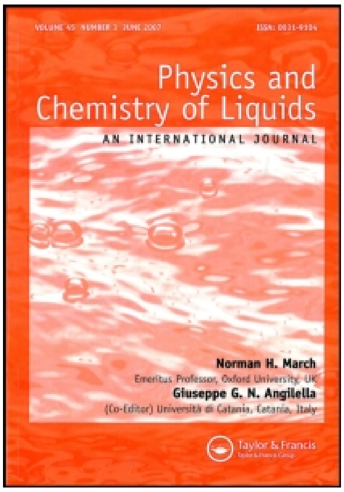

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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Michael Weinberg[a]
[a] Corporate Research Laboratories, Owens-Illinois, Technical Center, Toledo, Ohio

To cite this Article Weinberg, Michael(1974) 'Light scattering: landau-placzek ratio and total intensity', Physics and Chemistry of Liquids, 4: 2, 163 — 170
To link to this Article: DOI: 10.1080/00319107408084282
URL: http://dx.doi.org/10.1080/00319107408084282

Phys. Chem. Liq., 1974, pp. 163-170

Printed in Dordrecht, Holland

Light Scattering: Landau-Placzek Ratio and Total Intensity

MICHAEL WEINBERG

Corporate Research Laboratories, Owens-Illinois, Technical Center, Toledo, Ohio 43601.

(Received July 3, 1973)

The total light scattering intensity and the Landau-Placzek ratio are calculated, via thermodynamic arguments, from a model system representative of a single component relaxing fluid or a reactive binary mixture. Comparison is made with both previous thermodynamic calculations of the Landau-Placzek ratio and the results obtained from integration of the intensity distribution. In addition, the fluctuations of the dielectric constant are calculated, under varying conditions placed upon the dielectric constant, and the resulting expressions are discussed within the context of earlier works.

I. INTRODUCTION

The total light scattering intensity and the ratio of total central intensity to shifted intensity for a single component fluid was established many years ago.[1,2] Furthermore, these quantities have also been calculated for multicomponent fluids.[3,4] In recent years advances in experimental techniques have allowed detailed investigations of light scattering spectrum. Consequently, an interest has arisen in examining the details of the light scattering spectrum from more complex systems, such as multicomponent chemically reactive and relaxing fluids.[5] It will be the purpose of this work to compare the total scattering intensity and ratio of shifted to unshifted intensity for the latter systems with the type studied earlier. Furthermore, comparisons will be made with certain dynamical calculations wherever is appropriate.

It should be made clear from the outset that the results to be presented are valid only for a simple model system chosen. It is assumed that the local equilibrium ensemble appropriate for the description of a small subvolume is that one appropriate for an ordinary two component fluid. Furthermore, it is assumed that any relaxation process or chemical decay occurs slowly compared to the hydrodynamic decay.[6,7] Thus, one may envision the system under consideration as being either a binary mixture undergoing a slow chemical reaction or a single component system with a slow relaxation process. Several examples of such systems will be presented in the concluding section, however here it should be stressed that this system serves as a prototype for more complicated ones that have been investigated.[8,9]

In the following section the total light scattering intensity and ratio of intensities (Landau-Placzek ratio) will be calculated for the model system with several conditions placed upon the dependence of ϵ, the dielectric constant, on various thermodynamic quantities.

In the concluding section a discussion of the results presented in Section II will be given, and a comparison will be made to previous works. Finally, some comments will be made about the model system chosen.

II. THE TOTAL SCATTERING INTENSITY AND THE LANDAU-PLACZEK RATIO

Within this section the total light scattering intensity and Landau-Placzek ratio will be calculated for the system outlined above. For the present it will be assumed that $\left(\frac{\partial\epsilon}{\partial c}\right)_{n,T} = 0$; here c represents a concentration variable and n and T are density and temperature, respectively. The scheme of the calculation will be as follows. The fluctuations will be calculated as for a two component system, in both the case of a single component relaxing fluid as well as for the two component chemically reactive mixture. Since consideration is being given only to the case of small fluctuations, the thermodynamic derivatives that appear will be given, approximately, by their equilibrium values. However, at total equilibrium there exists a constraint, namely one of chemical equilibrium, which does not exist at some intitial time, t=0, in a small subvolume. Hence, as will subsequently become apparent the light scattering characteristics of this model system are in general different from a non-relaxing or rapidly relaxing single component fluid or a binary mixture which is unreactive. Specific comparisons will be made for the total intensity and the Landau-Placzek ratio in several cases.

