Law governing fall of the intensity in the far wings of molecular light-scattering lines

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An analysis is made of the consequence of the experimentally observed exponential fall of the intensity in the far wings of lines representing molecular scattering of light in gases and simple liquids. The physical origin of the fall is demonstrated to be the dynamics of the initial collisionless evolution of the scattering system. A study is made of the additional restrictions on the generalized susceptibilities and Green functions which follow from the existence of an initial collisionless stage in molecular dynamics. The restrictions reduce to the requirement of special high-frequency asymptotics of spectral functions which determine the frequency-dependent kinetic coefficients of the scattering system. A series of model functions possessing all the necessary properties is suggested.

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1. INTRODUCTION

Many experimental investigations of the far wings of lines representing the molecular scattering of light in gases and simple liquids have appeared in recent years and they have given unexpected results (for earlier work see Refs. 1–5; some of the more recent work with the relevant literature citations can be found in Refs. 6–9). The main results can be summarized as follows: in a very wide range of frequency shifts $\Delta\omega$, tens of thousands of time greater than the average line width, and for all the polarization components the fall of the intensity is basically exponential

$$I(\Delta\omega)\sim|\Delta\omega|^{q}\exp(-\tau|\Delta\omega|) \tag{1}$$

with approximately the same value of τ and similar values of the general coefficient in Eq. (1) for all the polarizations. Therefore, the degree of depolarization is comparable with unity instead of the usual value of $\sim10^{-3}$ at low frequencies. There have been no reports of any faster fall of the intensity in the line wing than that predicted by Eq. (1). The parameter τ varies from sample to sample, and depends on temperature and pressure, but it is always comparable with the characteristic time of molecular motion which is $\sim10^{-12}$ sec for liquids, $\sim10^{-11}$–10^{-10} sec for gases. At low temperatures there is a considerable difference between the intensities of the Stokes and anti-Stokes line wings due to quantum-statistical effects.

These results are incompatible with the existing semi-thermodynamic relaxation theory of the scattering of light, which is known to be invalid for short times[10] and which needs revision. Our aim will be to identify and consider the nature of the important information provided by the new experiments, and to attempt a provisional general analysis of the problem.

Let us assume that A, B, ... are the densities of the dynamic variables describing the collective motion in a medium and contributing to the scattering of light, and that $\chi''_{AB}(\omega,\mathbf{k})$ is the dissipative part of the matrix of the generalized susceptibilities associated with these variables. Then, the intensity of light scattered through a certain angle is given by the following expression, which is accurate apart from a universal factor,

$$I(\omega)\sim\frac{2\hbar}{1-e^{-\beta\hbar\omega}}\sum_{A,B}Q_{AB}(\mathbf{k})\chi_{AB}''(\omega,\mathbf{k}), \tag{2}$$

where $Q_{AB}(\mathbf{k})$ are slowly varying functions of ω, which are equal to the products of the mechanooptical coefficients and the appropriate functions of the polarization angles and of the scattering angle. Equation (2) is simplified by dropping the polarization indices; $\beta=(k_BT)^{-1}$; $\mathbf{k}$ is the change in the wave vector as a result of the scattering; $\omega=-\Delta\omega$. In terms of the above equation, the experimental results reduce basically to two items: 1) the functions $\chi''(\omega,k)$ have high-frequency asymptotes of the type

$$\chi''(\omega,k)\sim\text{const}\cdot\omega^{q}e^{-\tau\omega}\left(1+\frac{a_1}{\omega}+\dots\right),\quad \tau\omega\gg1, \tag{3}$$

at least at sufficiently low values of $\mathbf{k}$; 2) all the main terms in the sums of Eq. (2) are of the same order of magnitude in the range of validity of the asymptote (3).

2. DYNAMIC INTERPRETATION OF THE PARAMETER τ

The identity of the law (3) describing the high-frequency behavior of the functions $\chi''(\omega,k)$ in the case of liquids and gases means that this law must be based on general statistical relationships independent of the selection of the model of thermal motion of the medium or the mechanism of the scattering of light. The following considerations demonstrate the nature of the necessary general relationships.

