

LIGHT SCATTERING AS A TOOL

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The first to explain the blue colour of the sky as an accumulative result of scattering by the molecules of the air was Lord Rayleigh. He established that the intensity of the scattered light should be proportional to the reciprocal 4th power of the wavelength for particles which can be considered as infinitely small in comparison with the wavelength and have a constant polarizability independent of the wavelength. Implicitly contained in this calculation is the statement that we can count the number of molecules per cm^3 by observing the scattered intensity as compared to the primary intensity and provided we also know, as a measure for the polarizability, what the refractive index is¹.

Early after the start of the Second World War and in connection with the "Rubber Reserve Company" I recognized that the same reasoning could be applied to solutions. Instead of the total turbidity of the solution its excess turbidity over that of the solvent and instead of the refractive index of the solution its difference from that of the solvent have to be considered. A combination of these two experimental values then enables us to count the number of solute molecules per cm^3 or in other words to determine the molecular weight of these molecules². Since it turns out that the limit of the excess turbidity per unit of concentration which it tends to for very dilute solutions is proportional to the molecular weight, the scattering method is very appropriate for high molecular weight substances. The intensity of the scattering depends essentially on the change of refractive index per unit of concentration of the solute. It is proportional to the square of this quantity. If different single solvents are compared with each other this rule holds.

A peculiar effect was observed when a mixture of two liquids was used as a solvent. In the first experiment of this kind mixtures of benzene and methanol were used, the solute being polystyrene. If the molecular weight was then determined in the usual way it was not constant but seemed to increase with increasing percentage of methanol in the mixture. This could be shown not to be an effect of agglomeration. The appropriate explanation is that the mixture of benzene and methanol is in reality not homogeneous. In the vicinity of the polystyrene molecule the concentration of benzene is higher than it is further away; there is preferential adsorption of one of the liquids. In measuring the apparent molecular weight, determined in the usual way as a function of the concentration of the mixed solvent, a method is established to measure the degree of this preferential adsorption quantitatively³.

Another analogous effect is shown up when the solute is a copolymer of varying heterogeneity in the chain. This effect was investigated and discussed by Benoit. By measuring the scattering in three different solvents

(with three different refractive indices) it is possible to measure the polydispersity in chain composition⁴.

One of the conditions for the applicability of Rayleigh's reasoning is that the particles which scatter the light can be considered as infinitely small in comparison with the wavelength. If this is not so, light scattered from different parts of the particle reaches the point of observation with phase differences and so leads to interference effects. An observation of this kind was used by me in the thirties to establish a method for measuring atomic distances in single molecules by observing the angular intensity distribution of X-rays scattered by gases⁵. A primary radiation should be used with a wavelength comparable with the atomic distances to be measured. The main point to be recognized, however, is that an interference effect (which appears on a photographic plate as a number of rings concentric with the point where the primary ray hits the plate) persists, independent of the fact that the molecules which are subjected to the experiment are not standing still but take up all possible orientations at random. Shortly after the result of first experiments with X-rays on CCl_4 gas had been published, Mark and Wierl⁶ showed that the same effect could be easily obtained by the scattering of a beam of electrons, its wavelength being determined by de Broglie's relation.

Now considering again solutions of substances of high molecular weight and ordinary visible light it became important to make an estimate of the actual size of such molecules. If the formula for the random flight is applied to a polystyrene molecule of 1 million molecular weight for example, the calculated average distance between its ends comes out to be 300 Å, provided free rotation of the bonds is assumed. Taking 3000 Å as the wavelength of the visible light in, say, a benzene solution it seemed possible that an interference effect could be observed. However, polymer molecules like polystyrene differ essentially from molecules like CCl_4 . In solution they have no rigid geometrical structure. What can possibly be observed would only be an effect averaged over all the different forms such a molecule assumes in the course of time. The corresponding calculation shows that in this case no maxima and minima in the angular intensity distribution of the scattered light can be expected. What remains is a smooth decrease of intensity with increasing angle between primary and secondary ray. This decrease is more rapid the larger the average size of the molecule. In order to characterize this "angular dissymmetry" we took as a measure for it the quotient of the two intensities scattered at 45° and 135° . Bueche, working on solutions of polystyrene in benzene⁷ at Cornell, showed that this angular dissymmetry exists and increases proportionally to the molecular weight. It attains a value of 2 for a molecular weight of 1 million. From this it can be deduced that the average distance between ends of this molecule in a benzene solution is 1100 Å, instead of the 300 Å derived from the random flight formula with free rotation. Observations like this can be used to discuss for instance the hindering of the free rotation, the influence of the solvent-solute interaction and the effect of the excluded volume on the coil form of the molecule and on its extension.

