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Microscopic Theory of Rayleigh Scattering*

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A self-consistent, microscopic theory of scattering of light by molecular aggregates is evolved from the standpoints of random-phase-modulation theory and stochastic theory. Contemporary theory is founded on the premise that the scattered light spectrum is proportional to a four-dimensional Fourier transform of the molecular density-correlation function. This premise is justified only in a continuum representation of density, but it breaks down when the motion of discrete molecules is taken into account. The Rayleigh spectrum is shown to be a manifestation of translational degrees of freedom of molecules, much as the Raman spectrum is of internal degrees. Both the central and shifted components are attributed to propagating waves representing probability densities. Theoretical spectra are in agreement with experimental data in both the kinetic and hydrodynamic regimes, and the shifted frequencies are simply related to the rms speed of typical molecules. This theory also provides a mechanism which could account for deviations of total integrated intensity from that predicted by incoherent scattering. Such deviations are simply related to the ratio of intensities of the shifted and central components of the spectrum. Success of this theory, however, is not achieved without complete departure from conventional approaches of kinetic theory. By necessity, statistical aspects of the problem are approached through the use of a set of partial differential equations for the probability densities of continuous, differentiable stochastic processes. Statistical trajectories of molecules are characterized by a single function $h(\tau)$ defined as the logarithmic derivative of the conditional expectation value of velocity. Solutions based on the asymptotic behavior of $h(\tau)$ suggest the possibility for existence of other lines at the high-frequency end of the Rayleigh spectrum.

I. INTRODUCTION

The resurgence of interest in Rayleigh scattering of light in liquids and gases resulted to a large measure from invention of the laser and the analytical work of Komarov and Fisher,[1] who related the spectrum of scattered light to the function $S(\vec{K}, \omega)$, often called the structure factor, which is interpreted as a four-dimensional space-time Fourier transform of the molecular density-correlation function $G(\rho, \tau)$. It appeared possible, therefore, to infer some information on the dynamic structure of molecular aggregates through analysis of Rayleigh spectra.

In a series of papers, Yip and his co-workers[2-6] proposed a kinetic calculation of Rayleigh spectra by extension of developments in transport theory and neutron scattering. Almost concurrently, Mountain[7,8] developed a number of hydrodynamic calculations for the density-correlation function. It appears, however, that no attempt has been made at evolving a theory of light scattering from a unified set of principles. Although recent kinetic calculations of the spectra by Sugawara, Yip, and Sirovich[9,10]—based on approximate solutions of the Boltzmann transport equation for two specific interaction potentials—are in agreement with the observed spectra of Xe and CO_2 at a large viewing angle of 169.4°, they are not conclusive evidence that kinetic theory provides a truly microscopic theory of light scattering. Instead, these solutions essentially provide methods of calculation for the density-correlation function which, no doubt, are useful. As a theory of light scattering, however, composed of a self-consistent body of principles as a framework for interpreting observed phenomena, kinetic theory has neither explained the very existence of a Brillouin doublet as a manifestation of microscopic molecular events, nor predicted an analytical relation between the doublet frequencies and molecular quantities. In contrast, hydrodynamic theory interprets the doublet as a consequence of propagating density fluctuations and predicts the doublet frequencies in terms of acoustic velocity. To the extent that it attributes the observed phenomena to strictly collective or continuum aspects of the molecular aggregate, hydrodynamic theory is self-consistent in principle. But, as is to be expected, it is limited and, therefore, it fails to predict correctly the spectra at large angle, when the frequency shifts associated with individual molecules become comparable to a characteristic frequency such as collision rate. It is commonly accepted that at small viewing angle the gas behavior is hydrodynamic, but that it becomes collision dominated, and therefore kinetic, at large angle. Such dichotomy is not desirable in any theory, being a limitation of theory and not a consequence of the inherent nature of a gas.