Let us assume that $A(\mathbf{k})$ is the operator for one of the quantities occurring in Eq. (2) and $A(t,\mathbf{k})$ is its Heisenberg representation. We shall introduce an autocorrelation function

$$\langle A(t,\mathbf{k})A^{+}(\mathbf{k})\rangle=\lim_{V\to\infty}\left(\frac{1}{V}\left\langle\exp\left(-\frac{iHt}{\hbar}\right)A(\mathbf{k})\exp\left(\frac{iHt}{\hbar}\right)A^{+}(\mathbf{k})\right\rangle\right), \tag{4}$$

where H is the time-independent Hamiltonian of the system; V is the volume of the system; the angular brackets represent averaging over an equilibrium Gibbs ensemble. The limit $V\to\infty$ is reached for constant values of the density or chemical potential. For simplicity, the lower indices A, B, ... and the parameter $\mathbf{k}$ are omitted; moreover, it is assumed that going to the limit of V is included in the definition of the averages.

We shall begin by proving first a number of points which will be needed later. It is known (for example from the experimental results) that the spectral function $J(\omega)$ has asymptotes of the type

$$J(\omega)\sim A\exp\{-\tau\omega-\Omega(\omega)\},\quad \omega\to+\infty,$$
$$J(\omega)\sim A\exp\{-(\tau+\beta\hbar)|\omega|-\Omega(\omega)\},\quad \omega\to-\infty,$$

with $|\Omega(\omega)/\omega|\to 0$ in the limit $\omega\to\pm\infty$. It then follows from simple considerations that the correlation functions

$$\Phi^{(+)}(t)=\int_{-\infty}^{\infty}J(\omega)e^{-i\omega t}\frac{d\omega}{2\pi}=[\Phi^{(-)}(t)]^{*} \tag{5}$$

on the complex t plane are analytic in the bands $(\tau+\beta\hbar)<\mathrm{Im}\,t<\tau$ and $-\tau<\mathrm{Im}\,t<\tau+\beta\hbar$, respectively. This guarantees the existence of moments of any order of the spectral function

$$M(n)=\int_{-\infty}^{\infty}\omega^{n}J(\omega)d\omega, \tag{6}$$

and for high values of n, we obtain

$$M(n)\sim A\int_{0}^{\infty}\omega^{n}e^{-\tau\omega}[e^{-\Omega(\omega)}+(-1)^{n}e^{-\beta\hbar\omega-\Omega(-\omega)}]d\omega. \tag{7}$$

The second term in Eq. (7) is unimportant in an asymptotic estimate of the integral in this equation, so that we shall assume that

$$M(n)\sim\frac{An!}{(\tau+\Omega'(x_0/\tau))^{n+1}}\exp\left\{-\Omega\left(\frac{x_0}{\tau}\right)+\frac{x_0}{\tau}\Omega'\left(\frac{x_0}{\tau}\right)\right\}\times\left[1+\frac{x_0^2}{n\tau^2}\Omega''\left(\frac{x_0}{\tau}\right)\right]^{-1/2},$$

where x_0 is defined by

$$x_0\left(1+\frac{1}{\tau}\Omega'\left(\frac{x_0}{\tau}\right)\right)=n.$$

In the classical limit it follows from Eq. (7) that the only nonzero moments are even.

It is clear from Eq. (5) that in the case of sufficiently small values of t, we have the expansion

$$2\pi\Phi^{(+)}(t)=\sum_{n=0}^{\infty}\frac{M(n)}{n!}(-it)^{n}, \tag{8}$$

whose convergence radius is

$$R_t=\tau\lim_{n\to\infty}\left\{\left[1+\frac{1}{\tau}\Omega'\left(\frac{n}{\tau}\right)\right]\exp\left[\frac{1}{n}\Omega\left(\frac{n}{\tau}\right)-\frac{1}{\tau}\Omega'\left(\frac{n}{\tau}\right)\right]\right\}=\tau. \tag{9}$$