So far we have considered cases in which the effect of the single particle could be observed and analysed. There are, however, other important cases where this is impossible and the interference effects between neighbouring

molecules cannot possibly be neglected. A first case of this kind was that considered by Einstein in 1910⁸, when he calculated the light scattering power of liquids and solutions. In both these instances, instead of considering the single molecules, he reduced the problem to a discussion of the local fluctuation of density or concentration as the reason for fluctuations in the refractive index which ultimately are responsible for the scattering effect. In Einstein's paper the argument leads to the statement that the intensity of scattering is proportional to the average square of the amplitude of those fluctuations of the refractive index. This average then is derived by application of the equipartition law in statistical thermodynamics.

In his paper Einstein also derives a formula for the scattering due to concentration fluctuations in a liquid mixture. The last kind of formula is applicable here. Its advantage over the formula based on a reasoning similar to that of Rayleigh is that it can be applied to higher concentrations. The characteristic quality is the concentration-gradient of the osmotic pressure. In this context measurements on light scattering can be considered as absolute measurements of this gradient as a function of the concentration. For small concentrations the osmotic pressure can be represented as a series of ascending powers of this concentration and the coefficient of the second power term is the second virial coefficient, which measures in a first approximation the interaction of the solute molecules. This has been the concern of many publications since 1948. However, it should be kept in mind that Einstein's formula in its application to light scattering supposes essentially that the molecules can be considered as infinitely small in comparison with the wavelength. From the preceding it is evident that in order to determine a molecular weight by light scattering it is, in general, necessary to make a twofold extrapolation, first to the limit of zero concentration and secondly to the limit of zero angle. The usual way of performing this extrapolation is by a so-called "Zimm-plot"⁹.

As has been stressed already in 1916 by F. Zernike¹⁰ however, a fluctuation cannot be sufficiently characterized solely by its average amplitude. If we make a plot of, say, the refractive index along a line going from a point A to another point B at a distance r in the liquid, we have also to know how much correlation there is between the two fluctuations at these two points. This correlation can be mathematically measured by calculating the average product of the two fluctuations in points A and B in its dependence on their distance r . Dividing this product by the average square of the fluctuations one obtains a dimensionless function of r , which is sometimes called the auto-correlation function. It is clear that this function begins with 1 for $r = 0$ and tends to 0 for large values of r in which case both fluctuations will vary independently.

This correlation function in its dependence on the distance determines how the scattered intensity will depend on the scattering angle. There is a one-to-one correspondence between the two curves, the one representing how the correlation function depends on the distance, the other describing how the scattered intensity depends on the scattering angle. Essentially both curves are Fourier-transforms from each other. The behaviour of such a correlation can be roughly characterized by the distance over which it extends. This leads to the introduction of a "persistence" length L , which

can be defined with mathematical precision by the second moment of the correlation-curve. If this persistence length L is comparable with the wavelength of the light, angular dissymmetry will be observed. The scattered light will be stronger in the forward than in the backward direction and the observation of this effect will provide an opportunity for measuring the persistence length in terms of the wavelength of the primary radiation¹¹.