From the classical viewpoint, scattering of light by molecular aggregates involves principles of electrodynamics, mechanics, and probability. It is desirable, if not essential, that the roles each of these principles plays in determining the observed effects be segregated as much as possible. For example, even a single particle in a well-defined deterministic motion theoretically exhibits a scattered light spectrum which broadens with increasing viewing angle relative to the particle trajectory. Dependence of the observed spectra on angle, then, cannot be attributed unequivocally to a collective property of the aggregate. Moreover, the findings of Sugawara, Yip, and Sirovich,[9,10] showing virtually no difference in the results of calculations based on Maxwell and elastic-sphere molecules, suggest that statistical principles may be of greater significance than particular forms of mechanical forces. Since Rayleigh scattering offers the potential for investigating molecular aggregates, it is all the more imperative that observed phenomena be logically connected to their origins. Otherwise, any inferences on dynamic features of the aggregate would be open to question.

Principles of classical electrodynamics and stochastic theory can provide a firm basis if the probelm of scattering is so formulated that the underlying random processes are properly indentified and sufficient detail is included in the statistical description of these processes. As a rule, microscopic formulations of any problem are more realistic and contain greater detail than their macroscopic counterparts, and, when properly stated, they must tend to the latter as a limit. There being no question on the limitations of hydrodynamic theory, the puzzlement is with the failure of kinetic theory in not explaining the Brillouin doublet. In principle, as much detail can be included in the calculation of the density-correlation function as compatible with the kinetic model adopted, but the point of departure for both kinetic and hydrodynamic analyses of the aggregate has generally been the result given by Komarov and Fisher,[1] or its equivalent, relating the scattered field to the density-correlation function of the aggregate. The weakness lies in this analytical connection of scattered field to density, the latter being a space-time stochastic process pertaining only to the number of *any group* of molecules that happen to be in a volume element at a given point. Whatever analytical form the density takes, it remains a collective property of the aggregate but not of an individual molecule. A microscopic theory of scattering which is compatible with microscopic analysis of the aggregate is more appropriately founded on a viewpoint which considers the positions of individual molecules as explicit stochastic processes since they manifest themselves as random phases in the scattered field.

However, in this viewpoint, the sources of the radiation field are in motion, thus necessitating a formulation based on the electrodynamics of moving media. As such, the spatial Fourier-transform relationship between the scattered field and the density-correlation function is no longer tenable mathematically. This transform relationship is neither peculiar to Rayleigh scattering nor is it a consequence of the statistical nature of sources. It is a property, inherent in the Green function of the Helmholtz equation, which materializes if, and only if, the spatial coordinates of the source of radiation are independent of time. Thus, the weakness in contemporary theory is not so much in the kinetic calculations of the density-correlation function as in the improper formulation of the radiation field. There is, however, a fundamental inconsistency when the density of the scattering medium is treated from a microscopic standpoint and the radiation aspect is implicitly founded on a continuum description of the medium.

The work in this paper represents an attempt at evolving a self-consistent, explicitly microscipic theory of light scattering from a unified set of principles. Although it does not include effects of such refinements as molecular anisotropy and finite boundaries, it leads to remarkable quantitative agreement with experiment, in both the hydrodynamic and kinetic regimes, notably predicting correct values for the Brillouin frequencies in terms of molecular quantities. This success of theory, however, is not achieved without complete departure from conventional approaches of kinetic theory and statistical mechanics. The principal theme consists in formulation of the scattered field as a randomly phase-modulated field whose statistical properties are derived from the classical equations of motion of typical single molecules and pairs of molecules subject to general principles of stochastic theory.

The fact that random motion of the molecule affects the phase of oscillations of its dipole moment is far from being a new idea, dating to the pioneering work of Rayleigh.[11] Recently, Clark[12] also considered a formulation using random phases as a starting point. What the present work demonstrates, in addition to a new statistical approach, is a rigorous relationship (within constraints of the radiation zone and nonrelativistic approximations) between the scattered field and the random molecular motion. In this way, a certain parallelism to the Raman effect is achieved. It is recalled that the Raman spectrum is a manifestation of internal and rotational degrees of freedom of the molecule which affect its polarizability, whose temporal variation is viewed classically as amplitude modulation of the scattered field. The Rayleigh spectrum, as will become evident, arises principally from translational degrees of freedom of the molecule as a unit, which appear as phase modulation of the scattered field. Phase modulation naturally accounts for the broadening of spectrum with increasing viewing angle.

