PHYSICAL REVIEW VOLUME 135, NUMBER 5A 31 AUGUST 1964

Experimental Transition Probabilities for Six Oxygen Multiplets*

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(Received 8 April 1964)

The transition probabilities of six oxygen-I multiplets in the visible and near infrared region have been measured in a wall-stabilized high-current arc operating either in pure oxygen or in a nitrogen-oxygen mixture. Temperatures were obtained from intensity measurements of an oxygen or nitrogen line of known transition probability and by applying the arc equilibrium and conservation equations. Several independent runs were carried out. The results agree usually within 20% with those of other experimental and theoretical methods.

INTRODUCTION

A NUMBER of efforts have been undertaken to determine the transition probabilities of the strong lines of neutral oxygen.[1] A very extensive experimental investigation was done by Jürgens[2] in 1954 with a water stabilized arc in which he measured the transition probabilities of 18 oxygen multiplets in the region between 3900 and 8300 Å. Subsequent experiments showed, that this type of arc is subject to severe turbulence, i.e., the arc column wobbles around with very high frequencies by amounts as much as its diameter.[3,4] Hence Jürgens, using time-integrating photographic techniques, could only observe smeared-out averaged intensities. Secondly, it has been recently found that in arcs burning in gas mixtures local separations of the species due to the steep radial temperature gradients take place,[5,6] which change the relative concentrations of the different elements across the arc radius by as much as a factor of 2. This may also have influenced Jürgens' results, since he used the stoichiometric ratio of water vapor for his plasma diagnostics.

A redetermination of some oxygen transition probabilities with refined equipment and a method which circumvents the "demixing" problem seemed therefore to be desirable. In this paper the final results of such an investigation are reported. A first part of this work, an extensive study of the transition probability of the multiplet at 6157 Å, has been already reported.[7] It seems appropriate to outline again briefly the method employed in the earlier part: A refined version of the very stable and quiescently burning wall-stabilized arc was used. The demixing problem was circumvented by working with a plasma which consisted of practically pure oxygen with only a trace of hydrogen added. The plasma parameters could thus be determined from measurements of the Stark width of the hydrogen line H_β, combined with Stark broadening theory and the equilibrium and conservation equations for arcs. Only the measurement of the line shape of H_β was required, which did not require knowledge of the hydrogen concentration.

The second part of this investigation, the measurement of the transition probabilities of six strong oxygen multiplets in the visible and near infrared, is the subject of this paper. All reported values are based, more or less directly, on the 6157 Å multiplet measured earlier as comparison line.

METHOD

The total intensity I_{nm} of a spectral line emitted from an optically thin layer of plasma of length l is related to its transition probability A_{nm} by

$$I_{nm}=\int I_\lambda d\lambda=\frac{1}{4\pi}A_{nm}\frac{hc}{\lambda_{nm}}N_m l, \tag{1}$$

where N_m is the number density of atoms in the upper state m and λ_{nm} the wavelength. For a source in local thermodynamic equilibrium—the validity of this assumption needs to be checked later—the excited state populations are given by the Boltzmann factors. Thus N_m may be expressed through the total number density of this species of atoms and the temperature. Furthermore, the two latter quantities are related through a number of equilibrium and conservation equations, i.e., Dalton's law, the condition of local electrical neutrality and the Saha equations. This system of equations is relatively simple for a pure oxygen plasma under the desired excitation conditions. For such a one-element plasma at temperatures around 10 000°K, only the species O, O^+, and e^- need to be considered. All other species, like O_2, O_2^+, O^-, O^{++}, etc., are present in negligible concentrations, as has been checked from the appropriate mass-action laws.[7]

For a known pressure (in this experiment one atmosphere) the number densities may be obtained from this system of equations as explicit functions of the temperature. The inclusion of high-density corrections[8] introduces no additional complications. Thus,

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* This research was supported in part by project DEFENDER, sponsored by the Advanced Research Projects Agency, Department of Defense, through the U. S. Office of Naval Research.

[1] B. M. Glennon and W. L. Wiese, *National Bureau of Standards Monograph 50* (U. S. Government Printing Office, Washington, D. C., 1962).