On the other hand, Eq. (4) and the conditions for the stationary nature of the process $A(t)$ yield directly the expansion

$$\langle A(t)A^{+}\rangle=\sum_{n=0}^{\infty}\frac{(-1)^{n}t^{2n}}{(2n)!}\langle A^{(n)}A^{+(n)}\rangle+\sum_{n=0}^{\infty}\frac{(-1)^{n}t^{2n+1}}{(2n+1)!}\langle A^{(n+1)}A^{+(n)}\rangle, \tag{10}$$

where the upper indices in parentheses give the orders of the time derivatives:

$$A^{(0)}=A,\quad A^{(1)}=\frac{i}{\hbar}[HA],\quad A^{(2)}=\left(\frac{i}{\hbar}\right)^{2}[H[HA]],\ \text{etc.} \tag{11}$$

Comparing the series (8) and (10), we find that

$$M_{2n}=\langle A^{(n)}A^{+(n)}\rangle,\quad M_{2n+1}=-i\langle A^{(n+1)}A^{+(n)}\rangle, \tag{12}$$

so that all the moments M_n are the equilibrium averages of the products of certain operators taken at a given moment, and are therefore the equilibrium characteristics of the system describing its reversible properties. Therefore, the whole series (8) represents, within the limits of its radius of convergence, the initial and time-reversible (collisionless) stage of the evolution of the system.

We shall now obtain a result which is in a sense the reverse of that just obtained. Let us assume that $R_t\neq 0$ and that this quantity is finite. We shall now consider what restrictions this imposes on the behavior of $J(\omega)$ in the limit $\omega\to\infty$.

The series representing the function $\Phi^{(+)}(t)$ converges if $M(n)$ rises as $\Gamma(n+1)$ at high values of n. For an arbitrary value of n the n-th moment can be represented in the form

$$M_n=\Gamma(n+1)e^{\Omega(n)}.$$

The above expression defines (for given values of M_n) some function $\Omega(n)$ for a discrete set $n=0,1,2,\ldots$. The requirement of a finite convergence radius imposes the following restriction on the behavior of $\Omega(n)$ at high values of n:

$$\lim_{n\to\infty}\frac{\Omega(n)}{n}=a\,(\neq\pm\infty). \tag{13}$$

We shall now extend the definition of the function $\Omega(n)$ to values of the complex argument λ such that for $\lambda=n$ we have $\Omega(\lambda)=\Omega(n)$ and

$$\mu_s(\lambda)=\Gamma(\lambda+1)e^{\Omega(\lambda)}.$$

Since Eq. (5) is the definition of the direct Mellin transformation, Eq. (5) permits the inversion

$$J(\omega)=\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}\mu_s(\lambda)\omega^{-\lambda}d\lambda. \tag{14}$$

The integral on the right-hand side of Eq. (14) is determined easily by the steepest-descent method. The saddle point λ_0 is found using Eq. (13), and certain transformations give the asymptotic estimate

$$J(\omega)\sim\exp\{-\tau\omega+\eta(\tau\omega)\}\ \text{in the limit as}\ \omega\to 8. \tag{15}$$

The following notation is used in Eq. (15):

$$\tau=R_t=e^{-a},\quad \eta(x)=\Omega(x)-ax.$$

We shall now consider the physical meaning of the time τ. It follows from the above discussion that τ describes the duration of the prekinetic stage of the evolution of the system. During this stage the properties of the system can be described by the ergodic theory.[11] The main concept in this theory is the mixing time in the phase space τ_s, known as the stochastization time. We can assume that the times τ and τ_s are identical.[12] It is thus possible to obtain information on a fundamental phenomenon in statistical physics, which is the phase mixing in the ergodic theory, by investigating the profile of the high-frequency scattering wing.

The temperature and density dependences of the stochastization time τ_s for a hard-sphere gas are known from Ref. 11:

$$\tau_s=t_0/\ln\left(\frac{l}{d}\right);$$

here t_0 and l are, respectively, the mean free time and the mean free path; d is the diameter of a hard sphere.

