The researches of M. A. Leontovich in optics and acoustics[1]

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A brief review is given of M. A. Leontovich's researches in optics and acoustics betweeen 1926 and 1941. Particular attention is devoted to his work that laid the foundations for new fields of research in molecular acoustics and molecular optics. Three of M. A. Leontovich's experimental papers are also reviewed.

The scientific researches of M. A. Leontovich in optics and acoustics, performed by himself, with his teacher L. I. Mandel'shtam, or with his colleagues and pupils, constitute a considerable contribution to science and have served as the starting point and the foundation for new fields of research.

This original work has now led to the development of extensive fields of study in molecular optics and molecular acoustics.

1. SCATTERING OF LIGHT BY A SURFACE

The beginning[2] of M. A. Leontovich's researches in optics goes back to 1926 when, at the early age of 23, he collaborated with A. A. Andronov to develop a general quantitative theory of molecular scattering of light by the surface of a liquid.[1]

Thirteen years before this paper, L. I. Mandel'shtam laid the foundations of the theory of light scattering by the surface of a liquid. His results referred to the case where the scattered ray of light lay in the plane of incidence and made a small angle with the specularly reflected ray.

Leontovich and Andronov considered the most general case and obtained the corresponding formulas, the validity of which was confirmed experimentally. They examined fluctuational "roughness" whose amplitude ζ was much smaller than the wavelength λ of the radiation incident on the surface. This "roughness" was developed into a two-dimensional Fourier series and the problem was to determine the intensity of light reflected and refracted in different directions by the deformed surface.

It follows from the solution of the problem that there are reflected and refracted waves similar to those predicted by the Fresnel formulas for a perfectly smooth separation boundary. However, in addition to these waves there are also waves diffracted (scattered) by plane diffraction gratings (sinusoidal diffraction gratings or Fourier components of the above Fourier series).

When light is incident on a sinusoidal grating there is a unique diffracted wave whose direction depends on the angles and the wavelength. In practice, diffraction gratings have finite size, so that the diffracted light will include a set of diffracted waves from each "grating". This was taken into account by Leontovich and Andronov who found the resulting general formulas for the intensity of any scattered ray.

It is clear from the theory developed by them that the intensity of light scattered in any direction is a function of the angles and depends on the parameters of the material. It is given by

$$I\, d\Omega = I_0 \left(\frac{2\pi}{\lambda\Omega} \right)^4 \overline{|\zeta_{lm}|^2} s\Phi (\theta,\ \varphi)\, d\Omega, \tag{1}$$

where $d\Omega$ is a solid angle element within which the light flux is calculated, I_0 is the incident intensity, s is the area of a portion of the infinite grating, θ and φ are the polar angles, $\Omega = 2\pi/a$, a is the length of the side of the illuminated square, the mean square of the fluctuation is given by

$$\overline{|\zeta_{lm}|^2} = \frac{c_1 \left(\frac{\Omega}{2\pi}\lambda \right)^2}{c_2 + \sin^3 \theta_0 + \sin^2 \theta + 2 \sin \theta_0 \sin \theta \cos \varphi}\ ; \tag{2}$$

$c_1 = kT/4\pi\gamma^*$, $c_2 = (g\delta/4\pi\gamma^*)\lambda^2$, γ^* is the surface tension, g is the gravitational acceleration, and δ is the density difference between the media forming the separation boundary.

$\Phi(\theta,\ \varphi)$ in (1) is a complicated but known function. Since the term $\lambda^2 c_2\gamma^* = g\delta\lambda^4/4\pi$ can always be neglected in comparison with the other terms in the denominator of (2), the intensity of light that has undergone molecular scattering by the surface is shown by (1) to be inversely proportional to λ^2, whereas for bulk scattering the intensity is inversely proportional to λ^4 (Rayleigh's Law). This theory is distinguished by a considerable degree of generality. It is invalid only in a narrow temperature range near the critical point at which the "roughness" becomes appreciably greater than the wavelength. Outside this narrow range, the theory gives a full description of surface scattering by nonabsorbing media and predicts accurately both the intensity and the polarization.

In a separate brief note[2], M. A. Leontovich examined the scattering of light by the surface of mercury (a material of finite conductivity). He showed that, in this case, the scattered light was elliptically polarized, and

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[1] Translator's note: The Russian text uses combination instead of Raman. This is emphasized in this translation by placing Raman in parentheses.

[2] M. A. Leontovich's very first paper was published in Zeitschrift für Physik in 1925. It was entitled "On the Lewis equilibrium principle".

determined the ratio of the semiaxes of the ellipse as a function of the angle of scattering for normal and for 45° incidence on the separation boundary. The results of these calculations are in agreement with experimental data.

M. A. Leontovich did not confine himself to the comparison of his theory with experimental data, but decided to undertake himself the experimental verification of his general formulas, although he did limit this experimental work to the special case of scattering by static surface roughness.

M. A. Leontovich is usually considered to be a pure theoretician, but this was not the case. In the field with which we are concerned here, there are three experimental papers due to M. A. Leontovich himself but, of course, his main achievements have been in theoretical physics.

The first of these papers was devoted to the scattering of light by slightly matt surfaces.[3] M. A. Leontovich applied the results obtained with Andronov[1] to such surfaces, and analyzed the difference between scattering by static fluctuations and slightly matt glass surfaces. He concluded that, in the latter case, his calculations could be compared with experiment only for quantities that did not explicitly involve the mean square roughness "amplitude" $|\zeta|^2$ (see below). When this was so, the ratio of the characteristic size of surface roughness to the wavelength λ had to be small. This is how Leontovich himself wrote about the conditions of his experiment: "The experiments were performed with matt glass plates having good light transmission. These were in the form of unpolished glass plates intended as eventual mirrors. The degree of surface roughness depended on the precise time at which the surface polishing process was stopped.[3] As already noted, the following were investigated: (1) the state of polarization of diffusely scattered light and (2) the dependence of the relative intensity on the direction and wavelength of light.

Here it is important to note that, for the plates that I have used, which had the maximum transmission, the condition $\zeta/\lambda \ll 1$ could hardly have been regarded as satisfied, so that one would have expected only approximate agreement between experiment and theory.

To summarize, these experiments clearly showed that, firstly, the results of observations were increasingly closer to the calculations as the degree of roughness was reduced and, secondly, for the lowest degree of roughness that I have used, the agreement with the theory was satisfactory."

There follows a detailed account of the results of measurements of polarization and relative intensity. A table of measurements is reproduced and is accompanied by a careful discussion of these data. The fundamental paper containing improved theory and an account of the careful measurements concludes with acknowledgements to L. I. Mandel'shtam and G. S.

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[3] I was not able to produce the required slightly matt surfaces by treating the surface with hydrofluoric acid.

Landsberg whose merciless critique it evidently survived.

While M. A. Leontovich was working in the laboratory of L. I. Mandel'shtam in the Department of Physics of Moscow University (now the M. V. Lomonosov Moscow State University), the laboratory of S. I. Vavilov was enquiring into the nature of the quenching of the fluorescence of molecules observed in viscous liquids.

In a separate paper M. A. Leontovich solved the problem of fluorescence quenching by collisions between excited fluorescing molecules and other dissolved molecules. He considered the diffusion problem and obtained a formula for the mean time between the excitation of a molecule and its first collision, and derived the dependence of fluorescence energy on concentration and diffusion coefficient. The theoretical conclusion was compared with the experimental data of S. I. Vavilov and his collaborators.

2. RAMAN AND RAYLEIGH SCATTERING OF LIGHT

M. A. Leontovich began his work in L. I. Mandel'shtam's laboratory at the university at a time of unusually intensive and successful work at this laboratory on the experimental and theoretical examination of the scattering of light by solids.

After transferring, in 1925, to the Department of Physics of Moscow University, L. I. Mandel'shtam put forward the interesting and also at that time exceedingly difficult problem of detecting the change in the frequency of scattered light due to the modulation of the latter by the thermal elastic Debye waves that are always present in the medium at temperatures other than absolute zero.

The expected change in the frequency was of the order of 10^{-5} of the incident frequency.

It is now well-known that the Landsberg-Mandel'shtam experiment revealed that the change in frequency when light was scattered by a quartz single crystal was greater by three or four orders of magnitude, and this was readily observed in a simple (and by present standards, rather poor) spectrograph.

This was the phenomenon of combination (Raman) scattering—one of the most significant discoveries of the 20th century. The discovery was made in the presence of M. A. Leontovich who was working in the laboratory and could hardly avoid being party to these remarkable researches.

In fact, an experimental investigation by M. A. Leontovich,[5] performed together with G. S. Landsberg, appeared soon after and was devoted to the temperature dependence of the red and violet satellites in the combination (Raman) spectrum of quartz.

They base their results on the fact that the intensity of the Rayleigh or, as they call it, the fundamental, scattered line is proportional to absolute temperature.

They described the temperature dependence of the combination (Raman) line intensities as follows: "The intensity of the combination lines is probably deter-

mined by the number of elementary processes responsible for energy transfer between light and matter, and depends on temperature in a totally different way (quantum statistics and classical statistics)."

Leontovich and Landsberg continue to use the language of light quanta and proceed as follows: "From this point of view, one would expect the appearance of the red satellite when a light quantum interacts with either an excited or an unexcited system. Violet satellites can appear when the quantum collides with an excited system. The number of excited systems increases with temperature very rapidly, but the number of unexcited systems decreases with temperature very slowly.

As the temperature increases, one would therefore expect an increase in the intensity of the violet satellites, whereas the intensity of the red satellites should remain practically unaltered".

This quotation reproduces almost exactly, in words, the content of the formulas used in that paper.

Complex and laborious photographic photometry eventually yielded quantitative results that showed that the intensity of the 21.5-μm satellite varied in accordance with theoretical predictions in the range between 20° and 210°C, namely, the intensity of the violet satellite increased by a factor of three whereas the intensity of the red satellite remained practically constant. Moreover, the intensity of the fundamental line was proportional to the absolute temperature.

This was the first investigation of this kind and played an important role in the understanding of the mechanism responsible for the new phenomena. All its conclusions continue to be valid.

The third experimental paper by M. A. Leontovich is concerned with the following fundamental question: if the 9.13-μm satellite found in the first pioneering paper by Landsberg and Mandel'shtam for Iceland spar ($CaCO_3$) was due to the oscillations of the CO_3 group, does it also occur in the case of the water solution of potash (K_2CO_3) in which the CO_3 group is also present?

M. A. Leontovich carried out just such an investigation using an aqueous solution of potash. In this, he was forced to perform repeated filtration of the solution in order to free it from extraneous particles.

In his experiment he found a 9.26-μm satellite in a K_2CO_3 solution, which was very close to the wavelength of the satellite seen in Iceland spar, so that this result could be regarded as an experimental verification of the fact that this satellite characterizes the natural vibrations of the CO_3 group.

This was a difficult experimental investigation. Suffice it to say that 90-hour exposures were frequently necessary.