[2] G. Jürgens, Z. Physik **138**, 613 (1954).

[3] W. Lochte-Holtgreven, Rept. Progr. Phys. **21**, 312 (1958).

[4] E. W. Foster, Proc. Phys. Soc. (London) **A79**, 94 (1962).

[5] J. Richter, Z. Astrophys. **53**, 262 (1961).

[6] W. Frie and H. Maecker, Z. Physik **162**, 69 (1961).

[7] W. L. Wiese and J. B. Shumaker, J. Opt. Soc. Am. **51**, 937 (1961).

[8] H. R. Griem, Phys. Rev. **128**, 997 (1962).

the intensity of the oxygen lines I_{nm} may be expressed as a function of temperature only, and the temperature of the plasma may be determined by simply measuring the total intensity of an oxygen line of known transition probability. For this measurement the oxygen multiplet at 6157 Å was chosen, which had been studied extensively in the first part of this investigation.

By applying Eq. (1) to one line of known and one of unknown transition probability of the same element, one finds upon combining the two expressions

$$A_x = A_s \frac{I_x}{I_s} \frac{g_s}{g_x} \frac{\lambda_x}{\lambda_s} \exp\left(\frac{E_x - E_s}{kT}\right). \qquad (2)$$

The subscripts n and m have been dropped for simplicity. x refers to the line of unknown transition probability, s to the line of known transition probability, hereafter referred to as the standard line. E is the excitation potential and g is the statistical weight of the upper state. Thus A_x is determined by measuring I_s (in order to find T) and the intensity ratio I_x/I_s. Since two lines x and s of the same atom usually originate from nearby upper levels, i.e., $E_x \approx E_s$, the temperature does not enter the A_x determination in a very critical way.

For the two very strong near-infrared multiplets at 7774 and 8446 Å the oxygen concentration had to be greatly reduced to meet the requirement for application of Eq. (1) that the emission comes from an optically thin layer. Therefore, a plasma mixture of approximately 95% nitrogen and 5% oxygen was used. Nitrogen was chosen as the main constituent because, firstly, this element is similar to oxygen in several spectroscopically important properties like its excitation and ionization potentials; and secondly, there are lines with reliable transition probabilities available for the temperature determination, of which the multiplet $3s^4P - 3p^4S^0$ was selected.[9]

The plasma diagnostics was done analogously to the manner described above. First, the plasma was treated as a pure nitrogen plasma and the temperature determined from a nitrogen line of known transition probability. Then corrections for the small admixture of oxygen were made, taking experimental results on the demixing of the elements into account.

The transition probabilities of the two oxygen lines were again determined according to Eq. (2), but using now another oxygen line as a "standard" line. It turned out, that the 6157-Å multiplet was too weak for precise measurements, so that recourse had to be taken to the 7156-Å multiplet, which was studied earlier in this experiment.

EXPERIMENTAL PART

The light source used in this experiment was a wall-stabilized arc burning in oxygen or in a nitrogen-oxygen mixture with the atomic ratio 95:5. The arc chamber and the associated equipment have been described in detail in an earlier paper.[10] Thus, only a few specific details relevant to this particular experiment will be pointed out: The arc channels were chosen to be 5 mm and 4 mm in diameter for the oxygen plasma and the nitrogen-oyxgen mixture, respectively. The flow rates for the test gases and for argon, which was used to blanket the electrodes and surrounding regions, were approximately 100 ml/sec.

The plasma column was observed side on with an Ebert-type photoelectric spectrometer with a dispersion of 10 Å/mm. Photomultipliers of type RCA 1P21 were used for recording the lines in the visible, and type EMI 9588 B for recording the two near-infrared lines. The entrance slit of the spectrometer, which was parallel to the axis of the plasma column, was masked to accept radiation from a layer only 0.5 mm high. Any effect due to nonuniformity along the axial direction caused by bulging of the arc in the observed region was thus eliminated. But the measured intensities were still integrated over regions of various temperatures and densities across the arc and had to be spatially resolved. Utilizing the circular symmetry of the plasma column, the measured intensities were inverted into radial intensities by applying the Abel integral equation. During the course of this experiment an automatic data processing system capable of very high precision was constructed[11] and became available for part of the data inversion.

