coefficient. Consequently, a non-zero Q_0 implied a concentration-dependent diffusion coefficient. They also analyzed a binary system with a polynomial dependence of D on concentration C. They showed that if the concentration differences across the boundary are *small* enough, then D will correspond to the mean concentration at the boundary, Ω will also be zero everywhere, and thus Q_0 will be 0.

However, it was an open question whether Q_0 could be zero for a system where Ω was positive part way between $f(z)$=0 and $f(z)$=1, and balanced by being negative the rest of the way. We shall show here that this cannot be the case.

For 3 or more components, Ω in general should be non-zero, except for special concentration-difference ratios. In our *ternary* experiments, the Ω values seemed to be either all zero, all positive, or else all negative. However, occasionally there seemed to be cases where Ω values sometimes came below the horizontal line of Ω=0. When Ω was small, frequently the scatter of Ω from the different fringe patterns seemed to be responsible. When Ω values were large, there seemed to be some other error, usually an error in the measured total number of fringes J. Furthermore, there seemed to be a possible inflection point, also indicated in some of the early Ω graphs obtained by others **[9,11,14]**.

Simplified algebraic simulations of possible shapes for the Ω graph are shown in **Fig. 1**. Case 1 has a maximum without any inflection points. Case 2 has a maximum with an inflection point (here, after the maximum). Case 3 has Ω above and below the line of Ω=0, and thus a maximum and a minimum. These oversimplified drawings also include the equally oversimplified first and second derivatives of Ω with respect to $f(z)$.

Other variants are possible, for example with minimums instead of maximums or with multiple extrema, but Cases 1-3 are closest to the observed Ω graphs. Although Case 3 is shown as being symmetric, it is also conceivable to have variants of Cases 1 and 2 that dip below the $f(z)$=0 line closer to the ends, giving rise to an unsymmetric Case 3. However, we shall show below that this is not possible, and such cases when encountered must involve some type of experimental error.

Consequently it seemed desirable to investigate the detailed properties of the Ω graph. Fujita and Gosting **[8]** defined the quantity Ω_j for a particular interference fringe j as

$$\Omega_j = \mathrm{e}^{-z_j^2} - \frac{\sum_i \Gamma_i \, s_i \, \mathrm{e}^{-(s_i y_j)^2}}{\sum_i \Gamma_i \, s_i} \qquad (1)$$

or alternatively

$$\Omega_j = \mathrm{e}^{-z_j^2} - D_A^{1/2} \sum_i \Gamma_i \, s_i \, \mathrm{e}^{-(s_i y_j)^2} \qquad (2)$$

where D_A is an experimental quantity called the "height-area ratio" **[8]**, i is the index for the (n - 1) solutes, and j is the fringe number index.

The quantities s_i are related to the eigenvalues of the diffusion coefficient matrix **[7,12,15]**, and are functions only of the volume-fixed diffusion coefficients D_{kl}, where here k and l are the solute indexes. The Γ_i are functions of the D_{kl}, refractive index increments R_i, and refractive index fractions α_i. These quantities are described in Ref. **[1,2,7,12,15]**. The refractive index fractions depend on the solute concentration differences across the diffusion boundary, so are different for each experiment. Consequently, the Γ_i and in turn D_A are also different for each experiment. Thus the shape of the Ω graph depends on the Γ_i, as will be seen in **Fig. 2** below.

The $f(z_j)$ mentioned above is given for each fringe j by **[8,10]**

$$f(z_j) = erf(z_j) - \frac{2 z_j \, \mathrm{e}^{-z_j^2}}{\pi^{1/2}} \qquad (3)$$

and also by **[8,10]**

$$f(z_j) = \sum_i \Gamma_i \, f(s_i y_j) \qquad (4)$$

It is related to experimental quantities by

$$f(z_j) = \frac{j + 3/4 + \ldots}{J} \qquad (5)$$

where the + in the numerator includes an improved approximation **[8-10]**. The numerical value of $f(z_j)$ is obtained from Eq. (5) for each fringe using the fringe number j and the total number of fringes J. Then z_j is determined from $f(z_j)$ by iteration of Eq. (3), and y_j are in turn obtained by iteration from Eq. (4).