It seems to me that this paper contains a further very important result. The author mentions it in passing and only in parentheses: "Apart from this particular satellite [a weak diffuse band that is undoubtedly due to scattering in water ($\lambda \simeq 3 \mu$m)], there is no sign of other satellites in the K_2CO_3 solution although one

would have expected to see traces of a further satellite corresponding to $\lambda = 34.4 \mu$m, since this is also due to the internal oscillation of the CO_3 group". This is the first or, at any rate, one of the first, observations of the combination (Raman) band of water that has played such an outstanding role in the study of intermolecular interactions, including hydrogen bonding, and has revealed so much information about one of the most important materials on Earth, namely, ordinary water.

3. THEORY OF MOLECULAR SCATTERING OF LIGHT BY CRYSTALS

The range of M. A. Leontovich's scientific interests was very wide, and Mikhail Aleksandrovich worked hard and successfully. By the time he was 26, he had published 14 papers, mostly in Zeitschrift für Physik which was the leading physics journal of the day.

The principal achievement of the laboratory in which M. A. Leontovich worked at the time was the then recent discovery of combination (Raman) scattering of light, and the attention of the laboratory was largely directed toward the development of research on combination (Raman) scattering.

M. A. Leontovich began with the development of a classical theory of combination (Raman) scattering. The first theoretical paper was published by him jointly with L. I. Mandel'shtam and G. S. Landsberg,[7] but a more general problem arose, namely the development of a classical theory of molecular scattering of light by solids. M. A. Leontovich was a pioneer in this field and—this is particularly important—his work mapped out the correct general way ahead for theoretical studies in the molecular optics of solids, which is now an extensive branch of physics.

Leontovich, Mandel'shtam and Landsberg[7] realized that a complete theory of combination (Raman) scattering had to be a quantum mechanical theory but, at very high temperatures, a classical approach to intensity calculations could be attempted.

In the classical approach, the scattered light was looked upon as radiation diffracted by the elastic oscillations or waves propagating through the crystal, and the spectrum of such oscillations was known as a result of the theoretical work of Debye and Born. It is well known that these oscillations can be divided into acoustic (or Debye) and optical (or Born) oscillations or waves in the crystal.

The scattered light is none other than the light diffracted by the thermal waves propagating through the crystal and forming "diffraction" gratings.

Whereas acoustic oscillations are characterized by density variations, Leontovich, Mandel'shtam and Landsberg[7] pointed out that in optical oscillations ".....we are concerned not with density oscillations but with changes in the mutual distances of atoms or complexes of atoms in the lattice (structure oscillations)". They go on to point out that if such displacements lead to changes in the refractive index, the result should be an optical inhomogeneity due to this oscillation of the

diffraction gratings. The variation in the refractive index with time that accompanies such oscillations leads to a change in the frequency of the scattered light.

This qualitative picture suggests that the scattered light should contain a fundamental line, split as a result of the modulation of the scattered light by the frequencies of the elastic oscillations or by the acoustic branch of the frequency dispersion curve. These shifts should be small. Moreover, the scattered light should also contain highly shifted lines due to the modulation of the scattered light by the "structure oscillations" or the modulation by frequencies lying on the optical (infrared, as they preferred to call them[7]) frequency branches.

Of course, it is a far cry between the qualitative picture and the quantitative calculation, but this calculation is in fact performed in Ref. 7. The basic scheme is as follows.

It is assumed that the optical dielectric permittivity tensor ε_{ik} is distorted by the displacement u_r of the lattice elements, and the resulting change in permittivity is represented by

$$\Delta\varepsilon_{xx} = \sum_r g^r_{xx} u_r,$$
$$\Delta\varepsilon_{xy} = \sum_r g^r_{xy} u_r, \tag{3}$$

where $\mathbf{u}$ is the displacement of the r-th particle in the unit cell of the crystal lattice. The quantity $g^r_{x,y}\mathbf{u}$ is to be understood as representing $\Sigma g^r_{xy,\xi} u_{r\xi}$ (ξ assumes the values x, y, z) and the quantity $g^r_{xy,\xi}$ is a tensor of rank 3 for given r.

Following Born, the oscillation $\mathbf{u}(r)$ is represented by

$$u_r = \frac{1}{\sqrt{N}} \sum_{j,\mathbf{k}} \mathbf{a}_{rj} p_j \cos(\omega_j t + \varphi) \cos(\mathbf{k}r), \tag{4}$$

where N is the normalizing factor equal to the total number of cells in the crystal, p_j is the amplitude of natural oscillations, $\mathbf{a}_{rj}$ are eigenvectors defining the direction of the natural oscillations, $\mathbf{r}$ is the radius vector of the unit cell, and $\mathbf{k}$ is the wave vector.

The expression given by (4) also takes into account the frequency of acoustic oscillations but, since the authors were interested only in the optical or infrared part, they retained only ω_{0j} in the expansion $\omega_j = \omega_{0j} + \bar{\omega}_j k + \bar{\bar{\omega}}_j k^2$ ($k = |\mathbf{k}|$ is the wavenumber) and omitted the indices from there on (thus retaining a single structure oscillation in the description). The scattered intensity was then determined by introducing the fictitious electromotive force F defined by

$$\varepsilon_0 F_x = \Delta\varepsilon_{xx} E^0_x + \Delta\varepsilon_{xy} E^0_y + \Delta\varepsilon_{xz} E^0_z; \tag{5}$$

where $E^0 = \cos(\nu_0 t - s_0 x)$ and ν_0 is the frequency of the incident light.

For the light scattered by a volume element $d\tau$ in the direction of the y axis, the field strength is

$$E = \frac{d\tau}{4\pi R}\left(\text{grad div} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right) F\left(t - \frac{R}{c}\right), \tag{6}$$

where c is the velocity of light and R is the separation between volume element $d\tau$ and the point of observation. Substituting (3)–(5) into (6), we obtain the expression for

the electric field of the scattered wave. We shall omit all the intermediate steps, which can be found in Ref. 7, and merely note that the final result indicated that the scattered light contained fields with frequencies $\nu_+ = \nu_0 + \omega$ and $\nu_- = \nu_0 - \omega$. These are, in fact, the satellites or combination (Raman) lines. Classical theory shows that the amplitude ratio for the red and violet satellites is equal to $(\nu_0 + \omega)^2/(\nu_0 - \omega)^2$. This ratio is equal to unity when $\omega \ll \nu_0$, which means that classical theory assigns equal intensities to the violet and red satellites. This can be right only at very high temperatures, and is not valid for ordinary media at room temperature. Subsequent calculations showed that the ratio of the scattered light intensity $I(\nu)$ at frequency ν to the intensity I_0 of the incident light at frequency ν_0 yields the following result:

$$\frac{I(\nu)}{I_0(\nu_0)} = \frac{G_{\alpha\beta}\nu^4\tau}{(8\pi c^2 R_0)^2}\frac{\overline{W}}{\omega_0^2}, \tag{7}$$

where $G = \sqrt{\alpha^3}(g_{\alpha\beta,\xi}\mathbf{a}_{r\xi})$, α^3 is the volume of a unit cell of the crystal, $G_{\alpha\beta}$ is a measure of the change in the refractive index in the course of the oscillations (and is different for different frequencies), and $\overline{W}$ is the average energy of the oscillator. Hence it follows, in particular, that the behavior of the intensity of the satellites is also determined by the zero-point energy. Since G is unknown, the authors were unable to find a numerical value for the ratio (7).

This paper also contains a number of statements relating to the polarization of the combination (Raman) lines, but this problem is treated in detail in a separate paper by M. A. Leontovich[8], published in the following year by which time the quantum theory of combination (Raman) scattering had been developed.

Since both quantum and classical theories lead to the same result for the polarization of combination (Raman) components, M. A. Leontovich developed the classical theory of the polarization of Raman lines.[8]

It is noted in Leontovich's theory that all the polarization properties of the scattered radiation can be derived from the following expressions for the components of the electric vector of the scattered light:

$$E_x = A(G_{xy}E^0_y + G_{xz}E^0_z),$$
$$E_z = A(G_{zy}E^0_y + G_{zz}E^0_z). \tag{8}$$

The tensor $G_{\alpha\beta}$ is the same as in Ref. 7. M. A. Leontovich continues in the following words: "To determine the polarization of the scattered light, we must first establish the conditions that are satisfied by the tensor as a consequence of the symmetry of the crystal. These symmetry conditions have a different form for simple and multiple oscillations".

Leontovich then carries out an analysis that enables him to find, for simple natural oscillations, the components of the tensor that are nonzero for the triclinic, monoclinic, rhombic, tetragonal, trigonal, hexagonal, and cubic systems.

He then performs a still more complicated analysis to find the nonzero components of the tensor $G_{\alpha\beta}$ for doubly degenerate oscillations, and constructs the corresponding table (Table II) at the end of the paper.

Finally, he compares theoretical calculations with experimental results obtained by Cabannes (quartz and Iceland spar) and Menzies (quartz), and achieves qualitative agreement between the two.

In an annotation added in proof, he discusses the effect of the rotation of the plane of polarization in the crystal, and the influence it has on the determination of polarization in combination (Raman) scattering.

The next substantial step in theoretical research was made by M. A. Leontovich in collaboration with S. L. Mandel'shtam[9,10]. They considered the scattering of light by density fluctuations in a crystal by analogy with the Einstein theory of light scattering by density and concentration fluctuations in liquids and solutions.

They used the Einstein approach in which fluctuations are expanded into a Fourier series in space, and made a statistical calculation of the mean squares of the coefficients of this expansion. The problem then reduces to ensuring that the final formulas contain the measured quantities. They solved this problem and did, in fact, obtain the formulas for the relative intensity of light scattered by crystals of cubic and trigonal symmetry.

In the case of a cubic crystal, the relative intensity turned out to be (here and elsewhere in the paper we are retaining the original notation)

$$R = \frac{\pi^2 \tau k T \mu^8}{2\lambda^4 r^2} \left[\frac{2(p_{12}^2 + p_{44}^2)}{c_{11} + c_{12} + 2c_{44}} + \frac{p_{44}^2}{c_{44}} \right], \tag{9}$$

where τ is the scattering volume, k is Boltzmann's constant, μ is the refractive index, r is the separation between the scattered volume and the point of observation, p_{ik} are the optoelastic constants, and c_{ik} are elastic constants.

Subsequently, many workers followed the path indicated by the above paper, and we now have solutions for the scattering of light in the most general case for any crystal in any crystallographic direction.

The paper by M. A. Leontovich and S. G. Kalashnikov[11] was devoted to the effect of thermal oscillations on the scattering of x-rays by crystals, and in a certain sense belongs to the same range of investigations.

The theory of scattering of x-rays, in which the effect of thermal oscillations is taken into account, is due to Debye, Waller and Zener (1914–1936).

They represented the thermal displacements of the atoms by the superposition of the elastic Debye waves mentioned above.

The problem was solved by explicitly considering the normal oscillations of the lattice and the spectrum of these oscillations, which gave rise to a very considerable complication of the theory.