A comparison of the experimental values of τ for rare gases with the corresponding values of τ_s reveals full agreement.[12] We may assume that in the more interesting case of a liquid the exponential asymptote of the scattering wings represents the phase mixing (stochastization) processes in the scattering system.

3. DERIVATION OF THE EXPONENTIAL LAW OF THE FALL OF THE INTENSITY

The above discussion can be reversed and an attempt can be made to obtain the exponential law describing the fall of the spectral intensity with rising frequency from the general concepts of statistical physics. A fully rigorous derivation meets with considerable difficulties, but the qualitative aspects seem to be quite clear.

First of all, we note that almost all the approximately soluble physical problems relating to nonideal systems do not even give an asymptotic expansion of the type (4) for the correlation functions. This is due to the absence of the averages on the right-hand side of Eq. (12) resulting from the use of models with nonanlytic contributions to the Hamiltonian (particles with hard cores and other types of discontinuous interactions in the coordinate or momentum space) or due to unjustified extrapolation of the phenomenological form of correlations from the range of long times to $t\to 0$, which makes the correlations behave nonanalytically near $t=0$ [factors of the $\exp(-|t|/\tau)$ type then appear]. We shall be interested in the exact correlation functions of real systems which obviously cannot have such properties.

We shall assume that the Hamiltonian of the system under discussion is either rigorously analytic in respect to the particle coordinates and momenta, or it contains only such singularities which give rise to commutators (11) in a certain class of generalized functions, so that all the averages on the right-hand side of Eq. (10) (including those in the limit $V\to\infty$) are finite. It then follows from Eq. (12) that there is an infinite sequence of moments M_n and the function $J(\omega)$ in Eq. (5) should decrease in the limits $\omega\to\pm\infty$ faster than any negative exponent of ω. A fairly general estimate corresponding to large positive values of ω is given by

$$J(\omega)\sim\text{const}\cdot\omega^c\exp(-a\omega^p)$$

with certain positive constants a and p. In the case of high values of n, it follows from Eq. (5) that

$$M_n\sim\frac{\text{const}}{2\pi p}a^{-(n+c+1)/p}\Gamma\left(\frac{n+c+1}{p}\right),\quad n\gg 1. \tag{16}$$

Hence, the convergence radius of the series in Eq. (8) is

$$R_t=\lim_{n\to\infty}\left(\frac{n!}{M_n}\right)^{1/n}=\begin{cases}\infty, & \text{if}\quad p>1\\ a, & \text{if}\quad p=1.\\ 0, & \text{if}\quad p<1\end{cases} \tag{17}$$

Bearing in mind the reversibility of the evolution of the system described by the series (8), we find that the system can behave in three ways depending on the value of p.

1. If $p>1$, the series (8) and (10) converge absolutely for any value of t and the reversibility of the evolution of the system is retained indefinitely. Obviously, we are dealing here with idealized systems without any interaction between particles or excitations, with systems such as an ideal quantum or classical gas, a perfectly harmonic crystal, etc. All these cases have been thoroughly studied and, naturally, they give values $p>1$. For example, if we select A to represent fluctuations of the density in a classical ideal gas, we easily find $p=2$, and so on in other cases.

In real systems after going to the limit of infinite dimensions, the interaction between particles or excitations results unavoidably in dissipation processes which limit the duration of the collisionless stage. According to Eq. (17), this imposes serious restrictions on the possible values of the parameter p for real systems: $p\leqslant 1$.

2. If $p=1$, the reversible collisionless stage of the evolution of the system has a finite duration $\tau=a$, and it is followed by a dissipative stage.[1)] We may assume that all real systems belong to this "normal" class. If we redefine $a\to\tau$ and $c\to q$ for $p=1$, we are faced with the problem already discussed in connection with the experimental results. Naturally, the value of τ is common to all the properties $A, B, \ldots$ of a given system, whose dynamic behavior is governed by the same general type of interaction (the same group of terms in the interaction Hamiltonian). This agrees perfectly with the experimental observation of the constancy of the parameter τ in Eq. (1) for all the polarization components of the scattered light.