The quantities z_j, y_j, $f(z_j)$, and Ω_j are usually obtained from experimental data at round values of the measured fringe numbers j but all are actually continuous functions. The values of $f(z_j)$ run from 0 to 1 as z_j and y_j run from 0 to infinity.

We note in passing that the ternary data analysis method for Rayleigh interferometry was developed later **[2,16,17]** than for Gouy, and the D_{kl} are obtained from parameters extracted directly from fringe position data using least squares methods. An analogous Rayleigh Ω graph and Q_0 are not useful. This type of Rayleigh analysis is easily extended to any number of components **[12]**, and has been applied to a 4-component system **[18]**. It can also be adapted to non-interferometric solid-state measurements **[19]**. An analogy to the Rayleigh analysis has also been adapted to 3 or more component Gouy measurements **[12]**, and has also been applied to a 4-component system **[20]**. In this case, the Gouy Ω graph and Q_0 are not used to obtain the D_{kl}, but become useful diagnostic tools. In particular, if Q_0 is large for any of the concentration-difference ratios, that implies a large cross-term diffusion coefficient.

2. Examination of possible shapes of the Ω graph

We consider the Ω graph for an arbitrary but specific experiment.

We treat Ω as a continuous function and examine its first and second derivatives with respect to $f(z)$. The following analysis depends on the diffusion coefficients being constant. This will be the case if the concentration differences across the free-diffusion boundary are small, as is usual in both Gouy and Rayleigh measurements. (See ref. **[19]** for a brief discussion.)

The first derivative of Ω with respect to $f(z)$ is found implicitly by differentiating the first term of Eq. (2) with dz and the second term with dy. Then dz and dy are eliminated in terms of $df(z)$ by the derivatives of Eq. (3) and (4). The desired derivative Ω' is

$$\Omega' = \frac{d\Omega}{df(z)} = \frac{\pi^{1/2}}{2}\left[\frac{D_A^{1/2}}{y} - \frac{1}{z}\right] \qquad (6)$$

Maxima and minima occur where $\Omega'=0$. There are only two roots, one at

$$\frac{y}{z} = D_A^{1/2} \qquad (7)$$

The other is approached asymptotically as y and z go to infinity (together), i.e., where $f(z)=1.0$:

$$y=z=\infty; \quad f(z)=1.0 \qquad (8)$$

For certain values of Γ_i, it is possible for Ω to be 0 everywhere, and thus $\Omega'=0$ everywhere.

Equation (7) shows that there can only be a single maximum or minimum between $f(z)$ values of 0.0 and 1.0 whenever $\Omega\neq 0$ everywhere. Since the equations above apply to a system of *any number of components*, case 3, symmetric or otherwise, is impossible.

On the other hand, the Ω' root at $f(z)=1.0$ requires that as $f(z)$ increases, Ω' must pass through 0 at the $f(z)$ point corresponding to Eq. (7), and then turn back, itself going through a maximum or minimum, and returning to zero at $f(z)=1.0$. Consequently the second derivative Ω'' must have a root (i.e., be 0) between the maximum or minimum of Ω and $f(z)=1.0$. But this means that there must be an inflection point in the plot of Ω versus $f(z)$ after its maximum or minimum and before $f(z)=1.0$. Consequently case 1 is also impossible, and this conclusion also applies to a system of any number of components.

We have now shown that only case 2 is possible. Furthermore, either Ω must be zero everywhere or else must (a) have an extremum, (b) be either positive or else negative everywhere, and (c) have an inflection point between the extremum and $f(z)$=1.0. Consequently, if any Ω graph crosses the Ω=0 line, there must be a calculational or experimental error.