A first application of this line of thinking was the measurement of a catalyst's surface by means of small angle X-ray scattering¹². In a case like this, where the intention is to apply interference effects, it is necessary to decide on the kind of radiation which should be used. In practical cases of specific surfaces one has to consider for instance in gel-catalysts that they are of the order of, say, $100 \text{ m}^2/\text{cm}^3$ of the sample. This indication can be considered as determining a reciprocal length of 10^6 reciprocal cm or a length of 100 \AA . The wavelength of visible light (say 5000 \AA) would be much too large, no observable interference effect connected with the hole-sizes which characterize the specific surface can be expected. On the other end of the scale we have X-rays with a wavelength of say 1 \AA . They are possible, but then we have to concentrate our attention on the scattering at small angles of order of $1/100$ which corresponds roughly to 0.5° .

In the case of X-rays, what is important for the scattering is not the refraction index but the electron density in the material. Now as long as we are only considering small scattering angles, the atomic distribution in the material will be irrelevant and for our purpose we can consider the sample as consisting of regions of material with constant electron density adjacent to hole regions with electron density zero. This means that for the characterization of the sample only the geometry of the hole structure is important. In this case it can be shown that instead of the general correlation function we can substitute another function, which can be more easily visualized. Let us throw a stick of length r and end-points A and B into the medium and observe where these end-points are, either in a hole or in material. In a certain percentage of our throws the ends of the stick will be "dissimilar" meaning that if one end is in a hole the other will be in material. This percentage we call the "probability of dissimilar ends." Now this probability in its dependence on the length of the stick is a perfect substitute for our correlation function. Between this probability and the intensity distribution there is again a one-to-one correspondence.

In highly irregular hole structures, as those of catalysts, it turns out that the correlation function is often an exponential. If this is so, a very simple recipe results for the determination of the specific surface. It can be formulated as follows: Plot the reciprocal square root of the scattered intensity as a function of the square of the scattering angle. The result is a sloping straight line. The slope of this line determines the specific surface. In a certain sense this is a special case, namely that of perfect irregularity of the hole structure. Even if this perfect irregularity does not exist, it turns out that for larger angles (in the small angle region) the intensity decreases in proportion to the reciprocal 4th power of the angle. If now the intensity of the scattering is measured in this region of angles for different hole structures all of the same material the specific surface is proportional to the measured intensity. It is interesting to note that this is exactly what van Nordstrand found experimentally before

any theory of this kind of scattering experiment was available¹³. It should also be said that the same kind of conclusions were arrived at independently and nearly at the same time by Porod in Graz¹⁴.

In the case of polymers in solution the angular dissymmetry of the scattered light was due to the large size of the single polymer molecule comparable to the wavelength of that light. In 1950, observations of angular dissymmetry again for the case of visible light were reported by Zimm but this time for mixtures of liquids with regular small molecules of sizes about 1000 times smaller than the wavelength¹⁵. However this dissymmetry was only observed in experiments performed on the angular distribution of the strong critical opalescence which such mixtures show just before separating into two phases. The special mixture used by Zimm consisted of the two components: carbon tetrachloride and perfluorated methyl-cyclohexane, with a critical temperature of about 28°C. The curves for the scattered intensity plotted as a function of the square of the sine of half the scattering angle (which is the appropriate angular function according to the theory) determine by their slope at the origin for zero angle the persistence length L . Since such a slope is easily observed it is obvious that in this case L and the wavelength of the light must be of comparable magnitude.

In a case like this we can make a plot of the osmotic pressure for different temperatures of one of the components of the mixture $A + B$, say B , as a function of its concentration from 0 to 100 per cent. The theoretical form of such curves can be anticipated, at least in a qualitative way. Following Hildebrand's theory¹⁶, such isotherms are for our purpose equivalent to the van der Waals isotherms which can be plotted for a single gas in a diagram showing the pressure as a function of the volume for different temperatures. Both plots show for a definite concentration (or volume) an inflection point on the isotherm with a horizontal tangent. This is the critical point and in this point itself the work necessary to make a change in the concentration (or to change the volume in the case of single compound) is zero. This explains immediately the large amplitude of the fluctuations and consequently the large intensity of scattering¹⁷. On top of that, Zimm's experiment also showed that the persistence length of the fluctuations becomes large and increases continuously the nearer we approach the critical point. Obviously it is important to know what the law is which governs this increase of L . Let us suppose that the experiment is performed exactly at the critical concentration, but always at temperatures T higher than the critical temperature T_c . Zimm's experiments interpreted in terms of the persistence length L then show that the reciprocal of L^2 is proportional to the temperature difference $T - T_c$. Experimentally we therefore find a relation of the form

$$L^2 = \frac{l^2}{\frac{T}{T_c} - 1}$$

in which l is a new length which is constant. Zimm's experiments can be represented by making $l = 14.7 \text{ \AA}$.