A precise Abel inversion process is only possible if the source is stable and has rotational symmetry. These conditions were repeatedly checked and found to be closely fulfilled. To control the stability of the arc, its intensity was monitored throughout each experimental run ($\frac{1}{2}$ h) by a second recording spectrometer, located at the extension of the optical axis. The monitoring spectrometer was set at a fixed wavelength for the entire experiment. The intensity could be held within ±3% from the mean for each run with small adjustments of the current and gas flow rates.

The line intensity measurements were done with a broad exit slit, admitting a wavelength band of approximately 15 Å to the multiplier. For each line, measurements at three wavelength settings were required: One at the line center and one in the continuum on each side of the line, usually about 30 Å away. The exact location of the continuum band was dictated by the requirement that it had to be free from impurity lines. (The main impurity was argon diffusing in from the electrode regions.) Since the continuum is practically linear over the 60–100-Å wavelength region between continuum readings, the continuum intensity value under the line was obtained by linear

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[9] The mean value from the work of J. Richter [Z. Astrophysik **51**, 177 (1961)], Bates and Damgaard (Ref. 18), and Doherty (Ref. 17) was chosen.

[10] W. L. Wiese, D. R. Paquette, and J. E. Solarski, Phys. Rev. **129**, 1225 (1963).

[11] D. R. Paquette and W. L. Wiese, J. Appl. Opt. 3, 291 (1964).

TABLE I. Measured oxygen transition probabilities [in 10^7 sec^{-1}] and comparison with other experimental and theoretical results.

Multiplet	λ (in Å)	This experiment	Jürgens	Foster	Doherty	Bates Damgaard	Kelly	Kingsbury	Vainshtein	Buttrey Gibson
$3s^3S^0-3p^3P$	8446	2.6 ±27%	...	...	2.5	3.1	3.0	3.6	...	...
$3s^5S^0-3p^5P$	7773	3.1 ±27%	(3.7)	...	3.1	3.4	3.8	4.3	3.6	...
$3s'^1D^0-3p'^1D$	7157	4.8 ±25%	6.0	...	...	4.5	4.9	4.1	...	...
$3s''^1P^0-3p''^1S$	6654	6.7 ±30%	6.5	...	...	5.3	6.0	4.3	...	...
$3s^3S^0-4p^3P$	4368	0.059±23%	0.075	0.091	...	0.087	0.085	...	0.093	0.072
$3p^5P-4d^5D^0$	6157	0.73 ±20%	0.68	...	...	0.75	0.63	...	...	...
$3p^5P-5s^5S^0$	6455	0.76 ±25%	0.76	...	...	0.74	0.63	...	...	...

interpolation and subtracted from the reading at the line center to give the (uncorrected) line intensity. Corrections were then applied to include the intensity in the far line wings and for deviations from the mean monitoring intensity in each run. The wing corrections were similar to those applied in Ref. 7, where they have been explained in detail. They were based only on the assumption that the oxygen lines have dispersion-type profiles, which has been found to be generally the case under these conditions.[12] The wing corrections amounted to 1–6% of the total line intensities, with the exception of the broad line at 6455 Å where they amounted to 45%.

Since the 6157-Å standard line is very broad (≈16-Å halfwidth) with neighboring broad O I lines at 6046 and 6106 Å, a different technique was used to measure its intensity. With narrow entrance and exit slits corresponding to a wavelength band of 0.3 Å, the intensity was measured at 30 points across the line and the line profile plotted out. After determination of the background with the technique described in Ref. 7, the line intensity was obtained by graphical integration.

Several runs—always with the same settings for current, voltage, and gas flow rates—were performed to measure the total intensity of the investigated multiplets, and the mean values were used to obtain the intensity I_x. Since the multiplets at 6654 and 6455 Å were relatively weak, some additional runs for these were undertaken to reduce the statistical uncertainties.

The detailed intensity mapping of the very broad O I multiplet at 6157 Å proved to be so time consuming that it was done in separate runs, but under conditions identical to those for the other lines. In order to check the reproducibility of the arc conditions and to obtain a good statistical average, this was repeated four times. For the nitrogen-oxygen mixture the nitrogen line used for the temperature determination was measured with a broad exit slit in the same runs along with the oxygen lines.