3. If $p<1$, the series (8) and (10) diverge for all the values $t\neq 0$ and they are only asymptotic. The collisionless stage of the evolution of the system is not observed in the limit $V\to\infty$. No real systems exhibit this property, but without a further special analysis we cannot exclude this possibility.[2)]

We can thus see that the exponential asymptotes (3) can be regarded, from the theoretical point of view, as a natural and universal property of real systems reflecting the occurrence of a reversible collisionless stage of the evolution lasting for a finite time. This result can be strengthened in the following sense: the simple exponent $p=1$ in the exponential function of Eq. (3) represents not only an approximate but also the exact order of growth of the function $1/J(\omega)$. We can easily see that the replacement of the simple exponential function with the "refined" form $\exp[-\tau\omega l(\omega)]$, where $l(\omega)$ is any function rising monotonically but slowly at high values of ω, gives $R_t=\infty$ for the radius of convergence of the series (8) if $l(\omega)$ is a rising function, and $R_t=0$ if $l(\omega)$ is a falling function. It follows that any refinement of the simple exponential function takes the system in question outside the normal class, exactly as a replacement of $p=1$ with $p\gtrless 1$, and, therefore, it is not permissible.

We can formulate the problem of reconstruction of the functions $J(\omega)$ or $\chi''(\omega)$ from the moments M_n found using the experimental results. Then, the Carleman theorem on the classical problem of moments[13] shows directly that the cases when $p \geq 1$ in Eq. (13) belong to the determinate problem of moments, whereas the case $p<1$ belongs to the indeterminate problem. This provides additional support for the physical interpretation of the types of behavior considered above.

We shall conclude by noting that the results of the last two sections, given explicitly only for the diagonal elements of the matrices $J_{AB}(\omega)$ and $\chi''_{AB}(\omega)$, are readily generalized to these matrices as a whole and, therefore, can be extended to all the components of the scattered light in accordance with Eq. (2).

4. HIGH-FREQUENCY BEHAVIOR OF BREADTH FUNCTIONS

Let us assume that $\chi_{AB}(z, \mathbf{k})$ is the matrix of the generalized susceptibilities of the same set of quantities as above, considered here as a function of a complex frequency $z=\omega+i\eta$. Omitting again the indices and the parameter $\mathbf{k}$, and introducing as usual the susceptibility $\chi(\omega)=\chi'(\omega)+i\chi''(\omega)$, we find that

$$\chi(z)=\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\chi''(\omega)d\omega}{\omega-z}, \quad \mathrm{Im}(z)>0. \tag{18}$$

It follows from Eq. (2) that the above special nature of the asymptote of the function $J(\omega)$ imposes restrictions on the class of possible functions $\chi(z,\mathbf{k})$, which are additional to the familiar conditions. The functions $\chi(z,\mathbf{k})$ differ only by the constant coefficients from the retarded commutator Green functions in the $(z,\mathbf{k})$ representation, and the latter are related simply to other types of the Green functions in the same representation. Therefore, it is found that the various Green functions for the quantities $A, B, \ldots$ describing the collective processes in the investigated system subject to additional restrictions of exactly the same type as those applicable to the generalized susceptibilities.

It is natural to represent the generalized susceptibilities of the Green functions in terms of the breadth functions. Let us assume, for example, that are dealing with the diagonal matrix element $\chi_{AB}(z)$ corresponding to some diffusional or relaxational mode of motion. We then have the standard representation in the form

$$\chi(z,\mathbf{k})=(1-iz/\Gamma(z,\mathbf{k}))^{-1}. \tag{19}$$

In the theory of the scattering of light only the small values of $\mathbf{k}$ are important. If we expand $\Gamma(z,\mathbf{k})$ and restrict ourselves to the lower powers of $\mathbf{k}^2$, we obtain

$$\Gamma(z,\mathbf{k})=\nu\mathbf{k}^2\gamma(z) \quad \text{or} \quad \Gamma(z,\mathbf{k})=\frac{1}{\tau_1}\gamma(z), \quad \gamma(0)=1 \tag{20}$$