Obviously the next question is why such a relation should exist and what the significance is of the new molecular constant l introduced by it. Any theory which is relevant in this connection has to dig rather deeply into the

statistical thermodynamics of the subject. This means that in essence we have to know an expression for the free energy of a medium carrying fluctuations which is derived from a supposedly known representation of the mutual molecular interactions. No practically usable form of such an exact theory exists, but we have at our disposal classical approximations to the goal. For a single component we have van der Waals equation and for liquid mixtures Hildebrand's formulation. Both apply to the case of strictly homogeneous substances but can rather easily be generalized to cover also the non-homogeneous case of fluctuations¹⁸.

The problem of calculating the intensity and the angular distribution of the scattered light is twofold. We want to know first how a medium with local fluctuations of the refractive index reacts to the incoming light. This is a question of applying Maxwell's equations for the electromagnetic field to the case. Secondly, we must know enough about the amplitude and the geometry of those fluctuations. This is where the statistical mechanics aspect enters. For our purpose it is easier to discuss the first part of the problem not the way Einstein did, but to follow a reasoning introduced by L. Brillouin in the twenties¹⁹.

Let us consider the special case of density fluctuations. Brillouin takes these density fluctuations to be represented by a superposition of a large spectrum of sonic or supersonic waves which go through the medium in all different directions. Let us also fix our attention on the secondary radiation which leaves the medium in a direction making a definite angle θ with the primary ray. His calculation of the electrodynamic part of the problem then leads to the following statements.

(i) Of all the waves going through the medium only those are important for the scattering effect which have a front such that it can act as a mirror on which the primary ray is reflected. Waves of all other directions are not effective.

(ii) Of all the waves of different wavelengths going in the direction defined by statement (i) only those are important which have a wavelength Λ which is related to the wavelength λ of the light by Bragg's relation.

$$\frac{1}{\Lambda} = \frac{s}{\lambda}$$

in which

$$s = 2 \sin \frac{\theta}{2}.$$

This means of course that successive fronts of the supersonic wave with wavelength Λ have to reinforce the scattering effect by interference.

(iii) The intensity of the scattered beam is proportional to the intensity of the supersonic wave of wavelength Λ . As a matter of fact there exist two waves of this kind going in opposite directions. Each should create a Doppler effect of the order sound velocity to light velocity in the scattered frequency. So we should expect that monochromatic light will be split up into a doublet by Rayleigh scattering. The separation of the lines is of the order sound velocity to light velocity. Experiments of Ramm 30 years ago have shown that this effect exists²⁰. Brillouin's manner of representation of the problem very clearly shows that observing the scattered intensity as a function of the

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scattering angle really amounts to making a Fourier analysis of the spectrum of the supersonic waves which represent the thermal motion. This spectrum extends from $\lambda = \infty$ to a shortest wavelength which is of the order of the distance between two molecules. If visible light is used only a small part of this spectrum is being investigated, since the wave with the smallest accessible wavelength is effective for $\theta = 180^\circ$ and therefore has a wavelength which still is half the wavelength of the light.

The second part of the problem, concerning the amplitudes of the reflecting supersonic waves in thermal equilibrium is solved by Einstein by applying the principle of equipartition of energy. He concludes that all the waves have the same amplitude. So it follows theoretically that (after correction for the polarization effect) the scattered intensity should be the same for all angles.