Whether the extremum is a maximum or minimum depends on the sign of the second derivative of Ω at the root of Ω'. We get this second derivative by differentiating Eq. (6), and eliminating its resulting dy and dz terms using Eq. (3) and (4) to get everything in terms of $df(z)$, just as we did in getting Ω'. The result is

$$\Omega'' = \frac{d^2\Omega}{df(z)^2} = \frac{d\Omega'}{df(z)} = \frac{\pi}{8}\left[\frac{-D_A^{1/2}}{y^4 \sum_i \Gamma_i s_i^3 \mathrm{e}^{-(s_i y)^2}} - \frac{1}{z^4\,\mathrm{e}^{-z^2}}\right] \qquad (9)$$

At the extremum of Ω, the value of Ω'' is given by substituting Eq. (7) in Eq. (9), which gives

$$\Omega''(extremum) = \frac{\pi}{8z^4}\left[\frac{1}{\mathrm{e}^{-z^2}} - \frac{1}{D_A^{3/2}\sum_i \Gamma_i\, s_i^3\, \mathrm{e}^{-(s_i y)^2}}\right] \qquad (10)$$

The values of y and z are those at the extremum, and so one or the other can be eliminated by using Eq. (7). If Eq. (10) is negative then Ω has a maximum, and if positive then Ω has a minimum. Experience shows that both cases exist.

We note that at the other root of Ω', $y=z=\pm\infty$. The sign depends on the sign of the bracket in Eq. (10) at high values of z and y.

Let's turn to the inflection point, which is located at Ω''=0. From Eq. (9), this point is at

$$\left[\frac{-D_A^{1/2}}{y^4 \sum_i \Gamma_i s_i^3 e^{-(s_i y)^2}} - \frac{1}{z^4\, e^{-z^2}}\right] = 0 \qquad (11)$$

Numerical examples show that values of y and z exist such that there is an $f(z)$ between the Ω extremum and $f(z)$=1.0. Typically it is close to $f(z)$=1.0.

3. Examples of the Case 2 shapes

Fig. 2 shows three calculated Ω graphs for a ternary system with choices of s_i and three choices of Γ_1 modeled on experimental data for raffinose-KCl-H_2O **[4]**. (There is only one independent Γ_i for a ternary system, because it has been shown **[7,8]** that the sum of the Γ_i =1.0.) We note that D_A is a function of both s_i and Γ_l **[7,8]**. We have also calculated the Q_0 and Q_1 associated with the three graphs. (Q_1 is another integral that was once proposed for Gouy analyses by Fujita **[21]**, but has not actually been used.) Note that the 1st and 2nd derivatives for the model of a real system are far more complicated than the oversimplified illustration of Case 2 in **Fig. 1**.

We notice that the graph shapes depend on Γ_l, and the locations of the extremum and inflection point for each change with Γ_l. The inflection point is sufficiently slight for the third drawing that only the second derivative makes it clear that it exists.

4. Conclusions

We have shown for a multicomponent system that the Ω graph must have (a) either a maximum or else a minimum between $f(z)$=0 and $f(z)$=1 and (b) an inflection point between the $f(z)$ value at the extremum and $f(z)$=1. Consequently Case 1 and Case 3 cannot occur. If Ω changes sign with $f(z)$, there must be an error in the measurements or a wrong value of the total number of fringes J. Indeed, our experience with the highly accurate Gosting diffusiometer has always been that when an Ω graph has values both above and below the horizontal Ω=0 line, typically near $f(z)$=1, a wrong value of J had been used in the data analysis.

We note that it is possible for certain values of the Γ_i to have Ω=0 everywhere (and thus Ω'=0 everywhere), in which case the multicomponent diffusing system appears to act like a binary system.

Two final comments.

If the D_{ij} values for multicomponent systems have a concentration dependence, will small enough concentration differences across the boundary give effectively constant diffusion coefficients so our analysis will apply? The general case of a linear concentration dependence is not yet available. However, theoretical results for ternary systems, discussed in Ref. **[19]**, strongly suggest that this is true.

Three or more component systems can have both gravitational and dynamic instabilities for some refractive index fractions. Will those give rise to unusual Ω graphs? In these circumstances, the Gouy fringes are distorted **[22]**. Consequently, the experiment will be rejected, and the issue does not arise.

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footnote 1: This article is dedicated to Joseph. A. Rard, a friend, colleague, and outstanding experimentalist.

