Theorie van het rayleigh-verstrooidingstriplet van vloeistoffen. (afleiding van de formule van Landau en Placzek)

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ANKELIJKHEID VAN DE FLUCTUATIE. ELKE VOORNAAEMSTE BESTANDDEEL EEN VOLUMEUITGESTREKT OVER HET VERSTROOIENDE VOORBEELD VAN DEZE RE. IERZICHT

Hoofdstuk 1

In dit hoofdstuk geven we een korte historische introductie samen met enkele opmerkingen over de diffusie van de partiële of de continuïteitsmedia.

Hoofdstuk 2

In dit hoofdstuk geven we een beeld van de thermodynamische en statistische mechanica, die nodig zijn voor de volgende hoofdstukken.

Hoofdstuk 3

In dit hoofdstuk geven we een beeld van de fluctuatiepatronen die behandeld in Hoofdstuk III. Het fluctuatiepatroon toont een andere uitleg op verschillende momenten, en een coherentie tussen twee bijzondere patronen, die alleen binnen een zeer kleine periode van tijd bestaat. Volgens Leontowitsch ontwikkelen we de fluctuatie in ruimte-tijd Fourierreeksen. De ongezamenlijke gedraging

SUMMARY

Monochromatic incident light, scattered by liquids, shows a splitting up into three spectrum lines, two of which have been recognized as Doppler components. The origin of the undisplaced central line, however, has been an unsolved problem. In 1934 a hint for the solution was given by Landau and Placzek, who in a brief note predicted the ratios of intensities in the triplet to be $\frac{1}{3}c_a : (c_a - c_v) : \frac{1}{2}c_v$. In 1938 Biruš gave an experimental determination of the intensity relation for toluene and water.

In this thesis the supposed ratio is theoretically deduced in the case of low heat-conduction and viscosity. In 1931 Leontowitsch already treated the doublet in liquids. At that time a central line had not yet been found. He develops the density-fluctuation into Fourier series. He only considers viscosity as a damping influence on the density-waves and merely finds a doublet.

In the present paper his method is extended by introducing heat-conduction as a damping influence in addition to viscosity.

Chapter I gives a brief historical introduction together with some remarks on scattering either by particles or by a continuous medium.

Chapter II outlines some calculations and results of thermodynamical statistics and of statistical mechanics which are needed in the next chapter.

The density-fluctuation pattern which is dealt with in Chapter III shows a different picture at different moments, a coherence between two successive pictures existing only within a very small interval of time. Following Leontowitsch we develop the fluctuation into space-time Fourier series. The haphazard behaviour
of the density-fluctuation in a certain volume $V$ during a period of time $T$ is described by a very large number of complex coefficients, each term being characterised by four integers $r, h, k, l$, abbreviated by $(s)$. Combination of the terms $(s)$ and $(-s)$ gives a plane progressive density-wave of definite direction, phase-velocity, wavelength, phase and amplitude. These Fourierwaves have no separate real physical existence. The mathematical resolving of the density-fluctuation into Fourierwaves, however, is adequate because of the wave character of the traversing light.

In order to calculate the spectrum and the intensity of the scattered light we need: firstly $\overline{A_s^2}$, the mean square of the amplitude of the Fourierwaves, secondly $\overline{A_s A_{-s}^*}$, the correlation between the coefficients of different Fourierterms. To this end we consider the behaviour of the liquid from a definite initial pattern under the influence of damping forces, and without chance-forces causing fluctuations. The final state then is the thermodynamical equilibrium with equal density, temperature and pressure at all points. The dying out of the fluctuation-pattern is calculated from the hydrodynamical equations. We describe the fluctuation-state at a certain moment by a spatial Fourierseries, which has a simple relation to the space-time development. A simultaneous system of differential equations of the fifth order (10) is found, containing only the variables of a single Fourierterm separately, the total fluctuation being found by superposition. The general solution of the differential equations leads to an equation of the third degree. The existence of three roots (15) is the origin of the triplet structure of the scattered light. For the case of small heat-conduction and viscosity estimates of the roots are given.

The solution of the differential equations (16, 19) reveals that, in general, there are two kinds of density-waves:

1. progressive density-waves which by pressure-variation propagate with sound-velocity, the corresponding temperature-variation being adiabatically connected with the density-fluctuation.

2. temperature-fluctuations which are stationary for lack of pressure-variation, but which are accompanied by corresponding density-variations; here heat-conduction is the cause of the dying out of these waves with time.

The temperature-fluctuations of the waves

$$\delta T_1 = \frac{c_p}{c_v} \, .$$

$$\delta T_2 = \frac{c_p c_v}{c_s}$$

At equal $\delta T$ we have $\delta T_1 = -\delta T_2$ = a fluctuation-pattern at an arbitrary wave.

