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Abstract. The absorption and refractive index increments due to continuous distributions of resonances have been calculated for both Debye-type distributions and for distributions Gaussian in logarithmic frequency. Comparison of the results with the available experimental data shows that it is not possible to discriminate between the two types of distribution, but suggests that the damping constant of the individual resonances must be of the order of unity.

1. Introduction

The frequency dependencies of absorption and refractive index resulting from a super-position of three discrete resonances have been calculated (Hill 1968, Chamberlain 1968). The resemblance of the results of these calculations to the experimental results obtained for liquids at sub-millimetre wavelengths (Davies *et al.* 1968 a, b) is sufficiently close to encourage the investigation of the absorption and refractive index variation in the more realistic case of a continuous distribution of resonances.

The frequency dependencies of the permittivity ϵ' and loss ϵ'' due to a single damped simple harmonic resonance at frequency (wave number) σ_i are given by

$$\epsilon' - 1 = C\frac{\sigma_i^2 - \sigma^2}{(\sigma_i^2 - \sigma^2)^2 + (2\gamma\sigma)^2} \qquad \epsilon'' = C\frac{2\gamma\sigma}{(\sigma_i^2 - \sigma^2)^2 + (2\gamma\sigma)^2}$$

where σ is the measuring frequency, γ is a damping constant and C is a constant related to the strength of the oscillator. (The notation here is that used by Chamberlain (1968).)

If the resonant and measuring frequencies are both expressed in terms of a standard frequency σ_0:

$$\sigma = x\sigma_0$$

$$\sigma_i = y\sigma_0$$

these equations may be written

$$\epsilon' - 1 = \frac{C}{\sigma_0^2}\frac{y^2 - x^2}{(y^2 - x^2)^2 + (gx)^2} \qquad \epsilon'' = \frac{C}{\sigma_0^2}\frac{gx}{(y^2 - x^2)^2 + (gx)^2}$$

where $g = 2\gamma/\sigma_0$. (g is not to be confused with $r = 2\gamma/\sigma_i$, the damping coefficient used by Hill (1968).)

Provided that $\epsilon'' \ll \epsilon'$ (a condition which is satisfied for the sub-millimetre absorption in liquids) the refractive index n and absorption α are related to the permittivity and loss by

$$n = \epsilon'^{1/2}$$

$$\alpha = \frac{2\pi\sigma\epsilon''}{\epsilon'^{1/2}}.$$

Also, the increments, $\Delta\epsilon'$ and Δn, of both permittivity and refractive index through the dispersion region are small compared with their absolute values and are therefore related by

$$\Delta n = \frac{\Delta\epsilon'}{2\epsilon'^{1/2}}.$$

Hence

$$\Delta n = \frac{C}{2\epsilon'^{1/2}\sigma_0^2} \frac{y^2 - x^2}{(y^2 - x^2)^2 + (gx)^2}$$

$$= K'F'(x, y)$$

where

$$K' = \frac{C}{2\epsilon'^{1/2}\sigma_0^2}$$

and is constant, to a very good approximation, because the variation of ϵ' is very small. Similarly we may write

$$\alpha = \frac{4\pi\sigma_0 C}{2\epsilon'^{1/2}\sigma_0^2} \frac{gx^2}{(y^2 - x^2)^2 + (gx)^2}$$

$$= K''F''(x, y)$$

where

$$K'' = 4\pi\sigma_0 K'.$$

Thus the frequency dependence of the refractive index increment may be expressed by the function

$$F'(x, y) = \frac{y^2 - x^2}{(y^2 - x^2)^2 + (gx)^2}$$

and that of the absorption by

$$F''(x, y) = \frac{gx^2}{(y^2 - x^2)^2 + (gx)^2}.$$

(These functions are slightly different from Chamberlain's (1968) functions N' and N'', because it is now desired to vary the resonance frequency y continuously.)