The entire problem of light scattering is treated in classical terms. Classical analysis of the molecular statistics is necessary because the optical radiation fields, both incident and scattered, are formulated from the standpoint of classical electrodynamics. The formalism of the latter requires explicit characterization of the point sources of the field as functions $\vec{R}(t)$. In this context, it is important to distinguish the particle, as such, and the space in which the particle is described. We view the physical concept of the existence of a particle to be equivalent to the mathematical existence of a class of functions $\{\vec{R}(t)\}$ which map the domain set $\{t\}$ to the range set $\{\vec{r}\}$, so that if the element t_1 is mapped to $\vec{r}_1 = \vec{R}(t_1)$, under a particular mapping, one speaks of the particle being at $\vec{r}_1$ at time t_1. Mechanical laws are then merely the rules which restrict the mappings to specific classes which we call possible trajectories. However, existence of a mapping *does not* imply that the position $\vec{r}$ can be determined with accuracy, owing to one's imperfect knowledge of all the factors, including the act of measurement, which might influence the trajectory. Hence $\vec{R}(t)$ must be considered as a stochastic process such that the position is probabilistic, insofar as measurement is concerned, allowing specification only to the extent that $\vec{R}(t)$ lies in a finite interval $(\vec{r}, \vec{r} + d\vec{r}]$ with probability $p(\vec{r})d\vec{r}$. In this viewpoint, then, every particle has associated with it a mathematical mapping $\vec{R}(t)$, governed by mechanical laws and whose range set is $\{\vec{r}\}$, and a probablity measure density field $p(\vec{r})$, defined on the range set and governed by the axioms of probability theory.

Modern quantum theory, however, places a lower bound on the intervals within which position and momentum may be specified, through the Heisenberg uncertainty principle, for typical Cartesian components,

$$\langle \Delta P_X \rangle_{\text{av}} \cdot \langle \Delta X \rangle_{\text{av}} \geq \tfrac{1}{2}\hbar .$$

It is well, therefore, to estimate whether or not classical treatment of the translational degrees of freedom of a molecule is valid. To this end, we consider the square root of the variance of momentum of a single particle, resulting from the Gaussian probability density, as the uncertainty $\langle \Delta P_X \rangle_{\text{av}}$ (see Corollary 2.3 below). We find the corresponding uncertainity in position to be

$$\langle \Delta X \rangle_{\text{av}} \geq \hbar / 2(m k_B T)^{1/2} ,$$

where m is the mass of the molecule, k_B is the Boltzmann constant, and T is the Kelvin temperature. In terms of the gram molecular weight M, the uncertainty at $T = 300$ °K becomes

$$\langle \Delta X \rangle_{\text{av}} \geq 2.02 \times 10^{-9} M^{-1/2} \text{ cm}.$$

Consequently, even for the hydrogen molecule, $M \simeq 2$, the lower bound on the uncertainty in position is at least an order of magnitude smaller than molecular diameters, which are typically of the order of 10^{-8} cm. This bound is even smaller for heavier molecules. Thus, a molecule is a large object, in Dirac's sense, amenable to classical treatment insofar as translational degrees of freedom are concerned. Quantum effects are not expected to be significant, and representation of molecular motion by stochastic trajectories should lead to a reasonable description of observed phenonmena. A similar calculation of the energy variance shows the lower bound on the time scale to be of order 10^{-13} sec as compared with typical mean molecular collision times of 10^{-10} sec. Hence, throughout this paper, mathematical continuity of trajectories and the limit $\Delta t \to 0$ are understood as idealizations of the lower bounds imposed by quantum theory.