To determine the contribution of the thermal motion of lattice atoms to the scattering process, it is sufficient to know $\overline{\xi_j \eta_k}$ where ξ_j and η_k are the projections of the instantaneous thermal displacements of two atoms on a particular direction. Leontovich[12] gave a general method for evaluating quantities of the form

$\overline{\xi_j \eta_k}$, which reduces to the solution of a certain statistical problem.

By exploiting the Leontovich theorem, the authors of Ref. 11 were able to determine the temperature factor as a function of the mean square atomic displacement for crystals of arbitrary symmetry.

This led to a simpler theory, as compared with theories available before, and at the same time a more accurate calculation was made of the thermal scattering of x rays.

Leontovich[13,14] developed a quantitative theory which could be used to determine the intensity of light scattered by a nonuniformly heated crystal.

Almost 50 years ago, Mandel'shtam pointed out[15] that the intensity of light scattered by elastic waves with little damping in the medium is determined not only by the temperature at a given point, but also by the entire temperature distribution in the medium. Moreover, he noted that the difference increased with decreasing damping of the elastic wave responsible for the scattering of light.

M. A. Leontovich considered the quantitative theory of this interesting phenomenon twice. First[13] (1935) he developed a complex theory that actually applied to the special case of a one-dimensional model of a solid. Four years later he returned to this topic[14] and examined the more realistic case of a three-dimensional body that was infinite in the x, y plane and finite in the z direction. The temperature gradient was assumed to lie in the z direction.

M. A. Leontvich determined the intensity distribution of elastic waves in a medium in the same way that is used in optics to determine the light intensity distribution in a medium capable of absorption and emission, for example, as in the case of thermal emission. In the Leontovich theory, elastic waves are looked upon as a set of noncoherent rays of different direction. Energy transfer between these waves and high-frequency elastic waves in the crystal occurs through emission and absorption.

Leontvich's theory was concerned with the solution of the rigorous problem with realistic boundary conditions, and led to the following expression for the intensity due to molecular scattering of light. We reproduce the expression for the case where the temperature gradient $G_T = (T_l - T_0)/l$ is parallel to the direction of the incident beam of light and lies along the positive z axis (θ is the scattering angle):

$$I(z, \theta) = c \left\{ T + \frac{G_T \sin \frac{\theta}{2} \cdot \exp\left[\frac{2\alpha l}{2 \sin(\theta/2)} \right](1 + R)}{2\alpha \left[1 + R \exp\left(2\alpha l/\sin(\theta/2)\right)\right]} \operatorname{sh}\left[\frac{2\alpha \left(\frac{l}{2} - z \right)}{\sin(\theta/2)} \right] \right\} \tag{10}$$

where T_0 is the temperature at the lower end of the crystal, T_l is the temperature at the upper end of the crystal of thickness l, T is the temperature at the point z, α is the amplitude sound-absorption coefficient, R is the reflection coefficient for elastic waves on the

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4)M. A. Leontovich also found $I(z)$ for a parabolic dependence of the temperature of the body on the position coordinate.

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separation boundary, and c is a constant that includes all quantities that do not depend on temperature and absorption of elastic waves. When there is no gradient and the temperature is uniform, $I = cT$.

Experimental verification of this theoretical result could have been expected to reveal a fundamental new way of determining the damping coefficient in the ultrasonic part of the acoustic spectrum.

Experiments undertaken by G. S. Landsberg and A. A. Shubin, that were capable of about 10% accuracy, did not reveal any intensity difference between the uniformly heated quartz crystal and the crystal placed in a temperature gradient.

V. V. Vladimirskiĭ noted in 1942 that a nonuniformly heated body should exhibit an asymmetry between the red and violet Mandel'shtam-Brillouin components. This problem was ignored for a long time, and a suitable experiment was not put forward.

The problem surfaced again about three years ago, and has been widely discussed in the literature, mainly by theorists (see, for example, Ref. 17), but to some extent by experimentalists as well. However, it is still too early for any definite results.

4. RESEARCH IN ACOUSTICS

Interest in acoustic problems apparently arose both because of the unusual situation that emerged as a result of studies of molecular scattering of light (now known as Mandel'shtam-Brillouin scattering) and because of the discrepancy between the measured and calculated (from the hydrodynamic theory) absorption of sound in polyatomic gases and liquids.

New ideas—and they were purely qualitative at first—were put forward to overcome these fundamental difficulties.

In a lecture[18] that he gave just before the publication of his paper,[19] Leontovich states: "The Institute of Physics of Moscow University and the Physics Institute of the Academy of Sciences are engaged on several research projects on the absorption of sound in gases and liquids under the guidance of L. I. Mandel'shtam".

The theory of absorption of sound in gases with allowance for viscosity and thermal conductivity was developed as far back as 1868 by Kirchhoff, who showed that the absorption coefficient was proportional to the square of the frequency, viscosity, and thermal conductivity.

Experiments performed in the ultrasonic range confirmed the theoretical frequency dependence, but the measured absorption coefficient turned out to be much higher than the theoretical prediction.

The fine structure of the Rayleigh lines in crystals and liquids was discovered in 1930, and the Mandel'shtam-Brillouin components of this structure were found to be due to elastic thermal waves of frequency $f = 2nv \sin(\theta/2)/\lambda$ and half-width $\delta\omega = 2\alpha v$, where n is the refractive index of the medium, v is the velocity of ultrasound, and α is the amplitude absorption coefficient of the ultrasonic waves.

Estimates show that $f \simeq 10^{10}$ Hz. When the absorption coefficient α measured in the ultrasonic range at 10^7 Hz is extrapolated parabolically to 10^{10} Hz, it is found that α is so high that it is not meaningful to speak of a wave, i.e., the Mandel'shtam-Brillouin waves cannot be observed.

On the other hand, experiment shows that the Mandel'shtam-Brillouin waves *are* observed and are relatively narrow. This fact is in direct conflict with the hydrodynamic theory.

Difficulties in the interpretation of experimental data in terms of a theory that takes into account only shear viscosity and ordinary thermal conductivity were analyzed in detail by Mandel'shtam and Leontovich.[20] They came to the conclusion that both contradictions could largely be removed by taking volume viscosity η' into account in the hydrodynamic theory (which had been done before by Rayleigh) and by allowing for relaxation processes during the evolution of the frequency dependence.

The first careful examination of the hydrodynamic and kinetic theories of propagation of sound in polyatomic gases is due, as we have said, to Leontovich.[19] Generally speaking, both the first (η) and the second (η') coefficients of viscosity and the first (ν) and the second (ν') thermal conductivities have to be taken into account in the theory of propagation of sound.

Theoretical studies based on the kinetic theory of propagation of sound enabled Leontovich to show that, at low frequencies or, more precisely for $\omega\tau \ll 1$ (ω is the frequency of sound and τ is the mean free time between collisions between the gas molecules), allowance for the second viscosity was essential, whereas $\nu' = 0$. Moreover, it became clear that, in this frequency range, allowance for η' was entirely equivalent to allowance for ν', and that only one of them needed to be taken into account. At more or less the same time, Kneser pointed out a new mechanism for additional absorption of sound in polyatomic gases, namely, energy transfer from external to internal degrees of freedom, and developed a molecular theory of absorption of sound in gases, which was found to be in good agreement with experiment.

Leontovich showed that, in polyatomic gases and when $\omega\tau \ll 1$, losses accompanying energy transfer from external to internal degrees of freedom were represented by the second viscosity.

The hydrodynamic theory predicts that the amplitude sound absorption coefficient is given by[18]

$$\alpha = \frac{\omega^2}{2a^3}\left[\frac{4}{3}\frac{\eta}{\rho} + \frac{\eta'}{\rho} + \nu\left(1 - \frac{1}{\gamma}\right)\right]; \qquad (11)$$

where a is the Laplace velocity of sound ($a^2 = \gamma p/\rho$) and $\gamma = c_p/c_v$. From gas-kinetic data it follows that $\eta/\rho \simeq a^2\tau$ and hence $\alpha\Lambda$ (sound attenuation within one wavelength Λ) turns out to be of the order of l/Λ (l is the mean free path).

The hydrodynamic theory is valid provided only this ratio is small. The viscosity η' often plays a very important role.

For example, in liquid benzene, the value of α measured in the ultrasonic frequency range is greater by a factor of 90 than the value obtained when only η is taken into account.

In the Kneser theory of absorption of sound, only η and ν need be taken into account; as far as η' and ν' are concerned, they are already taken into account in an explicit form.

The expression obtained by Kneser for the sound absorption coefficient yields a quadratic dependence of α on frequency for $\omega\tau \ll 1$ and no dependence on frequency for $\omega\tau \gg 1$. Thus, inclusion of second viscosity brings about an agreement between theory and experiment, and difficulties connected with the quadratic extrapolation of α can be removed by deriving a Kneser type expression for α in liquids.

Sound absorption and dispersion in liquids were examined by Mandel'shtam and Leontovich in a broad frequency range.[20] The solution they obtained for this exceedingly difficult and general problem formed the beginning of a new branch of molecular acoustics.[21]

This purely theoretical investigation was complicated by the very nature of the problem. It is difficult to summarize it briefly, but we shall try to outline the overall scheme, and will then reproduce the most important results.

The second viscosity η' was not neglected in any of the cases considered. For liquids, this viscosity does not have the relatively simple significance that it has in polyatomic gases, and it is important to note that liquids were not treated as gases with liquid densities. It was clearly understood that the difference between a gas and a liquid was not only quantitative but—and this is more important—also qualitative.

Mandel'shtam and Leontovich write: "We assume that, in addition to the pressure p, density ρ, and temperature T, the equation of state also includes certain parameters ξ (or several such parameters) that are functions of p and T in the state of equilibrium. However, in the general case, when equilibrium does not obtain, they satisfy a certain 'reaction equation'. As expected, these assumptions lead to viscous stresses during uniform expansion".

The physical significance of the internal parameter, or internal parameters ξ_i, $i = 1, 2, 3, \ldots$, may be different in different cases. They may be the concentrations of components forming a liquid, or the concentrations of excited or associated molecules. "It may also be considered that the ξ determine, in some way, the internal structure of the liquid. As yet, there is little point in assigning any special meaning to these variables".

To simplify the problem, it is assumed in the first part of the paper that the internal state of a liquid can be described by a single parameter ξ. In equilibrium,

ξ is found from the condition $\partial\Psi/\partial\xi = 0$, where Ψ is the free energy per unit mass.

It is important to note that, in the limit of very low sound frequency, it may be considered that the liquid is in equilibrium at each instant of time, so that the velocity of sound is determined by the adiabatic compressibility. At high frequencies, on the other hand, the parameter ξ (internal state of the liquid) does not have time to change within one period of the sound wave, and the velocity of sound is determined by the adiabatic compressibility at constant ξ: "At intermediate frequencies, there is dispersion of sound". This is how the authors describe the overall picture of the phenomenon whose theory they are attempting to construct.