2. Continuous distribution of resonances

If we now consider a distribution of resonances, such that the fraction of resonances with resonance frequency in the range y to $y + dy$ is $f(y)\,dy$, the refractive index increment and absorption due to this distribution are respectively proportional to

$$F'(x) = \int_0^\infty \frac{f(y)(y^2 - x^2)}{(y^2 - x^2)^2 + (gx)^2}\,dy$$

and

$$F''(x) = \int_0^\infty \frac{f(y)gx^2}{(y^2 - x^2)^2 + (gx)^2}\,dy.$$

(It is assumed here that both the damping constant g and the oscillator strength are independent of frequency. This appears physically more reasonable than assuming $r\ (= g/y)$ and C/y^2 constant, as was done for three discrete resonances (Hill 1968).)

Two different types of distribution have been considered. The first is a Debye type of distribution:

$$f(y) = Ay^2 \qquad y \leqslant y_{\max}$$
$$f(y) = 0 \qquad \text{otherwise}$$

where A is a constant such that

$$\int_0^\infty f(y)\,dy = 1.$$

This is the distribution used by Debye in his theory of specific heats (Debye 1912). The assumption of a sharp cut-off of the distribution at $y = y_{\max}$ is, of course, an oversimplification. The assumption implicit in this distribution, that the vibrations to be considered are

the 'lattice' vibrations, gives the correct order of magnitude for the frequency of maximum absorption. The speed of sound in liquids is of the order 10^3 m s^{-1} and the intermolecular distance is of the order 10^{-10} m. Thus the cut-off frequency should be about 2×10^{12} Hz. This gives a wave number of the electromagnetic waves of the order 100 cm^{-1}. Experimentally, absorption maxima are found in the range 50 cm^{-1} to 100 cm^{-1}. In order to account for the sub-millimetre absorption, of course, these 'lattice' vibrations would have to be infra-red active.

The second type of distribution considered is a Gaussian distribution in logarithmic frequency:

$$f(y) = A \exp \left(- \frac{z^2}{W^2} \right)$$

where A and W are constants, A being again such that

$$\int_0^\infty f(y) \, \mathrm{d}y = 1$$

and

$$z = \ln y - \ln y_0$$

where y_0 corresponds to the most probable frequency.

For the Debye distribution σ_0 is taken as the maximum frequency, so that $y_{max} = 1$; for the Gaussian distribution σ_0 is taken as the central frequency, so that $\ln y_0 = 0$. The integrals were evaluated using the University of London Atlas computer.

3. Results

In the Debye distribution the only adjustable parameter is the damping constant g. In figure 1 the absorption (scaled to a maximum of unity) is shown for $g = 0.5$, 1.0, 1.5 and 2.0. In figure 2 the refractive index variation is shown for the same damping constants.
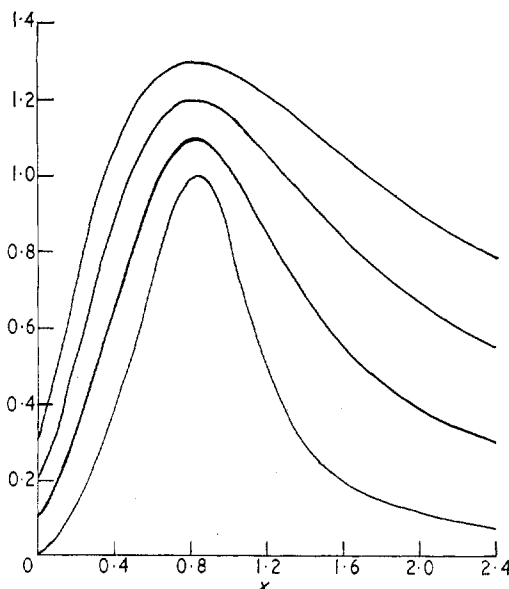

Figure 1. Absorption due to Debye distributions of resonances with damping constants $g = 0.5$, 1.0, 1.5 and 2.0. Successive curves are displaced vertically by 0.1.