The total light scattering intensity is proportional to fluctuations in the dielectric constant. In the usual manner, one may express these fluctuations in terms of fluctuations of other thermodynamic variables. Using the above condition $\left(\frac{\partial\epsilon}{\partial c}\right)_{n,T} = 0$, one may write

$$\Delta\epsilon = \left(\frac{\partial\epsilon}{\partial n}\right)_{T,c} \Delta n + \left(\frac{\partial\epsilon}{\partial T}\right)_{n,c} \Delta T \qquad (2.1)$$

Initially, the assumption that $\left(\frac{\partial \epsilon}{\partial T}\right)_{n,c} = 0$ will also be made. It is evident that in this case the light scattering intensity is proportional to the density fluctuations alone. Making use of Eq. (2.1) and the Landau and Lifshitz fluctuation theory,[10] it is easy to show that

$$<|\Delta\epsilon|^2> = \left(\frac{\partial \epsilon}{\partial n}\right)^2_{T,c} \left[\frac{n}{V} k_B T \left(\frac{\partial n}{\partial p}\right)_{T,c} + \frac{k_B T \left(\frac{\partial n}{\partial c}\right)^2_{T,p}}{\left(\frac{\partial \mu}{\partial c}\right)_{T,p}}\right] \qquad (2.2)$$

In the above equation k_B is Boltzmann's constant, μ is the chemical potential, and p is the pressure. With a bit of algebraic manipulation one can show that Eq. (2.2) agrees with the results obtained by Miller[4] if one invokes identical conditions upon the dielectric constant in the latter's work. Now one may use the fact that at equilibrium the affinity is zero. Following a procedure outlined by Mountain,[11] but using the variables T, p, and c, it can be shown that the above equilibrium condition leads to the relationship

$$\frac{n}{V} k_B T \left(\frac{\partial n}{\partial p}\right)_{T,c} = \frac{n}{V} k_B T \left(\frac{\partial n}{\partial p}\right)_T - \frac{\left(\frac{\partial n}{\partial c}\right)^2_{T,p} k_B T}{\left(\frac{\partial \mu}{\partial c}\right)_{T,p}} \qquad (2.3)$$

Using Eq. (2.3) in Eq. (2.2) one obtains,

$$<|\Delta\epsilon|^2> = \left(\frac{\partial \epsilon}{\partial n}\right)^2_{T,c} \frac{n}{V} k_B T \left(\frac{\partial n}{\partial p}\right)_T \qquad (2.4)$$

In the event that the system is only undergoing thermal relaxation or $\left(\frac{\partial p}{\partial c}\right)_{n,T} = 0$, then Eq. (2.4) is readily obtained from this condition and Mountain's Eq. (38a).[11]

One should note that two different types of partial derivatives appear in Eq. (2.3). Those with two subscripts are of the frozen equilibrium type while in the single subscript derivative the extent of reaction is not held constant. Alternatively, one may view Eq. (2.3) as providing a relationship between the fluctuations in two different type of systems; namely a reactive mixture and a pure fluid. Furthermore, it is easy to show that if one calculated the fluctuations in the dielectric constant from the "equilibrium system" directly (i.e., as a one component fluid), then one would obtain the expression given in Eq. (2.4.). This result has been assumed for the relaxation problem, although it is not at all an obvious result for the case of a slowly occurring general relaxation process. In addition, as one shall now see, if the temperature dependence of the dielectric constant becomes of importance, then, in general, agreement will not be found between an "equilibrium" calculation of $<|\Delta\epsilon|^2>$ and the method outlined in this work. The "equilibrium" calculation of the dielectric constant fluctuations yields,

$$<|\Delta\epsilon|^2>^{eq.} = \left(\frac{\partial\epsilon}{\partial n}\right)^2_{T,c} <|\Delta n|^2>^{eq.} + \left(\frac{\partial\epsilon}{\partial T}\right)^2_{n,c} \frac{k_B T}{\left(\frac{\partial S}{\partial T}\right)_n} \tag{2.5}$$

where S denotes the entropy and the superscript indicates the "equilibrium" calculation mentioned in the above. On the other hand, employing the "frozen" state calculation in conjunction with the equilibrium condition one finds,

$$<|\Delta\epsilon|^2> = \left(\frac{\partial\epsilon}{\partial n}\right)^2_{T,c} <|\Delta n|^2>^{eq.} + \left(\frac{\partial\epsilon}{\partial T}\right)^2_{n,c} \frac{k_B T}{\left(\frac{\partial S}{\partial T}\right)_{n,c}} \tag{2.6}$$

The difference between the two expressions for the dielectric constant fluctuations is exhibited solely in the appearance of the equilibrium constant volume specific heat in Eq. (2.5) and the frozen constant volume specific heat in Eq. (2.6). Thus, one may conclude that in the case of a relaxing system the fluctuations in the dielectric constant may be calculated in the usual way (in terms of "equilibrium" thermodynamic fluctuations) only under special circumstances. On the other hand, for a chemically reactive system the equilibrium condition simplifies the expression for the total intensity from the frozen value, appropriate for an unreactive two component system, and also only reduces to a one component form under certain conditions.