To construct this theory, they had to write down the equation for ξ. Mandel'shtam and Leontovich state that this equation can be obtained on the basis of the following considerations: "Firstly, since we are interested in small departures from the state of equilibrium (small sound amplitudes), we may expect this equation to be linear.

Secondly, the equation may be assumed to involve first-order derivatives of T, p, and ξ with respect to time ..... In general, this assumption signifies that changes in ξ occur instantaneously.

Thirdly, the condition of equilibrium for constant ρ, T, i.e., the condition for constant ξ, is that $\partial\Psi/\partial\xi$ must vanish."

The consequence of these conditions is that the required "reaction equation" must have the following form when the variable is appropriately chosen:

$$\dot{\xi} = -K\frac{\partial\Psi}{\partial\xi}, \tag{11'}$$

where K is a constant.

Equation (11') must be augmented with the energy equation which Mandel'shtam and Leontovich obtained on the assumption that the effect of shear viscosity and thermal conductivity on the absorption of sound was less than the effect due to the above processes (as they are reflected in bulk viscosity). In that case,

$$\rho\dot{E} - p\frac{\dot{\rho}}{\rho} = 0; \tag{12}$$

where E is the energy per unit mass and p is the pressure.

After evaluation of the relationships between E, p, ρ, Ψ, and their derivatives, it turns out that

$$\dot{\xi} = -\frac{1}{\tau}\left(\Delta\xi - \frac{E_\xi}{T\Psi_{\xi\xi}}\Delta T + \frac{p_\xi}{\rho^2\Psi_{\xi\xi}}\Delta\rho\right), \tag{13}$$

where $1/\tau = K\Psi_{\xi\xi}$, τ is a constant describing the time necessary to reach equilibrium, and the subscripts represent differentiation with respect to ξ or some other variable as the case may be. When $E(T, \rho, \xi) = \Psi - T\Psi_T$ and $p = P(T, \rho, \xi) = \rho^2\Psi_\rho$, equation (12) may be written in the form

$$E_\xi\dot{\xi} + E_T\dot{T} - \frac{Tp_T}{\rho^2}\dot{\rho} = 0 \tag{14}$$

where the derivatives with respect to T are taken at

constant ξ. For sound of frequency ω, the quantities ΔT, $\Delta\rho$, $\Delta\xi$ are proportional to $\exp(i\omega t)$, and equations (13) and (14) become

$$(1 + i\omega\tau)\Delta\xi = \frac{E_\xi}{T\Psi_{\xi\xi}}\Delta T + \frac{P_\xi}{\rho^2\Psi_{\xi\xi}}\Delta\rho,\tag{15}$$

$$E_\xi\Delta\xi = -c\Delta T + \frac{Tp_T}{\rho^2}\Delta\rho\tag{16}$$

where c is the specific heat $(=E_T)$. The square of the complex velocity of sound W is given by

$$W^2 = \frac{\Delta p}{\Delta\rho} = P_\rho + P_T\frac{\Delta T}{\Delta\rho} + P_\xi\frac{\Delta\xi}{\Delta\rho}.\tag{17}$$

If we now bring in (15) and (16), and also the standard thermodynamic expression for specific heats, we obtain

$$W^2 = v_0^2\left\{1 - \frac{i\omega\tau'\,[(v_\infty/v_0)^2-1]}{1+i\omega\tau'}\right\}.\tag{18}$$

The expression for the adiabatic velocity is obtained for $\omega\to 0$, and v_∞ corresponds to $\omega\to\infty$. It turns out that τ' differs from τ by the ratio $(\partial E/\partial T)_\xi/(\partial E/\partial T)_\mu$. The real velocity of sound and the amplitude absorption coefficient are given by

$$\frac{1}{v} = \mathrm{Re}\frac{1}{W}\qquad \alpha = \omega\,\mathrm{Im}\frac{1}{W}.$$

To a good approximation, all this leads to the following expressions:

$$\frac{v_0}{v} = 1 - \frac{1}{2}\frac{\omega^2\tau'^2\,[(v_\infty/v_0)^2-1]}{1+\omega^2\tau'^2},\tag{19}$$

$$\alpha = \frac{1}{2v_0}\frac{\omega^2\tau'\,[(v_\infty/v_0)^2-1]}{1+\omega^2\tau'^2}.\tag{20}$$

More generally, this theory predicts that

$$\left(\frac{v_\infty}{v_0}\right)^2 - 1 = \frac{1}{\rho^2 v_0^2}\left\{\frac{P_\xi^2}{\Psi_{\xi\xi}} + \frac{T(p_T-P_\xi E_\xi/T\Psi_{\xi\xi})^2}{c-E_\xi^2/T\Psi_{\xi\xi}} - \frac{Tp_T^2}{c}\right\};\tag{20'}$$

where c, p_T are thermodynamic variables referring to equilibrium, and are therefore known, and E_ξ, P_ξ are the derivatives of energy and pressure, which are determined by the nature of the variation of ξ in the course of reaction. These quantities can be obtained only under special assumptions about the nature of processes taking place in liquids, whereas $\Psi_{\xi\xi}$ can be found if we know the fluctuation $\overline{\Delta\xi^2} = kT/\Psi_{\xi\xi}$.

Equation (20) gives the expression for the absorption coefficient due to bulk viscosity which is the dominant coefficient in many liquids, including benzene. Equation (20) shows that $\alpha \propto \omega^2$ for low frequencies $(\omega\tau\ll 1)$, which is in agreement with the classical formula given by (11), whereas for high frequencies $(\omega\tau\gg 1)$, equation (20) assumes the form

$$\alpha = \frac{1}{2v_0}\frac{[(v_\infty/v_0)^2-1]}{\tau'},\tag{21}$$

and this signifies that α is independent of frequency at high frequencies, which provides a natural explanation of the presence of narrow Mandel'shtam-Brillouin lines in the scattered spectrum.

The relationship between η' and τ' can be readily established if we equate the expressions given by (20) and (11) for $\omega\tau' \ll 1$, having substituted $\eta = \nu = 0$. This yields

$$\eta' = \tau'(v_\infty^2 - v_0^2).$$

We also note that (11) is valid only if $\alpha\Lambda \ll 1$, whereas (20) is valid for any α. On the other hand, the relaxa-

tion theory formulas (19) and (20) are meaningful and describe sound propagation only in the presence of dispersion, i.e., if $v_0 \neq v_\infty$. Experimental studies of the Mandel'shtam-Brillouin spectrum have, in fact, revealed the presence of this dispersion ($\sim 10-15\%$).

The work of Mandel'shtam and Leontovich was the starting point of an extensive branch of molecular acoustics, which has continued to develop even since.

As has already been noted, Mandel'shtam and Leontovich assumed[21] that, in general, there may be a large number of the ξ parameters, and a corresponding number of the τ' parameters. They investigated this problem at the end of their paper, and obtained the following result:

$$W^2 = P_\rho + \frac{i\omega}{\rho^2}\sum_k\frac{P_k^2\tau_k}{1+i\omega\tau_k} + \frac{T}{\rho^2}\frac{\left(p_T - \frac{1}{T}\sum_k\frac{P_kE_k}{1+i\omega\tau_k}\right)^2}{C+\frac{1}{T}\sum_k\frac{E_k^2}{1+i\omega\tau_k}}.\tag{22}$$

The general relaxation theory of sound absorption in liquids, developed by Mandel'shtam and Leontovich[21], was applied by Leontovich[22] to the absorption of sound by strong electrolytes. "The internal state of a strong electrolyte is characterized by the 'ionic atmospheres' of its ions, which depend on temperature and density. The latter vary during sound propagation, which in turn affects the pressure in the solution. However, these atmospheres are not established instantaneously, and the time for this to happen is determined by the relaxation time τ."

M. A. Leontovich[22] went on to develop a complex theory which involved the Debye theory of strong electrolytes.

This theory enabled him to determine τ in the expression for the absorption coefficient and dispersion, and also the quantity $v_\infty^2 - v_0^2$. It turns out that this difference is proportional to the ion concentration raised to the power 3/2, whereas the absorption coefficient for $\omega\tau\ll 1$ is proportional to the square root of the concentration. The dependence of v and α on frequency is more complicated than is indicated by (19) and (20), because the state of the ionic atmospheres is determined by a distribution function and not by a single parameter.

Leontovich and Shaposhnikov[23] then developed the theory of sound propagation in weak electrolytes. They noted that "the theory of absorption and dispersion of sound in a weak electrolyte is an almost direct replica of the Einstein theory for gases." In reality, this "replication" is not all that simple. Absorption and dispersion can be expressed in terms of the degree of dissociation, which can be measured directly, so that it is possible to determine τ, which in turn depends on the rate of dissociation of the molecules of the electrolyte into ions.

5. RELAXATION THEORY OF THE SPECTRUM OF LIGHT SCATTERED BY ANISOTROPY FLUCTUATIONS IN LIQUIDS

The time-dependence "structure" of the medium, or the natural vibrations of its molecules, which modulate

incident light and are responsible for the appearance of the combination (Raman) lines, is now well understood, but the theory of the intensity of satellites is still being developed.

Scattering of light by pressure fluctuations gives rise to the Mandel'shtam-Brillouin components, whereas scattering by entropy fluctuations is responsible for the central or Rayleigh line. These types of scattered light have now been extensively investigated, and Leontovich's studies contributed in no small measure to our present understanding of this subject.

There is also light scattered by anisotropy fluctuations, which is represented in the spectrum by a broad continuous band with a maximum at the frequency of the exciting line. Although this scattered spectrum was discovered as far back as 1928, a theory of the phenomenon did not exist before Leontovich's work. Moreover, quite a few fanciful suggestions were put forward about the nature of the phenomenon itself.

The first rational pronouncement on the nature of the depolarized scattered spectrum, i.e., the wing of the Rayleigh line, is due to Landau and Placzek[24] who put it as follows: "The structure of this part of the Rayleigh line wing in the case of liquids is largely determined by the Debye relaxation time."

In 1941, just before World War II, M. A. Leontovich published the first quantitative theory of the depolarized scattered spectrum.[25] This paper was destined to play a major role in the subsequent development of the theory and in guiding experimental work that eventually led to quantitative measurements of the anisotropy relaxation time and to the discovery of new phenomena in the spectrum of depolarized scattered light.

Leontovich's theory established a relationship between such phenomena as depolarization of scattered light, the Kerr effect, and the Maxwell effect (flow birefringence).

Leontovich's quantitative theory is based on the Maxwell viscosity scheme, and takes into account scattering by pressure fluctuations (Mandle'shtam-Brillouin components) and the component of anisotropy fluctuations (orientation of anisotropic molecules) that is determined by deformational fluctuations.

It is assumed in the Leontovich theory that the state of the liquid at any point can be fully characterized by the temperature, the strain tensor e_{ik}, and the anisotropy tensor ξ_{ik}. Leontovich notes[25] that the introduction of only two tensors restricts the range of the theory but, since this was the first attempt at providing a theory of a complex phenomenon, this simplification was justified.