In the process of averaging in search of the values of the mean square of the correlation between the density-fluctuation we get the formula (44) for $A_s A_{-s}^*$ and $A_s A_{-s}^{*2}$ the wavelength of which is larger than the correlation space. We conclude the absence of Fourierwaves provided the Fourier terms.

The result for the mean square of the intensity (44) is represented graphically in particular:

1. Two Fourierwaves with equal wave-lengths have equal mean square amplitudes.

2. For small damping, condition $\nu \ll 1$, the phase-velocity is limited to two values at zero value and the other at zero value.

The second property may be expressed by saying that a wave of definite wavelength has only two possible orientations, namely at $v_s = 0$ and at $v_s = \pm \frac{c_s}{c_v}$.

In Chapter IV light scattering is applied to Einstein's solution with the only difference that we introduce a dependence on time. The solutions in which his formulae do not introduce a dependence on time is made to the dielectric quantity, which fluctuates with time.
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The temperature-fluctuations of the two waves are respectively

\[
\delta T_1 = \frac{c_v \rho_T}{c_v} \delta \rho_1, \\
\delta T_2 = -\frac{\rho_T}{c_v} \delta \rho_2.
\]

At equal \( \delta T \) we have \( \delta \rho_1 : -\delta \rho_2 = c_v : (c_v - c_s) \). In general the fluctuation-pattern at an arbitrary instant contains both these waves.

In the process of averaging in search for \( \overline{A_r A_r} \) and \( \overline{A_r A_r} \) we need the values of the mean square of the density-fluctuations, the correl-
between the density-fluctuation and its fluxion, and the cor-
relation between the density-fluctuation and the temperature-
fluctuation. In Chapter II these quantities have been discussed. The fact of \( \delta T \) being zero now proves to be the essential cause of the

The formulae (44) for \( \delta T_1 \) and \( \delta T_2 \) hold for all Fourierwaves
the wavelength of which is larger than the size of the corre-
lation space. We conclude the absence of correlation between two
Fourierwaves provided the Fourier time-interval \( T \) is large enough.
The result for the mean square of the amplitude is discussed
and represented graphically (fig. 4). Two properties are worth
mentioning in particular:

1. Two Fourierwaves with equal wavelength and phase-velocity
have equal mean square amplitude.

2. For small damping, condition (20b), the magnitude of the
phase-velocity is limited to two small intervals, one of which
lies at zero value and the other at that of sound-velocity.

The second property may be expressed otherwise: any Fourier-
wave of definite wavelength has only two narrow frequency-inte-
vals, namely at \( v_s = 0 \) and at \( v_s = \text{sound-velocity} : \text{wavelength} \).

In Chapter IV light scattering is treated in the same way as
Einstein's 30) with the only difference, however, that E. did
not introduce a dependence on time for the fluctuation, in con-
sequence of which his formulae do not show a spectrum. In the
equations of Maxwell the dielectric constant is a scalar
quantity, which fluctuates with time and space. The scattered light
caused hereby is indicated by the light vector \( \mathbf{\zeta} \) (52). In addition to the frequency \( v \) of incident light the Fourier frequency \( v_\mathbf{\zeta} \) now appears as a new element in the formulae for \( \mathbf{\zeta} \) (55). Elaborating \( \mathbf{\zeta}^2 \), by which the intensity of the scattered light is determined, it becomes clear that incident light waves only select a very small part of Fourier waves which possess a wavelength and direction very little differing from those of a wave given by Bragg's law. This fact is of great importance in determining the value of \( A_\mathbf{\zeta} A_\mathbf{\zeta}^* \) and \( A_\mathbf{\zeta}^2 \) and is also useful in calculating some integrals (p. 63, 65).

In the same way as the mean square of the amplitude of the Fourier waves the mean square of the scattering vector shows maxima, namely at incident frequency and at two frequencies which are symmetrical to it.

The calculation of the total intensity of scattered light leads to the formulae of Einstein (76b). For the intensities of the three components the Landau-Placzek relation is found, if the condition (20b) of small heat-conduction and viscosity is satisfied. The widths of the lines are also calculated.

For toluene of 25°Celsius at a scattering angle of 50° and with incident light of 4078 Å, we calculate the distances between the lines as 0.037 Å, and the width of the middle and the outer lines resp. as 0.54 and 2.2% of this line-distance (fig. 6). Obviously the values of line-width mentioned will escape observation, in view of the resolving power of the spectral apparatus and the line-width of the incident light.

LITERATUR

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