We have in this discussion been concerned with compression waves. The same can be done for concentration fluctuations and concentration waves. The only difference is that in the case of the concentration wave we have no more travelling waves. The complex concentration pattern of the fluctuation however can still be subjected to a Fourier-analysis and there will again be for every angle one component of wavelength which is responsible for the scattering. Due to this difference in the case of concentration fluctuations the spectral structure of the scattered light is different; we no longer expect a triplet. However, as to the total intensity of scattering we come in both cases to the conclusion, if we strictly follow Einstein's reasoning, that there is no angular dependence of the scattering in contradiction with Zimm's results.

Returning to the special case of density fluctuations we have now to investigate in more detail how the principle of equipartition is used in Einstein's reasoning. The only property of the liquid apart from its density which is considered in calculating the energy of the supersonic wave is the compressibility. The energy per cm^3 is taken proportional to the square of the amplitude and to the reciprocal of the compressibility. This makes the energy independent of the wavelength λ of the wave. The work which is necessary to create a density fluctuation becomes less and less the nearer we approach the critical point in which the compressibility becomes infinite. So for experiments in the vicinity of this point it becomes important to investigate whether the work of compression as such is the only work which has to be considered. Even if additional work exists we can certainly neglect it as long as it is small in comparison to the work of compression. However, this is no longer true in the vicinity of the critical point where the addition may persist but the compressional part vanishes. Now we know that work has to be done against the universal molecular attraction in order to create a surface. This implies that work of the same kind enters the picture as soon as we have to consider fluctuations in which local density changes occur. If such a fluctuation has the form of a wave of wavelength λ it is easily seen that the additional work will be proportional to the quotient l^2/λ^2 in which l is a measure for the range of molecular forces.

All in all therefore, we come to the conclusion that we still can accept the work involved in creating a compression wave of wavelength λ to be proportional to the square of its amplitude. The multiplication factor however

will now consist of two parts, a first part proportional to the reciprocal compressibility and a second part which has to be added proportional to l^2/λ^2 and therefore increasing in importance with increasing angles. In order to maintain equipartition it is now necessary that the amplitude of the reflecting supersonic wave and concurrently the scattered intensity decrease with increasing angle. The effect will be more pronounced the larger the compressibility and this means the nearer to the critical point the experiment is performed. Thirty years ago reasoning of this kind had already been introduced by Y. Rocard²¹. The same reasoning is applicable to concentration fluctuations where the reciprocal compressibility (which equals the product density times the rate of change of pressure with density) is to be replaced by the product concentration times the rate of change of the osmotic pressure with concentration. In the critical mixing point this last quantity is zero again.

The theory in this form suggest a simple representation of the experimental facts. If the reciprocal scattered intensity is plotted as a function of s^2 for different temperature-distances from the critical temperature a set of sloping parallel straight lines should result. The common slope of this set is a measure of l and l itself is a measure for the range of molecular forces. In the simple case of a gas of one component and in the generalized van der Waals theory of the effect l^2 is the second moment of the curve representing the mutual energy of two molecules as a function of their distance. The most simple case imaginable for testing these relations is that of gases with simple molecules in the vicinity of their critical points. Scattering experiments have been performed for Ar and N₂²². It is known that a very adequate representation of the mutual interaction is the assumption of hard spheres of diameter d which attract each other with a force derivable from a London-energy proportional to the 6th power of their reciprocal distance. If this assumption is accepted it turns out that l should be $\sqrt[3]{2}$ times the diameter. This is indeed the result of the experiment, d is about 3 Å and l about 5 Å. In the case of concentration fluctuations of two liquids A and B the definition of l^2 is somewhat more complicated. It contains ranges for the three interactions AA, BB, and AB. Several cases are now known of such linear plots. In Zimm's case the largest value of the correlation length was 1500 Å appearing at a temperature distance of 0.03°C from the critical temperature, leading to a range of interaction of 14.7 Å.