Absorption and reflection losses on the window of the arc chamber were taken into account experimentally. The condition of emission from an optically thin layer was checked by comparing constructed peak intensities of the lines to that of a blackbody of the arc temperature (using measured intensities and halfwidths, and the assumption of a dispersion-type profile). A correction of 3% was necessary for the 7156-Å multiplet, which turned out to be not quite optically thin ($\tau=0.15$ at the line center). The other lines were found to be optically thin as assumed—the 7774-Å and 8446-Å multiplets, of course, only in the nitrogen-oxygen mixture—and corrections were negligible.

The intensity measurements were placed on an absolute scale, when necessary, by comparison with a calibrated tungsten strip lamp. This lamp was also used for eliminating wavelength-dependent factors, like the sensitivity of the photomultipliers, in the relative intensity measurements for the other lines.

The assumption of local thermodynamic equilibrium (LTE) was checked by applying general equilibrium criteria[13] and was found very nearly fulfilled. It is also borne out by the results of other arc experiments done under similar conditions. Furthermore, the assumption of complete LTE is not critical for this experiment, since the temperature does not enter sensitively into the applied Eq. (2).

RESULTS AND DISCUSSION

The axis temperature of the pure oxygen plasma was determined as 11 980°K from four independent runs. The standard deviation from this mean value was 80°K. All measurements were carried out for the axis position only.

The three components of the nitrogen multiplet $3s^4P-3p^4S°$ at 7468, 7442, 7424 Å were used independently for the temperature determination of the nitrogen-oxygen mixture. Their intensities were measured in four runs, and a mean axis temperature of 12 550°K with a standard deviation of 40°K resulted.[14] The much smaller standard deviation in this case was due partly to the use of three lines instead of only one

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[12] W. L. Wiese and P. W. Murphy, Phys. Rev. 131, 2108 (1963).

[13] H. R. Griem, Phys. Rev. 131, 1170 (1963).

[14] This includes a correction for the oxygen admixture. In view of the demixing effect, an experimental determination of the mixing ratio was undertaken by measuring the ratio of an oxygen and nitrogen line of known transition probability for a number of radial distances. A gradual decrease of the oxygen concentration from 4.9% for the axial position to 3.8% for a radial position of 1 mm was measured. Because of the rather large uncertainty in the absolute values of these numbers and the relatively small change, a flat correction of 5% was applied.

before, and partly to the use of the automatic Abel processing system,[11] which had become available for this part of the investigation. For the mixture, measurements were carried out for several radial positions.

The final mean values of the measured transition probabilities, including wing corrections etc., are presented in Table I together with other experimental and theoretical results. For comparison, the value of the earlier measured multiplet at 6157 Å is also included. The standard deviations of the mean intensity ratios I_x/I_s are about 8% for the two strong multiplets at 4368 and 7157 Å and about 10% for the multiplets at 6455 and 6654 Å. For the 6455-Å multiplet an additional uncertainty, estimated as 5%, arises from the large wing correction. The transition probability of the 6157-Å standard line (A_s) is expected to have an uncertainty not to exceed 20%,[15] and $\Delta T/T$ is estimated to be 2%. The resulting overall uncertainties in the transition probabilities, obtained by treating the uncertainties in the intensity measurements and in the transition probability of the standard line as independent errors, are listed in Table I.

For the two infrared multiplets the 7157-Å multiplet had to be used as the standard line and contributed already an uncertainty of 25%. However, this disadvantage could be partly compensated by the improved experimental precision. Typical standard deviations of the mean intensity ratios were now only 2%. The total error for both multiplets is thus estimated not to exceed 27%. A good indication of the experimental precision is obtained from Fig. 1, where the measured transition probabilities for various radial positions are presented.

The remaining part of Table I contains other experimental and theoretical results. The agreement with other experimentally obtained values—from measurements by Jürgens,[2] Foster,[4] Buttrey and Gibson,[16] and Doherty[17]—is within 25%, except for Foster's value for the 4368Å line, where a difference of 50% occurs.