The time dependence of the anisotropy tensor is determined by the reaction equation [cf. equation (11')], which has the form

$$\dot{\xi}_{ik} = \frac{1}{\tau}\zeta_{ik}, \qquad (23)$$

where the anisotropy tensor is $\zeta_{ik} = e_{ik} - (1/3)\delta_{ik}\sigma - \xi_{ik}$ (σ is the expansion coefficient) and, as in the Maxwell theory of viscosity, it is assumed that

$$\eta = \mu\tau \qquad (24)$$

where η is the viscosity and μ is the shear modulus.

The scattered spectrum can be found by determining the time dependence of the fluctuations, which can be obtained from the equations of motion given in Ref. 25. These equations split into three groups.

The first group describes longitudinal waves responsible for the Mandel'shtam-Brillouin components. It also follows from these equations that the longitudinal wave is accompanied by a change in the ansiotropy.

The second group describes the propagation of transverse waves which, in the case of slow motion, form the usual "viscous" transverse waves whereas, for fast motion, they become transverse waves in a solid.

Finally, the third group of equations describes the perturbation of anisotropy that is not accompanied by the motion of the liquid. Purely conventionally, one can say that this group of equations describes transverse anisotropy "waves."

The intensity distribution in the scattered spectrum can be determined by first finding the scattered wave field. M. A. Leontovich seeks the light field scattered by a volume V in the following form:

$$\mathbf{E} = e^{i\omega_0 t}\mathbf{P}_i \int \Delta\varepsilon_{ik} e^{i(\mathbf{q}\mathbf{r})} \, dV; \qquad (25)$$

where ω_0 is the frequency of the exciting light, $\mathbf{P}_i$ is the polarization, $\mathbf{q}$ is the wave vector, and $\Delta\varepsilon_{ik} = \Delta\varepsilon\delta_{ik} + \Delta\varepsilon'_{ik}$. Moreover, in view of the fact that $\Delta\varepsilon'_{ik}$ is small, it can be assumed to be proportional to ξ_{ik} and, consequently,

$$\Delta\varepsilon'_{ik} = A\zeta_{ik}. \qquad (26)$$

Equations (26) and (23) lead us to the conclusion that the time for which birefringence is present, which is determined by $\Delta\varepsilon_{ik}$, is equal to the anistropy relaxation time τ. Consequently, τ determines the time necessary for the Kerr effect to become established or to vanish, or the corresponding time for flow birefringence (Maxwell effect).

For slow motion, for which ζ can be neglected, we have

$$\Delta\varepsilon_{ik} = \left(\frac{\partial e}{\partial \rho}\right)\Delta\rho\delta_{ik} + M\zeta_{ik}, \qquad (27)$$

where $M = A\tau$ is the Maxwell constant.

Equations (25) and (27) can now be used to determine the field $\mathbf{E}$. The intensity $I(\omega)$ is proportional to the mean square of the coefficients in the Fourier transform (25). Leontovich used this approach to determine the intensity distribution in the spectrum of the scattered light for different polarizations of the incident and scattered light. These formulas describe the Mandel'shtam-Brillouin components generated by the longitudinal and transverse waves, and also the intensity distribution in the spectrum due to anisotropy fluctuations (the Rayleigh line wing).

The formulas are relatively complicated and unwieldy, but they were used by Mikhail Aleksandrovich's wife, Tat'yana Petrovna, to obtain a graphical representation
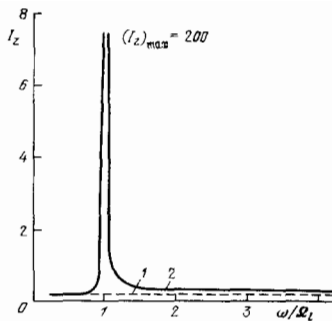
FIG. 1. Distribution of intensity in the spectrum of the scattered light:[25]

$1 - I_x$, $2 - I_z$; $A/(\rho\, \partial\varepsilon/\partial\rho) > 0$,
$\Omega_L \tau = 0.1$, $\Omega_T^2 = 0.075\Omega_L^2$.

of the depolarization coefficients over the spectrum. The results of these calculations are shown in Figs. 1–3. The intensity is plotted along the vertical axis and the frequency (in units of ω/Ω_L) along the horizontal axis (Ω_L is the frequency of a Mandel'shtam-Brillouin component).

The Rayleigh line wing extends over tens or even hundreds of reciprocal centimeters, whereas the Mandel'shtam-Brillouin components are confined to an interval of 1 cm^{-1} around the exciting line.

The Leontovich formulas become simpler for frequencies in the Rayleigh line wing that are much greater than Ω_L. The depolarized scattered spectrum is then given by

$$I(\omega) = \frac{13}{12}\, \frac{A^2 kT}{\mu}\, \frac{2\tau}{1+\omega^2\tau^2}. \tag{28}$$

Consequently, if the intensity distribution in the spectrum is in fact as given by (28), we have the real possibility of being able to determine the numerical value of the anisotropy relaxation time τ and then comparing it with the time constants for the Kerr and Maxwell effects.
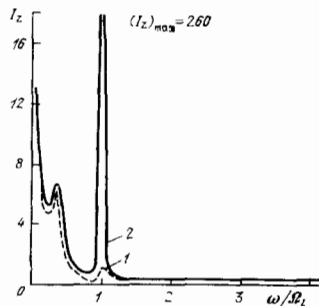

FIG. 2. Same as in Fig. 1:

$1 - I_x$, $2 - I_z$; $A/(\rho\, \partial\varepsilon/\partial\rho) > 0$,
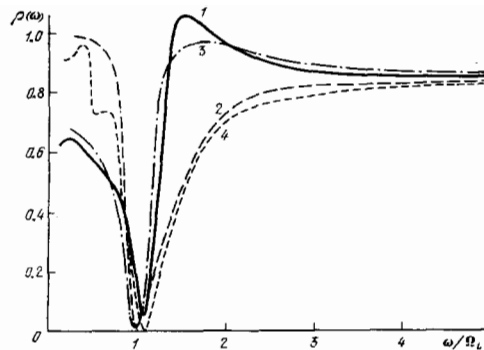$\Omega_L \tau = 10$, $\Omega_T^2 = 0.075\Omega_L^2$.

FIG. 3. Distribution of the depolarization coefficient $\rho(\omega)$ over the spectrum:[25]

$1 - \dfrac{A}{(\rho\,\partial\varepsilon/\partial\varphi)} < 0$, $\quad 2 - \dfrac{A}{(\rho\,\partial\varepsilon/\partial\rho)} > 0$, $\Omega_L\tau = 0.1$, $3 - \dfrac{A}{(\rho\,\partial\varepsilon/\partial\varphi)} < 0$, $4 - \dfrac{A}{(\rho\,\partial\varepsilon/\partial\rho)} > 0$, $\Omega_L\tau = 10$.

It is this theory that gave rise to a new line of research in molecular optics, which has been so successful and continues to develop both theoretically and experimentally.

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Dissipative equations for many-particle distribution functions

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This article deals with the papers by M. A. Leontovich on the subject of thermodynamics and statistical physics. Primary attention is given to the paper entitled "The fundamental equations of the kinetic theory of gases from the standpoint of the theory of random processes," which was published in 1935 in *Zhurnal Eksperimental'noĭ i Teoreticheskoĭ Fiziki*, No. 5. This paper is one of the basic works in the modern statistical theory of nonequilibrium processes.

Even a simple list of the papers by Mikhail Aleksandrovich Leontovich on the subject of thermodynamics and statistical physics[1-13] shows that his interests were very broad. But what is striking is not the breadth so much as the originality and depth of his analysis of these problems. The questions that occupied Leontovich many years ago remain current to this day.

For example, in an annotation to his article "On kinetics of fluctuations," which was published more than fifty years ago, we read:

A method is presented for determining the spectrum of fluctuations i. e., for determining the statistical averages of the squares of the spatiotemporal Fourier expansion of the fluctuations. The method is applied to concentration and density fluctuations in liquids. The consequences of the theory which bear upon the fine structure of the lines of the scattering spectrum are discussed in connection with the available experimental data.

This said it all, with the utmost clarity and precision.

Another paper by Leontovich, entitled "On the free energy of nonequilibrium states," might be carried over almost in its entirety to a contemporary course in statistical physics. Here also the goal and result are formulated with extreme clarity:

The free energy of a nonequilibrium state can be defined more generally than is ordinarily done by taking into consideration the additional potential energy in the presence of which the nonequilibrium state becomes as equilibrium state. The relationship of this definition to the Boltzmann principle is analyzed.

The method proposed in this article for describing a wide range of nonequilibrium states was given a more detailed exposition in Leontovich's book *Statistical Physics*.[8]

It is impossible here to analyze and evaluate from a modern point of view all of Leontovich's papers on thermodynamics and statistical physics.[1-13] Let us examine just one of them[6] in greater detail—"The fundamental equations of the statistical theory of gases from the standpoint of the theory of random processes." The choice of this particular paper, of course, was not accidental, as will become clear from this article.

This truly remarkable paper appeared in No. 5 of the journal *Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki* for 1935. Its ideas represented a significant departure from the existing level of the statistical theory of nonequilibrium processes.

Up to the time that this paper was written the statistical theory of nonequilibrium processes was based on the famous Boltzmann equation. This equation implied the law of increasing entropy (the *H* theorem of Boltzmann). It served as a basis for the equations of gas dynamics and the equations describing the free-molecular flow of a gas. This was indeed a triumph of the kinetic theory. It seemed that this theory was close to completion. Only a few prominant physicists of the time understood that this was only the first stage in the development of the statistical theory of nonequilibrium processes. In Leontovich's paper we read:

The kinetic theory treats processes in gases. It is a statistical theory, inasmuch as equation (1) [the Boltzmann equation] is based on the statistical proposition of the Stosszahlansatz. The structure of this theory, however, is undoubtedly very imperfect. The quantity $f d\omega do (d\omega = dv_x\, dv_y\, dv_z,\ do = dxdydz)$ must be assigned the value of some statistical average (mathematical expectation) of the number of particles in a volume $d\omega do$ of phase space μ—only then can the irreversible character of equation (1) and its consequences be understood. However, in the framework of the theory itself the meaning of this mathematical expectation remains extremely unclear, since one does not consider the probabilities which are used to generate these mathematical expectations. The theory is therefore also unable to give any information on the fluctuations in the gas and how they change in time.[1] (Ref. 6, p. 211).

In fact, the Boltzmann kinetic equation was treated as an equation for a determinate (not random) distribution function. Accordingly, in the transition from the kinetic equation to the gasdynamic equation, the gasdynamic functions—the density $\rho(r, t)$, the velocity $U(r, t)$, and the temperature $T(r, t)$—turned out to be determinate. As a result, effects due to fluctuations of the distribution function (kinetic fluctuations) and to fluctuations of the gasdynamic functions dropped out of consideration.