It is also of considerable interest to show that the Landau-Placzek ratio for the case of a slow relaxation may be calculated in the thermodynamic manner. If the variables S, p, and c are employed then application of the fluctuation formulas yield

$$\frac{I_c}{2I_B} = \frac{\left(\frac{\partial n}{\partial S}\right)^2_{c,p} k_B C_p{}^f + k_B T \left(\frac{\partial n}{\partial c}\right)^2_{T,p} / \left(\frac{\partial \mu}{\partial c}\right)_{T,p}}{\left(\frac{n}{V} k_B T\right) \left(\frac{\partial n}{\partial p}\right)_{S,c}} \tag{2.7}$$

In the above $C_p{}^f$ is the "frozen" constant pressure specific heat and $I_c/2I_B$ is the ratio of the unshifted (or central) intensity to the shifted intensity. In the case of pure thermal relaxation the second term in the numerator of Eq. (2.7) vanishes. After a bit of manipulation one obtains,

$$\frac{I_c}{2I_B} = \gamma_t - 1 \text{ (Thermal Relaxation)} \tag{2.8}$$

where $\gamma_t = C_p{}^f / C_v{}^f$

This result is identical to the one obtained by Mountain[12] and Stegeman, Gornall, Volterra, and Stoicheff[6] via calculations of the integrated intensity. In the general case,

$$\frac{I_c}{2I_B} = \gamma_t - 1 + \frac{\beta_T^0 - \beta_T^\infty}{\beta_S^\infty} \tag{2.9}$$

Here β_T^0, β_T^∞ and β_S^∞ are the zero frequency isothermal compressibility, infinite frequency isothermal compressibility, and infinite frequency adiabatic compressibilities, respectively.

In the case of a single component relaxing system it is a good approximation to neglect $\left(\frac{\partial\epsilon}{\partial c}\right)_{n,T}$. However, for a chemically reactive system $\left(\frac{\partial\epsilon}{\partial c}\right)_{n,T}$ may be non-negligible and must be considered in the expression for the total light scattering intensity. Once again calculating the fluctuations in the dielectric constant, as outlined in the beginning of this section, one obtains

$$\langle|\Delta\epsilon|^2\rangle = \left(\frac{\partial\epsilon}{\partial n}\right)^2_{T,c}\langle|\Delta n|^2\rangle^{eq.} + 2\left(\frac{\partial\epsilon}{\partial n}\right)_{T,c}\left(\frac{\partial\epsilon}{\partial c}\right)_{T,n}\cdot\left[\left(\frac{\partial c}{\partial n}\right)_T\langle|\Delta n|^2\rangle^{eq.}\right] + \left(\frac{\partial\epsilon}{\partial c}\right)^2_{n,T}\left[\left(\frac{\partial c}{\partial n}\right)^2_T\langle|\Delta n|^2\rangle^{eq.} + \frac{k_BT}{\left(\frac{\partial\mu}{\partial c}\right)_{T,n}}\right] \tag{2.10}$$

The "equilibrium" calculation gives,

$$\langle|\Delta\epsilon|^2\rangle^{eq.} = \left(\frac{\partial\epsilon}{\partial n}\right)^2_{T,c}\langle|\Delta n|^2\rangle^{eq.} + 2\left(\frac{\partial\epsilon}{\partial n}\right)_{T,c}\left(\frac{\partial\epsilon}{\partial c}\right)_{T,n}\cdot\left(\frac{\partial c}{\partial n}\right)_T\langle|\Delta n|^2\rangle^{eq.} + \left(\frac{\partial\epsilon}{\partial c}\right)^2_{T,n}\left[\left(\frac{\partial c}{\partial n}\right)^2_T\langle|\Delta n|^2\rangle^{eq.} + \left(\frac{\partial S}{\partial c}\right)_{n,T}k_BT\Big/\left(\left(\frac{\partial S}{\partial c}\right)_n\left(\frac{\partial\mu}{\partial c}\right)_{T,n}\right)\right] \tag{2.11}$$

So although the equilibrium condition allows a simplification from the two component result for the intensity (see for example Ref. 11), and the result given in Eq. (2.10) is quite close to the equilibrium value expressed in Eq. (2.11), the results will not be identical for the relaxation examples considered because of the inequality of the last term in the latter two equations.