Since the theory departs substantially from previous approaches, exposition of viewpoint and analysis is detailed. At this point, however, it seems appropriate to summarize the main body of experimental evidence, and to review briefly the evolution of contemporary theory and interpretations. This review is then followed by sections on scattering theory, statistical theory, and comparison to experiment, in that order.

II. REVIEW

Briefly and qualitatively, the salient experimental observations of Greytak, Benedek,[13,14] and Clark[12] are as follows. When a beam of monochromatic light, having frequency ω_0 and wave vector $\vec{k}_0$, is scattered by a neutral gas, the spectrum of scattered light manifests a finite width centered about ω_0. When the gas pressure and temperature and angle of observation relative to $\vec{k}_0$ are appropriately selected, a distinct fine structure appears in the spectrum consisting of three lines: the Rayleigh line with undisplaced frequency ω_0, and the symmetrically displaced Brillouin doublet at frequencies $\omega_0 + \omega_B$ and $\omega_0 - \omega_B$, the frequency shifts being of order 10^8 MHz. The angle of observation determines the wave vector $\vec{K}$, through the relation $\vec{K} = \vec{k}_0 - \vec{k}_s$, where $\vec{k}_s$ is the scattered field wave vector in the direction of observation. If ψ is the angle between $\vec{k}_0$ and $\vec{k}_s$, then to a good approximation $K = 2k_0 \sin(\frac{1}{2}\psi)$. According to current theory, the Brillouin doublet appears with a fair resolution when the ratio of $2\pi/K$ to the molecular mean free path is much greater than unity, i.e., under small angles for a given pressure. This ratio, y, is also considered as the parameter which determines the character of the gas as kinetic or hydrodynamic.[9,10]

More significantly, as the angle increases from near-forward to near-backward directions, the Brillouin doublet apparently loses resolution, and the entire spectrum broadens by as much as ten-to-one relative to the breadth at small angles.

Dependence of the total integrated intensity on viewing angle has thus far remained an open question. In xenon and argon, George *et al.*[15] observed marked departures from the angular dependence characteristic of dipole radiation of the Rayleigh theory; it is not clear how much of this deviation was due to their neglect of the cosecant correction owing to the changing effective volume. Watson and Clark,[16] on the other hand, report no angular deviations in nitrogen. Calculations by Thiemer[17] and Fieock[18] have led to the conclusion that the finite sizes of detector and scattering region cannot account for these angular deviations. Several authors have also observed a discrepancy in differential scattering cross section, the observed value being almost twice as large as that expected.[15,19] Implications of the above observations are discussed throughout the sequel; our attention is now turned to a brief review of theory.

In classical theory, Rayleigh scattering may be formulated from two viewpoints: the macroscopic or continuum viewpoint, and the microscopic or kinetic viewpoint. Validity of the fomer depends on how the wavelength and frequency of the incident wave compare with characteristic distances and times of the molecular aggregate, such as mean free path and time, and on the degree of detail to be included in the theory. In the macroscopic viewpoint, due to Smoluchowski[20] and Einstein,[21] light is scattered by local spatial inhomogeneity of dielectric constant or density, the mean values contributing to forward scattering only. When the inhomogeneity varies in time also, the effect is manifested in the spectral composition of the scattered light. Brillouin[22] resolved the time-dependent fluctuations into a set of random acoustic waves, which diffract the incident light and cause a Doppler shift in its frequency. In a more recent treatment, Pecora[23] starts with the fluctuation as a perturbation on the mean value, thereby showing that the first-order scattered field is caused by a continuous distribution of dipoles whose macroscopic moment density is proportional to the random fluctuation.