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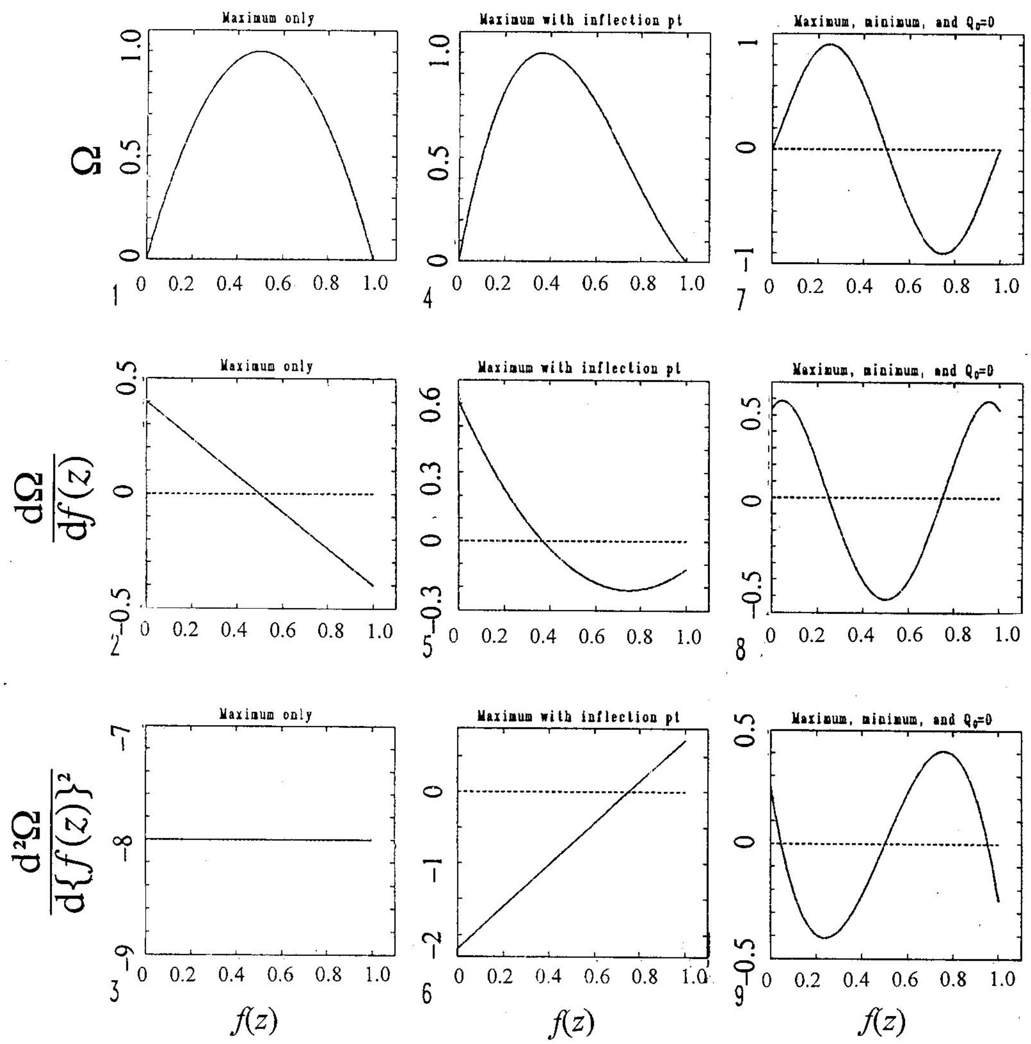

Fig. 1. Simplified algebraic simulations of possible shapes for the *Ω* graph. Case 1 (left column) has a maximum without any inflection points. Case 2 (center column) has a maximum with an inflection point (here, after the maximum). Case 3 (right column) has *Ω* values above and below the line of *Ω*=0, and thus a maximum and a minimum. The first row is *Ω*, the second is the first derivative *Ω*′, and the third is *Ω*″.