The situation was as follows: In the classical papers of Rayleigh, Planck, Einstein, and Smoluchowski it was shown that even in an equilibrium state fluctuations play a fundamental role in many phenomena. For example, density fluctuations govern the scattering of light, and fluctuations of the electromagnetic fields are manifested in thermal radiation. Without allowance for the fluctuations of the medium in which the Brownian particles move one cannot explain this "perpetual motion." This list could, of course, be extended. For example, in recent years we have come to understand the fundamental role of fluctuations in second-order phase transitions. Nevertheless, for many years nonequilibrium fluctuations remained outside the sphere of interest of kinetic theory. There were several reasons for this.

Working from Smoluchowski's equation, Leontovich obtained for the case of a rarefied gas a Markov-type equation for the most general distribution function f_N of a system of N particles. The equation which he obtained was irreversible right from the start. Here the question of the reasons for the irreversibility did not come up. Leontovich wrote:

> It should be noted that I have not touched upon the *basic physical question* of the extent to which the statistical description of the processes in terms of transition probabilities can be related to or put into correspondence with the description of quantum (or classical) mechanics. I think only that this statistical scheme is the most expedient for setting forth in a more complete form the *actual content* of the kinetic theory (Ref. 6, p. 213).

Thus, the matter of how the reversible equations of mechanics are related to the irreversible equations of the statistical theory of nonequilibrium processes remained an open question. This problem was promoted to the forefront. The problem of constructing a systematic fluctuational theory of nonequilibrium processes withdrew to the background and for a long time did not attract the attention of researchers.

Important contributions toward solving the problem of substantiating the kinetic theory were given in the papers by N. N. Bogolyubov, M. Born and H. S. Green, and J. G. Kirkwood. In Bogolyubov's now-classical monograph *Problems of Dynamical Theory in Statistical Physics* (1946) a method is developed for obtaining the Boltzmann kinetic equations (for a rarefied gas) and the kinetic equations of Landau and Vlasov (for systems of charged particles). Thanks to these papers, it became clear in what way and *at what cost* one can obtain from the reversible equations of mechanics the irreversible equations of kinetic theory.

As a result, many questions which had disturbed investigators simply went away. However, new questions, also of a difficult nature, arose. One of these was the question of nonequilibrium fluctuations.

In Bogolyubov's derivation of the kinetic equations — the closed equations for single-particle distribution functions — the hypothesis (*principle*) of total attenuation of the original correlations played an important role.

Here it was (*implicitly*) assumed that the long-lived correlations (with a time τ_{cor} of the order of, or larger than, the relaxation time of the single-particle distribution functions) do not play an appreciable role. The kinetic and hydrodynamic fluctuations thereby dropped out of consideration.

We note that Bogolyubov[14] cites Leontovich's article,[6] but not in connection with the question of fluctuations of the distribution functions. In §2 of this book[14] is the comment: "The study of the functions F_s in many cases can be simplified appreciably by the introduction of a special functional, the generalization of the generating functions employed by Leontovich[6] in the theory of stochastic processes with a discrete phase space."

Leontovich's paper[6] was subsequently almost forgotten, and it did not have an appreciable influence on the development of the theory of nonequilibrium fluctuations. The dissipative equations for the many-particle distribution functions were discovered anew by other authors—for example, in the works of I. Prigogine, R. Brout, and M. Kac (see Chs. 4 and 11 in Ref. 15, Ch. 10 in Ref. 16, Ch. 2 in Ref. 17, and Ch. 24 in Ref. 18).

For example, the study of the kinetic equations for many-particle distribution functions (master equations) occupies many pages in the splendid book[19] by the American mathematician M. Kac, which is a record of lectures on a number of problems in statistical theory. Kac, unfortunately, was not acquainted with Leontovich's paper at the time he was working on these lectures.[1] On the basis of Liouville's equation, V. N. Zhigulev[20] established a chain of dissipative equations for the sequence of distribution functions of a rarefied gas which is a direct consequence of Leontovich's equation. Attempts at approximate solution of this chain of equations for the purpose of studying the effect of turbulent fluctuations on the velocity distribution of the particles of a rarefied gas have recently been undertaken by Japanese investigators (see Ref. 21).

We shall return later to the discussion of dissipative equations for many-particle distribution functions. For now we shall only point out the following.

When large-scale and long-lived fluctuations are taken into account in kinetic theory, new contributions appear in addition to those incorporated in the Leontovich equation. These contributions are governed by fluctuations which have lifetimes much longer than the mean free time and so cannot be taken into account in the Boltzmann scheme. These additional contributions are particularly large for states which are far from equilibrium, such as in the presence of well-developed

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[1] During a school on statistical physics in Jadwisin, Poland, Kac told me that after his book appeared in Russian, a physicist from Leningrad had sent him a copy of Leontovich's article (Ref. 6). Kac asked me, "How could he [Leontovich] have known and understood all this back in 1935?" I felt that Kac's pride had been wounded. When later in the conversation I mentioned Leontovich's friendship and collaboration with A. N. Kolmogorov, Kac immediately replied, "Oh it was Kolmogorov who taught him this."

turbulence. Here both the thermodynamic functions and the kinetic coefficients are appreciably altered.

Let us now return to the question of fluctuations in the distribution function of a rarefied gas.

The first step in the kinetic theory of fluctuations was taken by B. B. Kadomtsev[22] in a calculation of the fluctuations of the distribution function of an equilibrium rarefied gas. The result was obtained by using a linearized Boltzmann kinetic equation as the relaxation equation in the theory of equilibrium fluctuations developed in the papers of H.B. Callen and T.A. Welton,[23] S. M. Rytov,[24] and L.D. Landau and E.M. Lifshits.[25] In an analogous way L. P. Gor'kov, I. E. Dzyaloshinskiĭ, and L. P. Pitaevskiĭ[26] calculated the equilibrium fluctuations for the Fokker-Planck equation and the linearized Landau equation.

Kadomtsev's formula was generalized to nonequilibrium states by various methods in the papers of Sh. M. Kogan and A. Ya. Shul'man, S.V. Gantsevich, V. L. Gurevich, R. Katilus, the present author, and others (see the review of Ref. 27, Chs. 5 and 11 in Ref. 15, and §19.20 in Ref. 28).

One of the ways of constructing a theory of nonequilibrium fluctuations is based on the use of the dissipative equation for a many-particle distribution function (§18 and Ch. 4 in Ref. 15). However, the starting point here is different from that of Leontovich's paper.

The initial equation in Ref. 15 is the Liouville equation—a reversible equation for the distribution function f_N. The transition from this equation to a dissipative equation for the smoothed many-particle distribution function $\tilde{f}_N$ is accomplished by averaging over a physically infinitesimal volume V_p. To make such a transition possible, Bogolybov's principle of total attenuation of the initial correlations is replaced by the condition of partial attenuation of the initial correlations: Only the small-scale correlations, for which

$$\tau_{\text{cor}} < \tau_p, \quad r_{\text{cor}} < l_p, \tag{1}$$

are attenuated: here τ_p and l_p are the intervals of time and length that are adopted as physically infinitesimal. For a rarefied gas, when the density parameter $\varepsilon = nr_0^3$ is much smaller than unity, the quantities τ_p and l_p in the kinetic stage of relaxation can be defined in the following way (§18 in Ref. 15 and Ch. 7 in Ref. 18):

$$\tau_p \sim \sqrt{\varepsilon}\tau \ll \tau, \quad l_p \sim \sqrt{\varepsilon}\,l \ll l, \quad N_p \sim \frac{1}{\sqrt{\varepsilon}} \gg 1 \quad \text{for} \quad \varepsilon = nr_0^3 \ll 1. \tag{2}$$

The introduction of the quantities τ_p and l_p enables one to separate correlations into large-scale and small-scale. As a result, on can write for $\tilde{f}_N$ the equation

$$\frac{\partial \tilde{f}_N}{\partial t} + \sum_{1 \leqslant i \leqslant N} \left(\mathbf{v}_i \frac{\partial \tilde{f}_N}{\partial \mathbf{r}_i} + \mathbf{F}_0 \frac{\partial \tilde{f}_N}{\partial \mathbf{p}_i} - \sum_{1 \leqslant j \leqslant N} \frac{\partial \tilde{\Phi}_{ij}}{\partial \mathbf{r}_i} \frac{\partial \tilde{f}_N}{\partial \mathbf{p}_i} \right)$$
$$= I_N(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N, t); \tag{3}$$

here we have introduced the notation I_N for the corresponding collision integral. This integral can be written either in the Bogolyubov representation [as in (18.10) of Ref. 15]

$$I_N = \sum_{1 \leqslant i, \, j \leqslant N} \delta(\mathbf{r}_i - \mathbf{r}_j) \int_{V_\Phi} d(\mathbf{r}_i - \mathbf{r}_j) \frac{\partial \Phi_{ij}}{\partial \mathbf{r}_i}$$
$$\times [\tilde{f}_N(\mathbf{r}_1, \mathbf{p}_1, \ldots, \mathbf{r}_i \mathbf{P}_i(-\infty), \ldots, \mathbf{r}_j, \mathbf{P}_j(-\infty), \ldots, \mathbf{r}_N, \mathbf{p}_N, t)$$
$$- \tilde{f}_N(\mathbf{r}_1, \mathbf{p}_1, \ldots, \mathbf{r}_i, \mathbf{p}_i, \ldots, \mathbf{r}_j, \mathbf{p}_j, \ldots, \mathbf{r}_N, \mathbf{p}_N, t)], \tag{4}$$

or, more conveniently for comparison with Leontovich's equation, in the Boltzmann representation

$$I_N = \sum_{1 \leqslant i, \, j \leqslant N} \int_0^{2\pi} d\varphi_{ij} \int_0^\infty \rho_{ij}\, d\rho_{ij} \, |\mathbf{v}_i - \mathbf{v}_j| \, \delta(\mathbf{r}_i - \mathbf{r}_j)$$
$$\times [\tilde{f}_N(\mathbf{r}_1, \mathbf{p}_1, \ldots, \mathbf{r}_i, \mathbf{p}_i', \ldots, \mathbf{r}_j, \mathbf{p}_j', \ldots, \mathbf{r}_N, \mathbf{p}_N, t)$$
$$- \tilde{f}_N(\mathbf{r}_1, \mathbf{p}_1, \ldots, \mathbf{r}_i, \mathbf{p}_i, \ldots, \mathbf{r}_j, \mathbf{p}_j, \ldots, \mathbf{r}_N, \mathbf{p}_N, t)]. \tag{5}$$

In expressions (4) and (5) the "width" of the function $\delta(\mathbf{r}_i - \mathbf{r}_j)$ is characterized by l_p.