In the Gaussian distribution there are two adjustable parameters: the damping constant g as before and the width parameter W. In table 1 the frequencies y_e at which $f(y)$ falls to $1/e$ of its maximum value are shown for various values of W. Figure 3 shows the
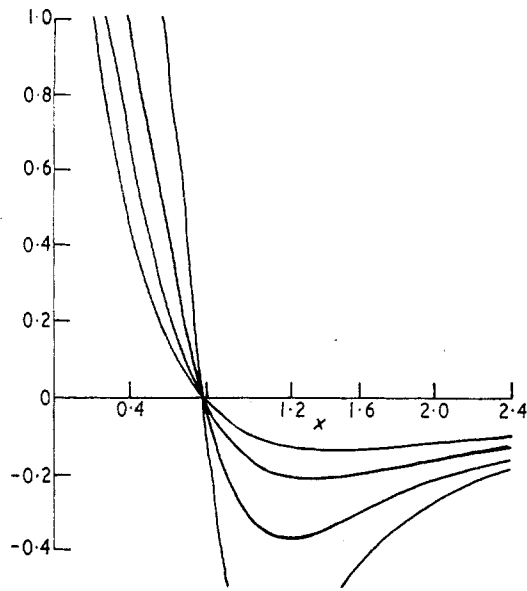
Figure 2. Refractive index increments due to Debye distributions of resonances with damping constants $g = 0.5, 1.0, 1.5$ and 2.0.

Table 1.

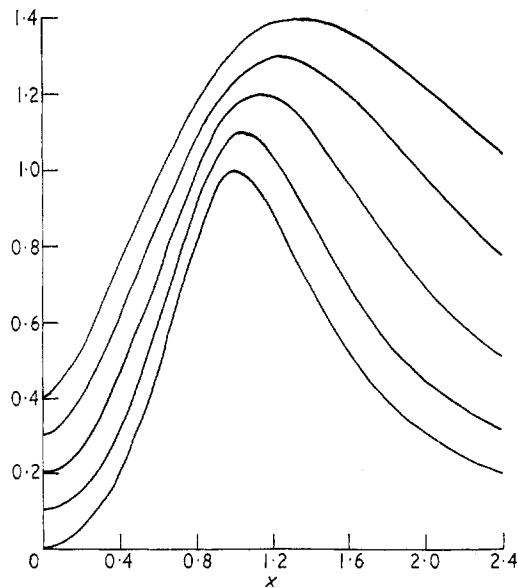| W	y_e
0.2	1.585 and 0.631
0.4	2.512 and 0.398
0.6	3.981 and 0.251
0.8	6.310 and 0.159

Figure 3. Absorption due to Gaussian distributions of resonances with damping constant $g = 1$ and width parameters $W = 0$, 0.2, 0.4, 0.6 and 0.8. Successive curves are displaced vertically by 0.1.

absorption curves (scaled to a maximum of unity) for $g = 1$ and $W = 0$ (a single resonance), 0·2, 0·4, 0·6 and 0·8. Figure 4 similarly shows the scaled absorption curves for $W = 0·6$, $g = 0·5$, 1·0 and 2·0, with the Debye distribution curve for $g = 1$ for comparison. (The frequency scales are adjusted so that the maxima coincide.) The refractive index variations for the Gaussian distributions with $g = 1$ and $W = 0$, 0·4 and 0·8 are shown in figure 5. (The curves for $W = 0·2$ and 0·6 are omitted for clarity.)
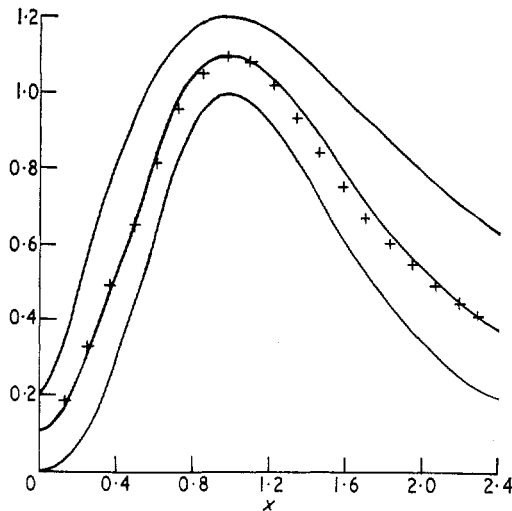