When it was clear that we had a new method in hand to measure directly ranges of molecular interaction, it was decided to apply it to polymer solutions. The example which was investigated was that of polystyrene in cyclohexane²³. It shows a critical temperature which varies from 19°C to 29°C when the molecular weight varies from 69,000 to 1,000,000, whereas at the same time the critical concentration varies from 7 to 2 volume-per cent. It was established that for the whole range of molecular weights the effect could be handled and represented the same way as for mixtures consisting of liquids with small molecules. This led to a table of l values for the interaction which starts with $l = 24$ Å for a molecular weight of 69,000 and ends with $l = 50$ Å for 1,000,000 molecular weight. The increase of l with increasing molecular weight is as expected. The absolute values of the interaction distance however, surprise us because they are rather small. In the case

of the highest molecular weight in which an original dissymmetry exists already in infinitely diluted solutions, which is further developed by an approach to the critical temperature, it was possible to make a simultaneous estimate of the interaction distance l and the radius of gyration r_g of the polymer coil. The quotient l/r_g is approximately 0.4.

In order to make certain that the relatively small values of l found by interpreting the angular dissymmetry are real, another method for determining the same interaction distance was conceived. Light passing through such a polymer solution loses its intensity as a result of scattering. Since it is believed that we know both intensity and angular distribution of this scattered light, we can calculate an apparent absorption coefficient by integrating the scattered intensity over all angles. This apparent absorption coefficient can be measured directly by a spectrophotometer, care being taken that secondary or tertiary scattering is avoided. If the reciprocal of this calculated apparent absorption coefficient is plotted for a definite colour as a function of the temperature a curve results which starts with 0 at the critical temperature and very soon goes over into a straight line. For another colour, say nearer to the blue end of the spectrum another curve results, which starts at the same point of the temperature axis but goes over in a straight line with less slope, as was to be expected from Rayleigh's law. In experiments with the spectrophotometer we avoid the immediate vicinity of the critical temperature and can then extrapolate the straight lines for the reciprocal apparent absorption coefficient backward until they cross the temperature axis. In this way we can define a different *apparent* critical temperature T_c^* for each colour. If now these temperatures T_c^* are plotted as a function of the reciprocal square of the wavelength of the light which is used for their determination a sloping straight line should result and the slope of this line determines l .

B. Chu made measurements of this kind²⁴ at Cornell and found for instance for a molecular weight of 147,000 a value of 29.1 Å. This is to be compared with a value of 28.4 Å derived from a direct measurement of the angular dissymmetry. This is convincing evidence that the small values of the interaction distance found in polymer solutions are essentially correct.

In order to understand this behaviour it seems necessary to assume that under the prevailing experimental conditions two coiling molecules have structures which are open enough for them to interpenetrate some distance before appreciable interaction occurs. A picture like this evokes the desire to determine more intimate features of such interactions. The theory, which has been used so far and which leads to a representation of the reciprocal intensity as a function of s^2 by a set of straight parallel lines, is only a first approximation in terms of the quotient l/λ . Taking as an example the case of one component again and of density fluctuations, what has been used is not the exact expression of the potential energy of a molecule with respect to surroundings in which the density varies periodically like in a wave. Nothing prevents us from using the exact expression instead of a first approximation in terms of l/λ . If this is done we can no longer expect the representation of the reciprocal intensity by a set of straight lines to hold²⁵. However, in order to detect such deviation we have either to come much

nearer to the critical temperature or to use wavelengths which are much shorter than those of visible light. In all these interference effects the essential variable is the product of a length (to be measured) and a reciprocal length which is s/λ .