for the diffusional and relaxational modes, respectively, where ν and τ_i are some coefficients whose meaning is self-evident. The function $\lambda(z)$ has a representation analogous to Eq. (18):

$$\gamma(z)=\frac{1}{i\pi}\int_{-\infty}^{\infty}\frac{\gamma_0(\omega)d\omega}{\omega-z}, \quad \mathrm{Im}(z)>0, \tag{21}$$

and on the real axis this function is given by

$$\gamma(\omega)=\gamma_0(\omega)+\frac{i}{\pi}\fint_{-\infty}^{\infty}\frac{\gamma_0(x)dx}{\omega-x}. \tag{22}$$

The spectral function $\gamma_0(\omega)$ is real, nonnegative, and even: $\gamma_0(-\omega)=\gamma_0(\omega)$. Now, these familiar properties are supplemented by the requirement of an exponential fall of increase in ω:

$$\gamma_0(\omega)\sim\omega^q e^{-\tau\omega}, \quad \omega\to+\infty. \tag{23}$$

In fact, it follows from Eq. (19) that, for example, for a diffusional mode of motion

$$\chi''(\omega)=\nu\mathbf{k}^2\omega\gamma_0(\omega)\left[\left(\omega-\frac{\nu\mathbf{k}^2}{\pi}\fint_{-\infty}^{\infty}\frac{\gamma_0(x)dx}{\omega-x}\right)^2+\nu^2\mathbf{k}^4\gamma_0^2(\omega)\right]^{-1}, \tag{24}$$

and at high values of ω, the required asymptote is

$$\chi''(\omega)\sim\frac{\nu\mathbf{k}^2}{\omega}\gamma_0(\omega)\sim\nu\mathbf{k}^2\omega^{q-1}e^{-\tau\omega}. \tag{25}$$

In the case of a relaxational mode of motion, Eqs. (24) and (25) should be modified by replacing $\nu\mathbf{k}^2$ with $1/\tau_1$.

Similarly, in the case of the wave mode of motion, we have the standard representation

$$\chi(z,\mathbf{k})=\frac{\omega_0^2(\mathbf{k})}{\omega_0^2(\mathbf{k})-z^2-iz\Gamma(z,\mathbf{k})}. \tag{26}$$

If we assume that, at low values of $\mathbf{k}$,

$$\omega_0(\mathbf{k})=c k, \quad \Gamma(z,\mathbf{k})=\mu\mathbf{k}^2\gamma(z), \quad \gamma(0)=1, \tag{27}$$

it follows from the previous condition (23) that

$$\chi''(\omega)\sim c^2\mathbf{k}^2\frac{\mu\mathbf{k}^2}{\omega^3}\gamma_0(\omega)\sim c^2\mu\mathbf{k}^4\omega^{q-3}e^{-\tau\omega}. \tag{28}$$

If for the mode in question the functions $\omega_0(\mathbf{k})$ and $\Gamma(z,\mathbf{k})$ have nonzero limits for $\mathbf{k}\to 0$, only the coefficient in front of the frequency-dependent factors changes in Eq. (28). It should be noted that the functions $\gamma_0(\omega)$ and the numbers q will naturally be different for different problems.

At low values of ω or z, the property $\gamma(0)=1$ means that we obtain the usual results for the generalized susceptibilities in the limit of low values of $\mathbf{k}$ and ω, which are well known from the phenomenological theory.

In general, the arbitrary functions $\chi_{AB}(z,\mathbf{k})$, which may be encountered in the scattering of light, can be represented by simple combinations of two typical functions given by Eqs. (19) and (26). Therefore, we always find that the requirement (23) applicable to the width functions is necessary and sufficient to ensure the required asymptote of the functions $\chi(z,\mathbf{k})$. This is thus the necessary additional condition that the generalized susceptibilities or Green functions have to satisfy.