Equation (3) with collision integral (5) corresponds to equation (42), (43) of Leontovich's paper (the quantity I_N in (42) is defined in Ref. 6 on p. 231). The difference lies in the following:

In equation (42) of Ref. 6 the collision integral lacks the second term in the square brackets in (5) [with the function $\tilde{f}_N(x_1, \ldots, x_i, \ldots, x_j, \ldots, x_N, t)$], which is important, for example, in proving the law of increasing entropy of the entire system (see below). However, in going over from equation (42) to the Boltzmann equation, Leontovich[6] does, of course, include the contribution of this term.

On the left-hand side of equation (3) there is an additional term that does not appear in (43) of Ref. 6; this term takes into account the interaction of the particles. This term, as we shall see, is important in the study of the contribution of the large-scale fluctuations.

Let us consider the most important consequences of equation (3) with collision integral (5) [or (4)].

With the aid of equation (3), we shall find an equation for the single-particle distribution function:

$$f_1(\mathbf{r}_1, \mathbf{p}_1, t) \equiv \tilde{f}_1$$
$$= V \int \tilde{f}_N(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N, t)\, d\mathbf{r}_2 \ldots d\mathbf{r}_N\, d\mathbf{p}_2 \ldots d\mathbf{p}_N. \tag{6}$$

In the integration over $\mathbf{r}_2, \ldots, \mathbf{r}_N, \mathbf{p}_2, \ldots, \mathbf{p}_N$, all the terms with $i \neq 1$ drop out. All the terms in the sum $\sum_{1 < j \leqslant N}$ under the integral over $\mathbf{r}_j, \mathbf{p}_j$ are on equal footing; one may therefore set $j = 2$ and replace the summation by a factor $N - 1$, which is the number of terms in the sum over j. Finally, we let $(N - 1)/V \to N/V = n$. This results in the following equation:

$$\frac{\partial f_1}{\partial t} + \mathbf{v} \frac{\partial f_1}{\partial \mathbf{r}_1} + \mathbf{F}_0 \frac{\partial f_1}{\partial \mathbf{p}_1} = n \int \frac{\partial \Phi_{12}}{\partial \mathbf{r}_1} \frac{\partial}{\partial \mathbf{p}_1} \tilde{f}_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t)\, d\mathbf{r}_2\, d\mathbf{p}_2$$
$$+ n \int_0^{2\pi} d\varphi_{12} \int_0^\infty \rho_{12}\, d\rho_{12} \int d\mathbf{p}_2 \, |\mathbf{v}_1 - \mathbf{v}_2| \, [\tilde{f}_2(\mathbf{r}_1, \mathbf{p}_1', \mathbf{r}_1, \mathbf{p}_1', t)$$
$$- \tilde{f}_2(\mathbf{r}_1, \mathbf{p}_2, \mathbf{r}_1, \mathbf{p}_1, t)], \tag{7}$$

which corresponds to equation (63) in the paper by Leonotovich. The only difference is that on the right-hand side of equation (7) there is an additional term (the first term on the right-hand side) which takes into account the contribution from large-scale fluctuations (see below).

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Let us introduce the two-particle correlation function. By definition, with allowance for the fact that $f_1 \equiv \tilde{f}_1$, we have

$$\tilde{f}_2 = f_1 f_1 + \tilde{g}_2. \tag{8}$$

It can then be said that equation (7) is not closed, since it contains the correlation function $\tilde{g}_2$ in addition to the function f_1. For this reason, even when the first term on the right-hand side is neglected this equation differs from the Boltzmann equation. It is the first equation of a chain of coupled equations for the smoothed (over a physically infinitesimal volume V_p) functions $f_1, \tilde{g}_2, \tilde{g}_3, \ldots$ (see Ref. 15). In contrast to the Bogolyubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy of equations for the ordinary distribution functions, the system under study is approximate because of the smoothing over the volume, and for this reason is dissipative.

In equation (7) the correlation function $\tilde{g}_2$ enters in two ways which are, in a sense, complementary. In the second term on the right-hand side of equation (7) the function $\tilde{g}_2$ appears inside the integral that takes into account the contribution of binary collisions. In order to obtain the Boltzmann collision integral, one must set $\tilde{g}_2 = 0$ inside it. Now how is one to justify such an approximation? In this regard Leontovich writes:

> This relation [relation (7) without the first term on the right-hand side, auth.] will have the same form as the "fundamental equation of the theory of gases" [the Boltzmann equation, auth.] if one replaces [in our notation, auth.] $\tilde{f}_2(p_2', p_1')$ by $f_1(p_2')f_1(p_1')$ and, correspondingly, $\tilde{f}_2(p_2, p_1)$ by $f_1(p_2)f_1(p_1)$. Such a replacement might be justified if it were proved that as the total number of particles goes to infinity, the quantities giving the dispersion of the numbers of particles in definite states increase in proportion to N. By analogy with the "limit theorem" proved for a discrete series of states, such a behavior of the dispersion and, hence, the validity of such a limit theorem in this case as well seem probable to me, although I have not been able to prove it. As a result of the indicated replacement, equation (63) [our Eq. (7) without the first term on the right-hand side, auth.] goes over to equation (1) [the Boltzmann equation, auth.]

Thus Leontovich assumed $\tilde{g}_2 = 0$ in the collision integral only in the thermodynamic limit: $N \to \infty$, $V \to \infty$, but N/V finite. In Bogolyubov's book[14] the Boltzmann equation is a closed equation for a single-particle distribution function obtained on the basis of the principle of total attenuation of the initial correlations. One can discern a certain connection between these approaches. In both cases we arrive at a closed equation for a determinate (not random) distribution function. For this reason, as we have already mentioned, all phenomena governed by kinetic and hydrodynamic fluctuations drop out of consideration.

To estimate the role of the function $\tilde{g}_2$ in the collision integral, let us use the condition of partial attenuation of the initial correlations [condition (1)]. Assuming (for small-scale correlations) that the correlation length $r_{cor} \sim r_0$ (r_0 is the diameter of an atomic sphere),

we obtain the estimate

$$\tilde{g}_2 = \int g_2(r) \frac{dr}{V_p} \sim \frac{r_0^3}{V_p} \sim \frac{\varepsilon}{N_p} \sim \varepsilon^{3/2}, \quad \text{since} \quad N_p \sim \frac{1}{\sqrt{\varepsilon}}. \tag{9}$$

This is what provides the grounds for dropping the functions $\tilde{g}_2$ inside the collision integral. The large-scale correlations are included in the first term on the right-hand side of (7). As a result, the equation for the function f_1 assumes the form [Eq. (18.6) in Ref. 15)

$$\frac{\partial f_1}{\partial t} + \mathbf{v}_1 \frac{\partial f_1}{\partial \mathbf{r}_1} + \mathbf{F} \frac{\partial f_1}{\partial \mathbf{p}_1} = I_B(\mathbf{r}_1, \mathbf{p}_1, t) + \tilde{I}(\mathbf{r}_1, \mathbf{p}_1, t); \tag{10}$$

here

$$I_B = n \int_0^{2\pi} d\varphi_{12} \int_0^{\infty} \rho_{12} d\rho_{12} \int d\mathbf{p}_2 |\mathbf{v}_1 - \mathbf{v}_2| \\ \times \{f_1(\mathbf{r}_1, \mathbf{p}_2', t) f_1(\mathbf{r}_1, \mathbf{p}_1', t) - f_1(\mathbf{r}_1, \mathbf{p}_2, t) f_1(\mathbf{r}_1, \mathbf{p}_1, t)\} \tag{11}$$

is the Boltzmann collision integral, and

$$\tilde{I} = n \int \frac{\partial \Phi_{12}}{\partial \mathbf{r}_1} \frac{\partial}{\partial \mathbf{p}_1} \tilde{g}_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2 t) d\mathbf{r}_2 d\mathbf{p}_2 \tag{12}$$

is an additional integral determined by the large-scale fluctuations. The force F in Eq. (10) is given by the expression

$$\mathbf{F}(\mathbf{r}, t) = \mathbf{F}_0 - n \int \frac{\partial \Phi(|\mathbf{r} - \mathbf{r}'|)}{\partial \mathbf{r}} f_1(\mathbf{r}', \mathbf{p}', t) d\mathbf{r}' d\mathbf{p}'. \tag{13}$$

Thus, under the condition of attenuation of small-scale correlations, the equation for f_1 is of the form (10). This equation is dissipative. Here the dissipation due to the exclusion of small-scale correlations enters explicitly through the Boltzmann collision integral. Additional dissipation due to the functions $\tilde{g}_2$ (the integral $\tilde{I}$) is also possible. Before discussing this matter, let us make the following remark.

Instead of using Eq. (3) for the function $\tilde{f}_N$ as the initial equation, one can use the equation for the microscopic phase density smoothed over a volume V_p:

$$N(\mathbf{r}, \mathbf{p}, t) = \sum_{1 \leq i \leq N} \delta(\mathbf{r} - \mathbf{r}_i(t)) \delta(\mathbf{p} - \mathbf{p}_i(t)). \tag{14}$$

Let us denote this by $\tilde{N}$. Averaging this equation (see §22 in Ref. 15) and using the equality $\langle \tilde{N} \rangle = nf_1$ and the condition of attenuation of the small-scale correlations, we again arrive at Eq. (10). Now, however, the integral $\tilde{I}$ is represented in a different, but equivalent form:

$$\tilde{I}(\mathbf{r}, \mathbf{p}, t) = \\ = \frac{1}{n} \int \frac{\partial \Phi(|\mathbf{r} - \mathbf{r}'|)}{\partial \mathbf{r}} \frac{\partial \langle \delta \tilde{N} \delta \tilde{N} \rangle_{\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}', t}}{\partial \mathbf{p}} d\mathbf{r}' d\mathbf{p}' \equiv -\frac{1}{n} \frac{\partial \langle \delta \tilde{F} \delta \tilde{N} \rangle}{\partial \mathbf{p}}; \tag{15}$$

here $\delta \tilde{N} = \tilde{N} - nf_1$ and

$$\delta \tilde{F} = -\int \frac{\partial \Phi(|\mathbf{r} - \mathbf{r}'|)}{\partial \mathbf{r}} \delta \tilde{N}(\mathbf{r}', \mathbf{p}', t) d\mathbf{r}' d\mathbf{p}'. \tag{16}$$

In this approach Eq. (10) must be supplemented by an equation for the correlator of the fluctuations of the phase density $\tilde{N}$.

Of course, the equation for such a correlator, by virtue of the nonlinearity of the system, will contain a more complex, ternary correlator. This sequence of equations can be closed under the condition that the fluctuations are small. This condition is valid for a

wide class of problems if the averaging volume V_p is suitably chosen so that it contains many particles ($N_p \gg 1$).

One may, of course, turn not to the equations for the moments of the fluctuations $\delta \tilde{N}$, but instead use Eq. (12), which expresses the integral $\tilde{I}$ in terms of $\bar{g}_2$. The equation for $\tilde{g}_2$ is of the form given by (18.25) in Ref. 15. In (18.25) the condition that the fluctuations $\delta \tilde{N}$ be small corresponds to the approximation $\tilde{g}_3 = 0$, $\tilde{g}_2 \ll f_1/f_2$.