Jürgens' experiment and its shortcomings, which led to this investigation, have already been discussed in the introduction. It is somewhat surprising to find that his and the present values agree so well. The only detectable tendency is that his values, on the whole, are slightly higher. It appears that because of the turbulence in his arc no significant separations of the elements could take place. This is consistent with the fact that demixing effects have only been observed in the quiescently burning wall-stabilized arcs. Furthermore, Jürgens' method of determining the transition probabilities by comparing the oxygen line intensities with the hydrogen line H_β is quite insensitive to turbulence in the arc, since the temperature dependence of most of these lines and of H_β is very similar. It is suggested by the results of this experiment that the other values measured by Jürgens should be accurate within 25%. But the narrow error limits given in his paper are not justified.

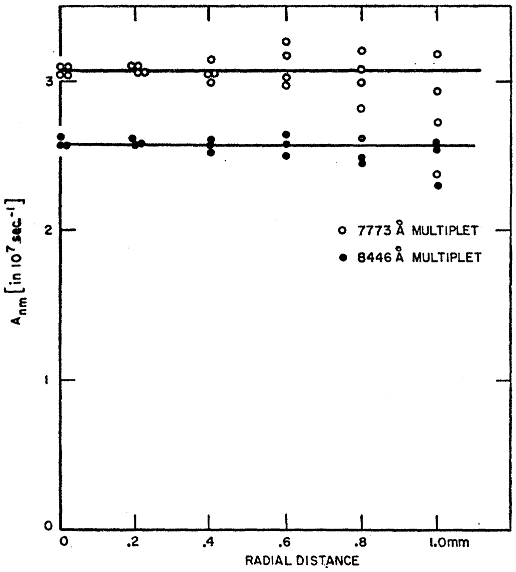

FIG. 1. Transition probabilities for the 7773- and 8446-Å multiplets, measured at several radial positions. Since the intensity at a radial position of 1 mm is only of the order of 10% of the axial value, the results for the larger radial distances were given less weight in the analysis.

Foster's measurements[4] were done with a light source and diagnostic method very similar to that of Jürgens. He discussed the turbulence and demixing problems, but concluded that they were not very significant. The present disagreement with his result for the 4368-Å multiplet is in the same direction as with Jürgens' value but more pronounced.

The transition probability of this multiplet has been measured very recently also in a conventional shock tube by Buttrey and Gibson.[16] This light source, in which the plasma is generated in the region behind the shock front, is fundamentally different from an arc and thus not subject to the aforementioned difficulties. The authors filled the tube with pure oxygen and observed photoelectrically. The plasma conditions were obtained from the Rankine-Huginot equations. Their result, still higher than the present one, but lower than the other arc values, was estimated to have an uncertainty of 30%.

The transition probabilities of the two infrared multiplets at 7774 and 8446 Å have recently been measured by Doherty,[17] again with a conventional shock tube. He employed a gas mixture of neon with

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[15] An earlier error estimate of 30% for this line (Ref. 7), which was based primarily on the accuracy of Stark-broadening calculations, could be revised downward, since recent experimental checks (e.g., Ref. 10) indicate a higher accuracy for these particular Stark parameters. The transition probability was also slightly changed (by 4%) to take these experimental results into account (see also Ref. 12).

[16] D. E. Buttrey and J. B. Gibson, Technical Documentary Report RTD-TDR-63-3047, Defense Documentation Center, Cameron Station, Alexandria, Virginia, 1964 (unpublished).

[17] L. R. Doherty, thesis, Michigan, 1963 (unpublished).

small amounts of oxygen and hydrogen and measured photographically the oxygen line intensities relative to some neon lines, which, in turn, were calibrated against H_β as radiation standard. He estimated uncertainties of 40% for both lines. His numerical values are in remarkable agreement with the present ones. Jürgens' results for the 7774-Å multiplet contain an inconsistency between the f value and transition probability by a factor of 1.7. The new results suggest, that the transition probability quoted by Jürgens rather than the f value is correct. This number has been included in Table I in parentheses.