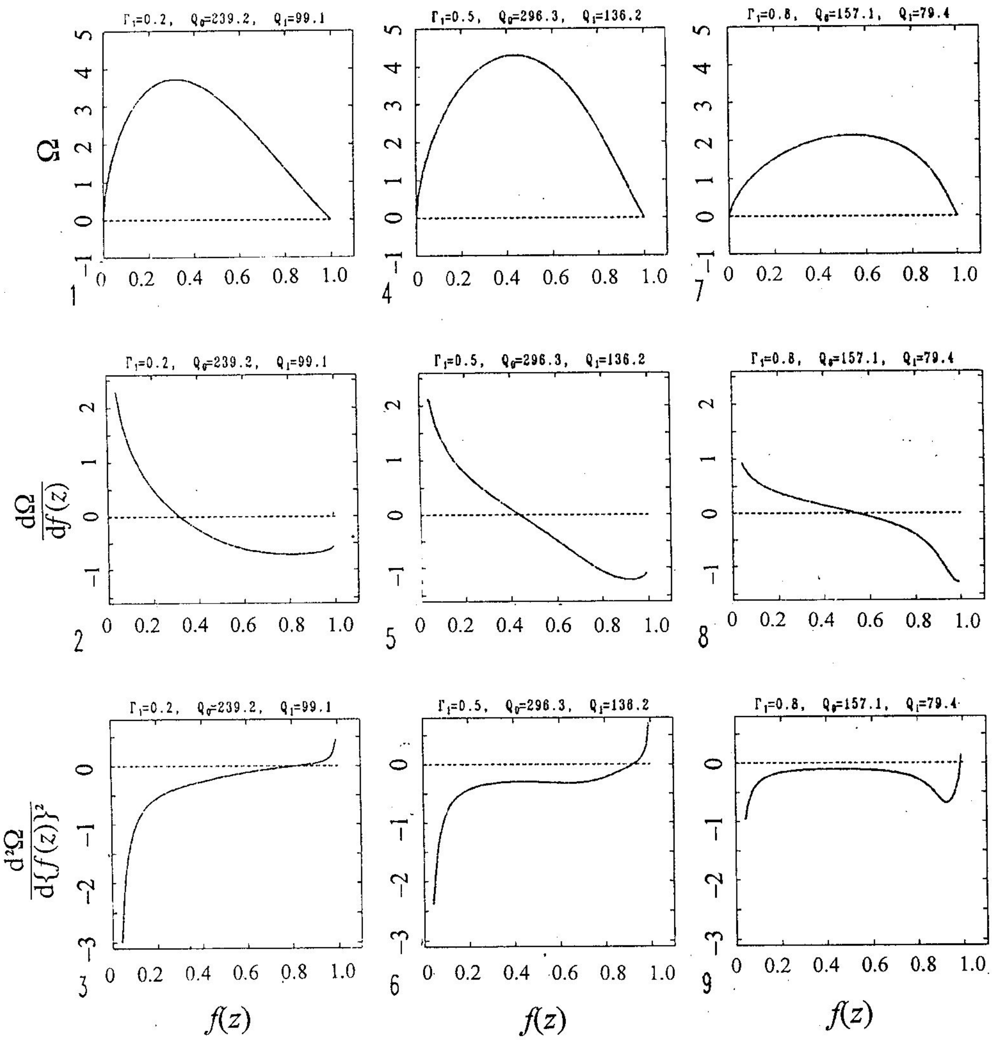

Fig. 2. Three calculated Ω graphs for a ternary system modeled on experimental data for raffinose-KCl-H_2O **[4]**, with its values of s_i and three choices of Γ_1. We note that D_A is a function of both s_i and Γ_1 **[7,8]**. We have also calculated the Q_0 and Q_1 associated with the three graphs (Q_1 is not used here.) Column 1 has Γ_1=0.2 with a corresponding Q_0=239.2. Column 2 has Γ_1=0.5 and Q_0=296.3. Column 3 has Γ_1=0.8 with a corresponding Q_0=157.1. Rows 1-3 are Ω, Ω', and Ω'', respectively. Note the complicated forms of Ω' and Ω'' when based on experiment.