In the zeroth order approximation in the fluctuations, the integral $\tilde{I}$ in (10) is zero, and we return to the kinetic equation of Boltzmann. In the next approximation the equation for the correlator $\langle \delta \tilde{N} \delta \tilde{N} \rangle$ can be written in the form of an equation with a source $A(x, x', t)$—a function determined by the single-particle distribution function [Eq. (22, 21) in Ref. 15]. The source is represented as a sum of two terms:

$$A(x, x', t) = A_B(x, x', t) + \tilde{A}(x, x', t). \qquad (17)$$

The first term A_B is determined by the atomic structure of the subsystem in the physically infinitesimal volume V_p. The collisions of the particles of volume V_p are not a continuous process. A shot effect is present.

The second term on the right-hand side of (17) is due to the dissipative effect of the large-scale fluctuations $\delta \tilde{N}$, and so the function $\tilde{A}$ can be expressed in terms of the integral $\tilde{I}$ [(22.23) in Ref. 15].

In summary, there is a sort of dual superstructure on top of the level of description by means of the Boltzmann equation.

The "first level" is governed by the molecular structure, which leads to a shot effect in the collision processes. For this reason the source $A_B(x, x', t)$ is called *molecular*.

The "second level" is governed by the large-scale fluctuations and is not directly related to the molecular structure of the system. The source $\tilde{A}$ might therefore be called *turbulent*.

In specific situations one of these two factors may be dominant. Then one can distinguish two more particular generalizations of the Boltzmann equation. Let us first consider the case in which source $\tilde{A} = 0$. In this approximation one has $\tilde{I} = 0$ in (10), and equation (10) coincides with the Boltzmann equation. Thus the function $f_1(r, p, t)$ can be determined independently of the problem of calculating the fluctuations of the distribution function.

However, since the function f_1 is introduced, as was proposed in Leontovich's paper, in the form of a "mathematical expectation" ($nf_1 = \langle \tilde{N} \rangle$), there exists fluctuations $\delta \tilde{N} = \tilde{N} - \langle \tilde{N} \rangle$. In the present case the source $A(x, x', t)$ in the equation for the correlator $\langle \delta \tilde{N} \delta \tilde{N} \rangle$ is specified completely by the function $A_B(x, x', t)$. This function can be expressed as follows in terms of the function f_1 [(10.12) in Ch. 11 of Ref. 18]:

$$A_B = [(\delta \hat{I}_p - \delta \hat{I}_{p'}) - (\delta \hat{I}_p + \delta \hat{I}_{p'})_0] n \delta(r - r') \delta(p - p') f_1(r, p, t); \qquad (18)$$

here $\delta \hat{I}_p$ is an operator determined by the linearized Boltzmann collision integral. The subscript zero on the second term in the square brackets indicates that the collision operators act only on the distribution function [and not on the function $\delta(p - p')$].

The correlator $\langle \delta \tilde{N} \delta \tilde{N} \rangle_{x, x', t}$ can serve as an initial condition ($t = t'$) for calculating the double-time correlator, which satisfies the equation

$$\left(\frac{\partial}{\partial t} + v \frac{\partial}{\partial r} + \delta \hat{I}_p + F \frac{\partial}{\partial p} \right) \langle \delta \tilde{N} \delta \tilde{N} \rangle_{x, t, x', t'} = 0, \; t > t'. \qquad (19)$$

The system of equations for the single-time and double-time correlators is equivalent to the Langevin equation for the function $\delta \tilde{N}$:

$$\left(\frac{\partial}{\partial t} + v + \frac{\partial}{\partial r} + \delta \hat{I}_p + F \frac{\partial}{\partial p} \right) \delta \tilde{N}(r, p, t) = y(r, p, t). \qquad (20)$$

The left-hand side of this equation is of the same form as the linearized Boltzmann equation. The moments of the Langevin source are given by the formulas

$$\langle y(r, p, t) \rangle = 0, \qquad (21)$$
$$\langle y(r, p, t) y(r', p', t) \rangle = A_B(x, x', t) \delta(t - t').$$

Thus the intensity of the Langevin source in the linearized Boltzmann equation for the fluctuations $\delta \tilde{N}$ is given by expression (18). The latter in turn serves as a source in the equation for the single-time correlator of the fluctuations $\delta \tilde{N}$ for $\tilde{A} = 0$.

For an equilibrium state the second term (with subscript zero) in formula (18) drops out, and we arrive at the result of Kadomtsev's paper on kinetic fluctuations in an ideal gas under equilibrium conditions. For a nonequilibrium state formulas (21) and (18) are equivalent to those given in Refs. 27, 28, and 15.

It follows from what we have said that results (18)–(21) can be obtained on the basis of the dissipative equation introduced by Leontovich, together with collision integral (5).

Let us now establish the connection between formula (5) [or (4)] and the well-known Prigogine-Brout expression for the collision integral in the equation for the many-particle function of a gas which is spatially homogeneous with respect to the coordinates of all the particles. These distribution functions are defined by

$$\tilde{f}_N(r_1, p_1, \ldots, r_N, p_N, t) = \frac{1}{V^N} \tilde{f}_N(p_1, \ldots, p_N, t). \qquad (22)$$

The expression for the integral $I_N(p_1, \ldots, p_N, t)$ follows from (5) and is of the form:

$$I_N(p_1, \ldots, p_N, t) = \frac{1}{V} \sum_{1 \leqslant i, j \leqslant N} \int_0^{2\pi} d\varphi_{ij} \int_0^\infty \rho_{ij} d\rho_{ij} |v_i - v_j|$$
$$\times [\tilde{f}_N(p_1, \ldots, p_i', \ldots, p_j', \ldots, p_N, t) - \tilde{f}_N(p_1, \ldots, p_i, \ldots, p_j, \ldots, p_N, t)]. \qquad (23)$$

By using Eq. (4), one can also write this integral in the Bogolyubov representation.

Formula (23) incorporates binary (Boltzmann model), but strong interactions. In the approximation of a perturbation theory in the interaction, it implies the result of Prigogine and Brout (Ch. 2 in Ref. 17). The corresponding equation for the single-particle distribution

function (neglecting large-scale correlations) coincides with the kinetic equation of Landau.

Let us turn now to the other limiting case, in which the turbulent source $\tilde{A}$ is dominant on the right-hand side of (17). In this case, as we know, equation (10) does not reduce to the Boltzmann equation.

The additional contribution to the dissipative characteristics that is determined by the integral $\tilde{I}$ can be significant. In particular, this contribution governs the anomalous electrical conductivity of a plasma.[29,18]

Let us now return to equation (3) for the many-particle distribution function $\tilde{f}_N$ and consider some of its properties.

In an equilibrium state the collision integrals (4) and (5) go to zero when the multidimensional Maxwellian distribution

$$\tilde{f}_N (\mathbf{p}_1, \ldots, \mathbf{p}_N, t) = \frac{1}{V^N} \frac{1}{(2\pi m k T)^{3N/2}} \exp \left(- \sum_{1 \leqslant i \leqslant N} \frac{p_i^2}{2mkT} \right) \quad (24)$$

is substituted into them.

If the collision integral (5) [or (4)] is multiplied by the function $-k \ln \tilde{f}_N(\mathbf{r}_1, \mathbf{p}_1, \ldots, \mathbf{r}_N, \mathbf{p}_N, t)$ and integrated over all the variables, we then have

$$- k \int \ln \tilde{f}_N \cdot I_N \, d\mathbf{r}_1 \, d\mathbf{p}_1 \ldots d\mathbf{r}_N \, d\mathbf{p}_N \geqslant 0. \quad (25)$$

This property provides for the undiminishing of entropy of the insulated system

$$S(t) = -k \int \ln \tilde{f}_N \cdot \tilde{f}_N \, d\mathbf{r}_1 \, d\mathbf{p}_1 \ldots d\mathbf{r}_N \, d\mathbf{p}_N, \quad (26)$$

i.e.,

$$\frac{dS}{dt} \geqslant 0. \quad (27)$$

The equal sign corresponds to an equilibrium state.

With the aid of equation (3) together with the collision integrals (4) and (5) [or (23) for the spatially homogeneous case] one can estimate the relaxation times in the various stages of the time evolution. For example, in the kinetic stage, which is described by the Boltzmann equation, we obtain for the relaxation time the familiar expression

$$\tau_{rel} \sim \frac{l_{rel}}{V_\tau} \sim \frac{1}{V_\tau n r_0^2}. \quad (28)$$

The relaxation time is thus determined by the mean free time of some *given* particle [such as particle number 1 in Eq. (10)].

With the aid of expression (23), for example, one can estimate the minimum relaxation time $(\tau_{rel})_{min}$—the time in which *any* single particle of the system "forgets its path." This is sufficient for the system as a whole to be unable to return to the initial state when the signs of the velocities of all the particles of the system are reversed. It follows from (23) that

$$(\tau_{rel})_{min} \sim \frac{1}{N} \tau_{rel} \sim \frac{1}{N V_\tau n r_0^2}. \quad (29)$$

Thus, the minimum relaxation time is smaller by a factor of N than the mean free time. This time characterizes the initial stage in the onset of irreversibility.

One can see from what we have said that Leontovich's paper had great potential. The author regrets that he first read this paper when Leontovich was already gravely ill and unable to discuss any questions. One can only be amazed at how much Leontovich was ahead of his time in his understanding of the fundamental questions of statistical physics.

In conclusion, the author wishes to point out that other types of dissipative equations are possible for many-particle distribution functions.

Dissipative equation (3) is written for the distribution function of the complete set of variables $\mathbf{r}_1, \mathbf{p}_1, \ldots, \mathbf{r}_N, \mathbf{p}_N$ of the N-particle system under consideration. Dissipation arises in this system when small-scale correlations are excluded. This is what dictates an incompleteness in the description.

A different situation is considered in Ch. 10 of Ref. 16 (see also Ch. 24 of Ref. 24). An equation is sought for the distribution function of the variables of the main system, which consists of N particles with an arbitrarily strong interaction between them. Here dissipation is established by the incompleteness of the description in the auxiliary variables of the extended system. In contrast to the case of (3) with the collision integral (5), here one obtains an equation for the many-particle distribution function which is nonlinear in the function $\tilde{f}_N$.

In the equilibrium state the "collision" integral in this equation goes to zero when the Gibbs canonical distribution with the Hamiltonian of the main system is substituted into it. Here the H theorem of Boltzmann is also valid. The minimum relaxation time, as in (29), is proportional to $1/N$.

The kinetic equations for the many-particle distribution functions are too complicated to solve. However, they can prove extremely efficient for constructing approximate equations corresponding to different levels of description and are well suited for describing the kinetics of coherent states during nonequilibrium phase transitions.

Basic to these studies is Leontovich's paper[6] on "The fundamental equations of the kinetic theory of gases from the standpoint of the theory of random processes." This paper will no doubt be studied for many years to come by students of the development of the statistical theory of nonequilibrium processes.

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