Figure 4. Continuous curves: absorption due to Gaussian distributions of resonances with $W = 0·6$ and $g = 0·5$, 1·0 and 2·0. Successive curves are displaced vertically by 0·1. + absorption due to a Debye distribution of resonances with $g = 1$(vertical scale displaced by 0·1).
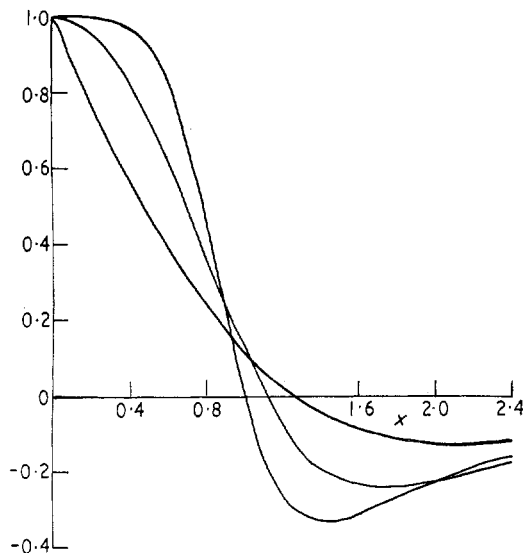

Figure 5. Refractive index increments due to a Gaussian distribution of resonances with $g = 1$, $W = 0$, 0·4 and 0·8.

The characteristics of these curves are conveniently summarized by three parameters. Let x_{max} be the frequency at which the absorption is a maximum, x_+ be the frequency at which the absorption falls to half its maximum value on the high-frequency side and x_- be the corresponding frequency on the low-frequency side. Then useful parameters are the

relative frequencies at the half amplitude points, $r_+ = x_+/x_{max}$ and $r_- = x_-/x_{max}$, and the relative frequency of the refractive index minimum $r_{min} = x_{min}/x_{max}$. These parameters are listed in table 2 for the distributions considered, together with the experimental values (corrected where appropriate for the contribution of the dipole relaxation) found by Davies *et al.* (1968a, b) for chlorobenzene, methyl chloroform, toluene, 1-4 dioxane and benzene.

Table 2.

Distribution	x_{max}	r_+	r_-	r_{min}
Debye				
$g = 0.5$	0·85	1·41	0·54	1·29$_5$
$g = 1.0$	0·82	1·84	0·45	1·49
$g = 1.5$	0·82	2·30	0·35	1·66
$g = 2.0$	0·82	2·93	0·30	1·80
Gaussian				
$g = 1.0, W = 0$	1·00	1·62	0·62	1·41
$W = 0.2$	1·05	1·64	0·58	1·43
$W = 0.4$	1·15	1·72	0·51	1·48
$W = 0.6$	1·25	1·87	0·44	1·56
$W = 0.8$	1·32	2·09	0·40	1·67
$g = 0.5, W = 0.6$		1·74	0·52	1·50
$g = 2.0, W = 0.6$		2·20	0·32	1·65
Experimental				
chlorobenzene	48	1·75	0·25	1·50
methyl chloroform	34	1·8	0·44	—
toluene	80	1·51	0·42	1·14
1–4 dioxane	69	(1·78)	0·44	1·17
benzene	68	—	0·42	0·55