A number of theoretical results are also available for comparison. However, only those from the more advanced methods will be discussed here. There is, first, the Coulomb approximation by Bates and Damgaard.[18] This method has been applied to many transitions of the lighter elements with great success, and its results compare very well with those from much more elaborate calculations. With the exception of the 4368-Å multiplet, the agreement with the present experimental results is within 25% or better, which is as good or better than generally encountered. For the 4368-Å transition, the Coulomb approximation is not expected to give a reliable value, because the positive and negative contributions to the transition integral nearly cancel in this instance. The same applies, incidentally, to the other theoretical methods to be mentioned below. It is therefore felt, that the present experimental value for this line is the most accurate one.

Another widely used theoretical method, the self-consistent field approximation, has been applied to oxygen by Kelly[19] and Kingsbury.[20] The important exchange effects between the electrons were included in Kelly's work in a simplified manner by using Slater's approximations.[21] Under the assumption of LS coupling Kelly's transition integrals were converted into transition probabilities by applying the Goldberg tables.[22] The agreement with the measurements is as good as in the case of the Coulomb approximation. In addition to the transition integrals, Kelly has tabulated their area ratios, i.e., the ratios of positive to negative contributions. The value applicable for the 4368-Å multiplet turns out to be close to 1 (1.28), which means that a rather uncertain transition probability will result.

Kingsbury[20] also carried out self-consistent field calculations, but he neglected the exchange effects entirely, which makes his values less reliable.

Finally, some results of semiempirical calculations by Vainshtein[23] are available. Vainshtein obtained numerical values for a number of elements and found that his method compared well with experiment and with more elaborate theoretical approximations, such as self-consistent field calculations. He observed that on the whole his approximation has led to overestimates.

All theoretical values are obtained under the assumption of LS coupling. While this assumption is in general supported from energy separations etc.,[24] some deviations occur. For instance, intercombination multiplets $3s^5S^0-3p^3P$ and $3s^3S^0-3p^5P$ have been observed.[25] Although they were found to be of very low intensity, they nevertheless subtract a small fraction from the strength of the 8446-Å and 7774-Å multiplets, which originate from the same upper levels. Since this is not taken into account in the theoretical values, these should appear slightly too high.

CONCLUSION

It appears that Jürgens' values were not significantly affected by the turbulence and demixing problems. There seems to be only a slight tendency detectable—they are, on the whole, somewhat large. The values of the additional 11 multiplets measured by him may thus be considered reliable within 25%. However, for

TABLE II. Suggested transition probabilities.

Multiplet	λ (in Å)	g_n	g_m	Transition probability (10^7 sec^{-1})	Absorption oscillator strength	Line strength (a.u.)
$3s^3S^0-3p^3P$	8446	3	9	2.80	0.895	75.6
$3s^5S^0-3p^5P$	7773	5	15	3.40	0.925	118
$3s'^1D^0-3p'^1D$	7157	5	5	4.73	0.363	42.8
$3s''^1P^0-3p''^1S$	6654	3	1	6.00	0.132	8.74
$3s^3S^0-4p^3P$	4368	3	9	0.0655	0.00561	0.243
$3p^5P-4d^5D^0$	6157	15	25	0.703	0.0665	20.2
$3p^5P-5s^5S^0$	6455	15	5	0.710	0.0148	4.71

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[18] D. R. Bates and A. Damgaard, Phil. Trans. Roy. Soc. (London) **A242**, 101 (1949).
[19] P. S. Kelly, J. Quant. Spectry. Radiative Transfer **4**, 117 (1964).
[20] R. F. Kingsbury, Phys. Rev. **99**, 1846 (1955).
[21] J. C. Slater, Phys. Rev. **81**, 385 (1951).
[22] L. Goldberg, Astrophys. J. **82**, 1 (1935); **84**, 11 (1936).
[23] L. A. Vainshtein, Opt. i Spektroskopiya **3**, 313 (1957).
[24] Ch. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949), Vol. I.
[25] K. B. S. Eriksson and H. B. S. Isberg, Arkiv Fysik **24**, 549 (1963).

the presently investigated multiplets, the results of this experiment should be regarded as superseding his and Foster's values.