In the event that $\left(\frac{\partial c}{\partial n}\right)_T \approx 0$, one finds a rather simple result for the ratio of intensities,

$$\frac{I_c}{2I_B} = \gamma_t - 1 + \left[\frac{\left(\frac{\partial \epsilon}{\partial c}\right)_{n,T}}{\left(\frac{\partial \epsilon}{\partial n}\right)_{c,T}}\right]^2 \frac{\gamma_t}{\left(\frac{\partial \mu}{\partial c}\right)_{n,T}\left(\frac{n^2}{V}\right)\beta_T{}^0} \tag{2.12}$$

III. DISCUSSION

In the past there has been the assumption made that the concentration fluctuations in a multicomponent reactive system will be identical to those in an unreactive multicomponent fluid.[13] On the other hand, for a relaxing system there has been the implication that the total intensity may be calculated in terms of equilibrium fluctuations just as for a single component system without a relaxation process.[12] From the results of Section II., however, the following observations may be made. The equilibrium condition which enables one to express the total light scattering intensity for a relaxing fluid, under the condition $\left(\frac{\partial \epsilon}{\partial T}\right)_{n,c} = 0$, in terms of the equilibrium density fluctuations is also responsible for the simplification of the result for the intensity of a reactive binary mixture. This simplification casts the results for the total light scattering intensity for this latter system quite close to the equilibrium calculation. In fact, the dependence of ϵ on c, in a sense, introduces the temperature fluctuations which "spoils" the exact agreement. In a quite similar manner, in a one component relaxing system (when $\left(\frac{\partial \epsilon}{\partial T}\right)_{n,c} \neq 0$) the term involving the temperature fluctuations disallows a simple "equilibrium" calculation of the total intensity. Finally, it should be emphasized that the above discussion is only valid when a thermodynamic description of the light scattering is adequate. A rapid relaxation or chemical reaction will not be amenable to this discussion.

Cummins and Gammon[14] have attempted to use thermodynamic arguments to predict the Landau-Płaczek ratio for relaxing systems. Stegeman, *et al.*,[6] have indicated the reasons for errors in early experimental measurements of the Landau-Placzek ratio, and have quite correctly shown that, in general, the distribution of spectral intensity may not be described by thermodynamic considerations. However, as was illustrated in Section II., in the limit of slow relaxation the correct Landau-Placzek ratio may be obtained via thermodynamic arguments. In addition, it is now clear why previous attempts have yielded incorrect results. The arguments used went something as follows.[15] The constant pressure fluctuations decay quite slowly so that one may use the static equilibrium fluctuations in entropy to obtain the central intensity, but one must use the "partially relaxed" or dynamic value of the adiabatic compressibility to find the rapidly decaying adiabatic fluctuations. The results of such an argument leads to an expression for the Landau-Placzek ratio such as

$$\frac{I_c}{2I_B} = \frac{\left[n^2 \left(\frac{\partial \epsilon}{\partial n}\right)_T^2 \beta_T - \beta_S\right]_{\text{static}}}{\left[n^2 \left(\frac{\partial \epsilon}{\partial n}\right)_T^2 \beta_S\right]_{\text{h.s.}}} \tag{3.1}$$

where $\beta_S{}^{\text{h.s.}} = \dfrac{1}{n\upsilon^2{}_{\text{h.s.}}}$ and $\upsilon_{\text{h.s.}}$ is the measured hypersonic velocity. As was mentioned previously, Stegeman, et al., have shown quite explicitly that $I_c/2I_B$ cannot be calculated thermodynamically in the regime where the relaxation processes does not decay very slowly (in fact in many cases there is strong overlapping of the peaks and the ratio is ill-defined). Hence, unless $\beta_S{}^{\text{h.s.}}$ is close to β_S^∞ Eq. (3.1) should be held suspect. However, even in the event that the limiting high frequency sound velocity has been reached it should be noted that Eq. (3.1) implies that the total light scattering intensity is not proportional to the equilibrium value of the density fluctuations. This invalid conclusion is arrived at due to the fact that the role of the concentration fluctuations has been ignored in evaluating the central peak.

Finally several comments will be made upon the nature of the system chosen for investigation. First, however, it should be re-emphasized that the model used was picked primarily for its simplicity, and served as a prototype to illustrate certain features concerning the light scattering from relaxing or chemically reactive fluids. On the other hand, this model could represent adequately certain simple systems. For example, a substance undergoing an isomerization reaction in which its two forms have a significantly different effective polarizability could typically represent the chemically reactive system. Most isomerizations are rapid, however, and thus one would have to consider such a reaction under conditions (perhaps low temperature) where the time scale requirements are satisfied. It is quite clear that a two level, single component, relaxing fluid is well represented by the model chosen in this work. However, one should note that this model is not restricted in its validity to merely this type of simple relaxing system. For example, it has been shown that it is applicable to a many level system under certain circumstances.[7] Finally, one may note that even if the detailed description of the spectrum is quite complicated and is not describable in terms of a single relaxation time, it is possible that the thermodynamics may be adequately described in terms of a single additional thermodynamic parameter. Currently, this work is being extended to derive expressions for the total light scattering intensity and the Landau-Placzek ratio for viscous fluids below the glass transition temperature.

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