From table 2 it can be seen that, with a suitable choice of the parameters g and W, either type of distribution can fit the experimental results moderately well. In figure 6 the experimental absorption results are shown fitted to the Gaussian curve for $g = 1$, $W = 0.6$. (The experimental results are obtained as continuous curves: discrete points are plotted in figure 6 for the sake of clarity.) In figure 7 the experimental refractive index curve for chlorobenzene is shown fitted to the Gaussian curve for $g = 1$, $W = 0.6$. The adjustment
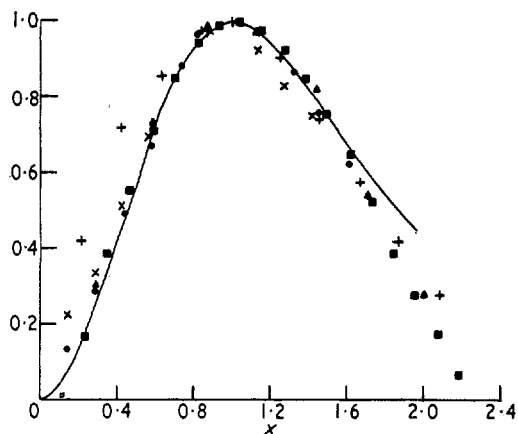

Figure 6. The experimental absorption curves for chlorobenzene, methyl chloroform, toluene, 1-4 dioxane and benzene, with the theoretical curve for a Gaussian distribution of resonances with $g = 1$, $W = 0.6$: + chlorobenzene, ■ methyl chloroform, ▲ toluene, ● 1-4 dioxane, × benzene.

of the two scales of the absorption curve determines the scale factor of the refractive index curve and the value of the refractive index at which the increment is zero. From the absorption curve the frequency of maximum absorption (48 cm^{-1}) corresponds to $x = 1.25$.
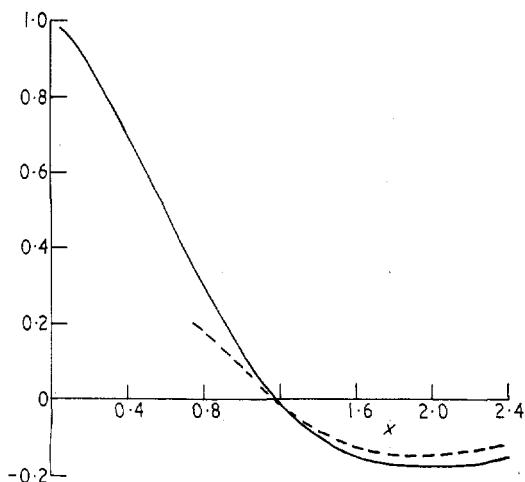

Figure 7. The experimental refractive index curve for chlorobenzene, with the theoretical curve for a Gaussian distribution of resonances with $g = 1$, $W = 0.6$: —— theoretical; — — — experimental.

Hence from the theoretical refractive index curve the zero of the refractive index increment occurs at a frequency of 45.3 cm^{-1} (corresponding to $x = 1.18$). The experimental value of the refractive index at this frequency is 1.5287. This value must be subtracted from the refractive index values at other frequencies to obtain the refractive index increments. The maximum absorption of 12.6 neper cm^{-1} corresponds to a theoretical maximum of $F''(x)$ of 0.659. The constant K'' is thus 19.1. K' can now be calculated as $K''/4\pi\sigma_0$, where σ_0 is the standard frequency (48/1.25 cm^{-1}). Thus $K' = 0.040$.

Toluene, 1-4 dioxane and benzene all have much lower values of r_{min} than can be accounted for by this theory, that for benzene even being less than unity. It would be of great interest to know whether this is a general characteristic of non-polar and weakly polar liquids.

4. Conclusion

It can be seen that the experimental results can be represented quite satisfactorily by a continuous distribution of resonances. Although it is not, with the experimental evidence at present available, possible to discriminate between the two types of distribution, it is clear that, certainly in the case of the Debye distribution and probably also in the case of a Gaussian distribution, the damping parameter of the individual resonances must be of the order of unity.

Acknowledgments

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