By way of illustration of possible permissible functions $\gamma_0(\omega)$, we may mention all functions of the type

$$\gamma_0^\nu(\omega)=\frac{1}{2^\nu\Gamma(\nu+1)}\frac{(\tau\omega)^\nu}{I_\nu(\tau\omega)}, \quad \nu>-1, \tag{29}$$

where $I_\nu(x)$ are modified Bessel functions and ν is a real quantity. All of them have the necessary properties and are characterized by the asymptote

$$\gamma_0^\nu(\omega)=\frac{(2\pi)^{1/2}}{2^\nu\Gamma(\nu+1)}(\tau\omega)^{\nu+1/2}e^{-\tau\omega}. \tag{30}$$

The functions $\gamma^\nu(z)$ generated by them from Eq. (21) are found to be, after analytic continuation to the half-plane $\mathrm{Im}(z)<0$, transcendental meromorphic functions with an infinite series of simple poles located on the negative imaginary half-axis at asymptotically equidistant positions. For $\nu=\pm\frac{1}{2}$, the functions $\gamma^{\nu}(z)$ can be expressed quite simply in terms of the logarithmic derivative of the Γ function.

We can show that, in general, the requirement of an exponential fall of the functions $\gamma_0(\omega)$ on increase in ω generates functions $\gamma(z)$ whose all distant singularities approach asymptotically the negative imaginary half-axis (or lie on this axis), and have an asymptotic uniform distribution. This means that the functions $\chi(z,\mathbf{k})$ have the same properties, at least at low values of $\mathbf{k}$.

5. CONCLUSIONS

The main and direct conclusion of our study relating to the spectroscopy of the molecular scattering of light is that the exponential profiles of the far wings of the scattering lines represent the initial reversible and collisionless stage of the evolution of the scattering system. The exponential line profiles are not related to any specific mechanisms of collisions (or interaction) of particles in the medium or any specific scattering event, and in theoretical investigations they should be obtained for any correctly selected model of the process. A study of the scattering spectra in the transition region with moderately large frequency shifts, corresponding to the dynamics of decay during the collisionless stage and transition to the hydrodynamic stage of the molecular motion, would give more interesting physical results. Unfortunately, systematic investigations of this kind have not yet been made.

An equally important conclusion of our work is that the scattering line profiles should be described by transcendental meromorphic functions. For comparison it should be noted that in semithermodynamic theories any profile is interpreted as a super-position of real relaxation processes. A comparison with the experimental results then frequently gives such short relaxation times that they clearly lie outside the range of validity of the thermodynamic approach.

In the theory developed by us each of the functions $\chi_{AB}(z,\mathbf{k})$ can also be expanded as an infinite series of elementary fractions on the basis of the Mittag–Leffler theorem. However, only one characteristic time τ or several such times are retained and the series as a whole describes one or several processes, and not an infinite set of processes.

It seems to us that the above and related considerations together with rigorous methods of statistical mechanics, should be sufficient to develop a complete and correct theory of the spectra of the molecular scattering of light in gases and liquids with one or few atoms per molecule.

In statistical physics itself the main conclusion following from the above analysis is the feasibility of deriving simple laws for the asymptotic behavior of the generalized susceptibilities and Green functions in the many-body problem at the high-frequency limit. If $\mathbf{k}\to 0$, then for a wide class of systems, it follows from the above analysis and from the experimental results that the law reduces basically to an exponential decrease in the dissipative parts of the generalized susceptibilities at high real frequencies. It would be highly desirable to investigate asymptotic laws of this kind for arbitrary values of k and different classes of the system. The considerations given in Sec. 3 make it very likely that there should be some universal exponential law applicable to all the normal systems.

1)More rigorously, the above analysis shows only that the duration of the collisionless stage is no less than R_t. We can identify these two times and leave open the question of possible pathological cases, when they differ significantly.

2)The values $p<1$ were obtained theoretically in Ref. 2 only for a very rough estimate of the "close-collision" effect in the case of depolarized scattering of light in a gas. These values are obtained on the basis of the most naive description of the elasticity of electron shells of atoms with the aid of the Lennard-Jones potential, and the results are unreliable.

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