For all multiplets except the one at 4368 Å the spread between the most recent theoretical and experimental results, namely those of Bates and Damgaard, Kelly, Vainshtein, Buttrey and Gibson, Doherty and this experiment, does not exceed 26%. One of the rare cases is encountered, where the agreement between several independent methods is so good that one may consider the mean values from the above mentioned methods reliable to within 10%. These mean values are recommended for future applications and are assembled in Table II.

The comparison indicates, furthermore, that for the lighter elements the advanced theoretical methods give results as reliable as experiments. Since the former involve less time and effort (the Coulomb approximation by Bates and Damgaard is generally available), they should be extensively applied. On the other hand, experimental determination of transition probabilities should be concentrated on transitions where interferences in the transition integrals or deviations from *LS* coupling occur.

PHYSICAL REVIEW VOLUME 135, NUMBER 5A 31 AUGUST 1964

Application of a Kinetic Model to Time-Dependent Density Correlations in Fluids*

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(Received 8 April 1964)

The kinetic model of Bhatnagar, Gross, and Krook is used to study the double Fourier transform of the time-dependent density correlation function $G(r,t)$. The results are appropriate to a dilute fluid for arbitrary ratio of wavelength to mean free path. The results of the model calculations are compared to those derived from the linearized hydrodynamic equations. Since neutron and light-scattering experiments can be analyzed in terms of $G(r,t)$, this comparison indicates that the hydrodynamic description should be applicable for momentum transfers less than $(\hbar/2\lambda)$, where λ is the collision mean free path in the fluid.

I. INTRODUCTION

THE theory of nonequilibrium phenomena has been significantly extended by the development of relationships between the linear response of a system to an external disturbance and the time-dependent correlation functions expressing the propagation of equilibrium fluctuations in the system. These developments have been primarily used to give exact expressions for transport coefficients in terms of time-dependent correlation functions.[1] It is, however, sometimes profitable to use our knowledge of the linear response to determine certain properties of those correlation functions that are directly measurable.

In recent years inelastic scattering of slow neutrons has become an important process for the study of molecular dynamics in condensed states of matter.[2] In a well-known work Van Hove[3] showed that the energy and angle differential cross section is proportional to the double Fourier transform of a time-dpendent correlation function $G(\mathbf{r},t)$. By definition, $G(\mathbf{r},t)$ is the equilibrium ensemble average of a product of two time-dependent density operators and is therefore closely related to the linear response of the system to an externally induced density disturbance. As recently emphasized by Kadanoff and Martin,[4] connections of this type can be usefully exploited, particularly in the limit of slow space and time variation. In the present work we consider arbitrarily fast space and time variation, but are restricted to the limit of low density.

Since $G(\mathbf{r},t)$ is in general complex its interpretation as a time-displaced, density-density correlation function has no simple physical meaning.[5] On the other hand, the physical content of this function is simply revealed when it is considered in classical terms. For then $G(\mathbf{r},t)$ gives the probability per unit volume of finding an atom at $(\mathbf{r},t)$ given an atom at the origin at $t=0$ and clearly describes the space-time evolution of density correlations in the system. In the following sections we make explicit use of this physical interpretation; consequently, the calculation concerns only classical systems.[6]

When a system initially in equilibrium is perturbed very slightly, its behavior, except for short-time transients, can be described in terms of the variations of a small number of macroscopic quantities. Moreover,

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* Work supported in part by the U. S. Atomic Energy Commission.

[1] R. Kubo, *Lectures in Theoretical Physics* (Interscience Publishers, Inc., New York, 1959), Vol. I, Chap. 4.

[2] *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961); also Vol. I, 1963.

[3] L. Van Hove, Phys. Rev. **95**, 249 (1954).

[4] L. Kadanoff and P. C. Martin, Ann. Phys. (N. Y.) **24**, 419 (1963).

[5] For an interpretation of the imaginary part of $G(\mathbf{r},t)$, see L. Van Hove, Physica **24**, 404 (1958).

[6] The relation between neutron scattering and the classical correlation function has been studied by R. Aamodt, K. M. Case, M. Rosenbaum, and P. F. Zweifel, Phys. Rev. **126**, 1165 (1962).