In order to obtain details of the interaction curve it is necessary to observe the scattering curve over a large range of values of that product. In the case of polymers we cannot go very far by working much nearer to the critical temperature because the samples we can investigate are never monomolecular but always cover a rather extended range of molecular weights, even if we are able to use fractions of which the quotient weight average to number average molecular weight is not very different from unity. On the other hand, the use of X-rays instead of visible light is promising since in this way we can decrease the wavelength by a factor larger than 1000. What we are striving at is to obtain a curve for the scattered intensity which extends over a large range of values of s/λ . Theory predicts that such a curve can be transformed into another curve which will represent in essence the interaction energy of two polymer coils as a function of the distance of their centres of gravity. If we take as an example $l = 30 \text{ \AA}$ then, for a wavelength of 3000 \AA of visible light, the maximum value of the dimensionless variable ls/λ obtainable for a 180° angle is 2×10^{-2} . If copper X-ray radiation is used the equivalent angle to start with is 10^{-3} or 3.4 minutes of angle. So very small angle X-ray scattering has to be considered. On the other hand, a range of a few degrees of angle under these circumstances, if compared with the visible light case, means a very extended range of the dimensionless variable. Critical opalescence for X-rays means an abnormally large scattering for small angles which increases the nearer the critical temperature is approached but extends only over a small angular range. Experiments of this kind have now been performed both for a mixture of small molecules²⁶ and for a polymer solution²⁷. If, as in the case of light, the reciprocal scattered intensity is plotted as function of $(s/\lambda)^2$ a curve results which is nearly a straight line for a considerable range of values of $(s/\lambda)^2$, a range much larger than that which can be covered by visible light. Moreover, this straight line has the same slope as that obtained for visible light. However, for still larger values of the variable, deviations from the straight line occur and the curve shows a well pronounced curvature downward. Even so, since the experimental results for the reciprocal intensity can very well be represented by a power series in $s(\lambda)^2$ which is cut off at the 4th power term, we can derive not more than the fourth moment next to the second moment of the interaction curve from these experiments.

Investigating the angular distribution of the scattered intensity has provided the opportunity to measure the correlation of the concentration fluctuations in space. Obviously we can also question at a given point in space their correlation in time. If the illumination is made with strictly monochromatic light characterized by a sharp line in the spectrum, the spectral investigation of the scattered light will answer that question. Such experiments have recently been performed for light scattered by both density fluctuations²⁸ and concentration fluctuations²⁹. In the latter case it was found experimentally that the line was broadened and that the broadening obeyed the following two rules:

(i) at a given temperature–distance the width of the line varies with the angle of scattering proportional to s^2 ;

(ii) at a given angle of scattering the width increases in proportion to the temperature–distance from the critical temperature. It can be shown³⁰ how the first of these rules follows from the concept that variations in time of the fluctuations are connected with a diffusion process. The second rule expresses the fact that measuring the width of the line is a method for the determination of the diffusion-constant and, moreover, that this constant becomes zero at the critical point. This last point can be understood as following from the fact that the “driving force” for the diffusion is proportional to the rate of change of osmotic pressure with concentration, a quantity which becomes zero in the critical point itself.

Finally the large number of theoretical papers about the critical point itself which appeared in recent years should be mentioned. The classical way since Einstein to discuss fluctuations is to consider them as small deviations from the equilibrium. If one approaches the critical point their amplitude increases and theoretically becomes infinite in that point itself.

It is obvious that in this region a better theory has to be constructed. It turns out that this is a very difficult mathematical problem, which today has not yet been solved. However, enough has been done to make certain that in the immediate vicinity of the critical point the classical formation will not be adequate for the description of the phenomena.

How near the critical point has to be approached practically can at this imperfect stage of the theory only be determined by experiment. In the case of concentration-fluctuations in liquids it has been impossible to find indications of this non-classical behaviour³¹ until very recently when, in an experiment especially designed for this purpose, a non-classical anomalous increase of the scattered intensity was observed with visible light for small scattering angles at a temperature difference of 0.002°C from the critical point³².

References

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- ^{1b} J. W. Rayleigh. “On the Transmission of Light Through an Atmosphere Containing Small Particles in Suspension and the Origin of the Blue Sky,” *Phil. Mag.* **47**, (5) 375 (1899); he was induced by a letter of J. C. Maxwell in which the possibility of determining the number of molecules by using both turbidity and refractive index is clearly expressed. Maxwell’s letter is reproduced by Lord Rayleigh, the essential part of it reads as follows: “If you can give us (1) the quantity of light scattered in a given direction by a stratum of certain density and thickness, (2) the quantity cut out of the direct ray and (3) the effect of the molecule on the index of refraction, which I think ought to come out easily, we might get a little more information about these little bodies.” It is in this second paper that Lord Rayleigh comes to the conclusion that the scattering particles in the air are the molecules.
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