In the microscopic viewpoint of Rayleigh,[11] which historically predates the macroscopic one, each molecular dipole is an independent scatterer, neglecting correlations in the random molecular motion, so that the total intensity is proportional to the number of molecules, and its spectrum is a replica of the incident light, except for the multiplicative factor ω_0^4. The argument for independent scattering is precisely that the phases of oscillation of the molecules are completely uncorrelated, owing to their random motion. Because the phase correlation is neglected, no mechanism is provided for the spectral composition of scattered light. Komarov and Fisher[1] reverted to the microscopic viewpoint, but considered some details of molecular motion, concluding that the scattered intensity is proportional to the space-time Fourier transform of the molecular density-correlation function. Thus, analytical effort shifted to calculation of this correlation function by both kinetic and hydrodynamic methods.

Even as the density-correlation function is calculated by a kinetic-microscopic method, however, contemporary interpretation of what causes the phenomenon of light scattering is basically the macroscopic viewpoint, the doublet arising from scattering by propagating density fluctuations, and the central component from nonpropagating fluctuation. In addition to the duality in viewpoint, this division of fluctuations into propagating and nonpropagating components seems to be somewhat artificial because any dynamic field process (including a diffusion process) is resolvable into propagating waves via the Fourier integral in four dimensions, i.e., the space-time analog of the Wiener-Khinchin theorem.[24] Strictly speaking, the only component of the spectrum which is nonpropagating is that at zero frequency.

Mathematically, the essential difference between macroscopic and microscopic formalisms of radiation from a source distribution lies in the role of spatial coordinates of the source. In the macroscopic case, the source of the radiation field is an actual or an equivalent current density field $\vec{J}(\vec{r}, t)$. Even when $\vec{J}(\vec{r}, t)$ is a stochastic process, the spatial coordinates are additional indices on equal rank with time *and independent of it*. In molecular scattering, the current density is simply related to the number density $n(\vec{r}, t)$, and it is this continuum stochastic process that characterizes the scattered field. In the microscopic case, the coordinates of the moving point sources are functions of time. In molecular scattering one deals with N stochastic processes $\vec{R}_i(t)$, representing molecular coordinates, and it is they that determine the character of the scattered field. A consistent treatment of the radiation field must deal with the motion of the sources explicitly.

Contemporary theory of light scattering is founded on the premise that the scattered light intensity is the space-time Fourier transform of the molecular density-correlation function. Inasmuch as this relationship is valid only when the source of radiation is a continuum, which is at rest relative to the observer, and since it fails when the source is a collection of moving points, contemporary theory is implicitly founded on the macroscopic viewpoint of scattering, and it must be regarded as such. What kinetic theory has introduced is a computational refinement into the continuum theory but not a fundamental change of viewpoint.

It is reasonable to conclude that, to date, a self-consistent, dynamic, microscopic theory of light scattering has not been proposed. In the following exposition, we attempt to lay the framework in which such a theory can evolve.

III. SCATTERING THEORY

A. Preliminary Considerations

There is no basis in purely statistical theory which can attribute the broadening of spectrum with increasing angle to statistical properties of the aggregate which is generally assumed to be isotropic. This phenomenon, then, must be occuring on a molecular level; that is, it cannot be a manifestation of some collective property of the aggregate, such as density or temperature, if the viewpoint is to be consistently microscopic. Since the frequency spectrum is a property of oscillations, and these are characterized by a phase and an amplitude, the broadening effect must be attributed to either the amplitudes or phases of oscillations of individual molecular dipoles. Experience with phase-modulation theory indicates that the broadening of the spectrum must be related to the molecular phases. For it is well known that the spectrum of any phase- or frequency-modulated oscillating function depends strongly on a parameter called index of modulation, and the breadth of the spectrum for large index can be as much as 100 times that for small index. Physically, the effective phase of the incident field that the molecule experiences is determined by its position in the wave field, and in turn, the phase of the scattered field depends on the position of the molecule relative to the observer. Thus, if $\vec{R}_i(t)$ is the position vector of a nonrelativistic molecule, $\vec{k}_0$ and $\vec{k}$ are the wave vectors of the incident and scattered fields, respectively, the effective phase apparent to the observer is $(\vec{k}-\vec{k}_0)\cdot\vec{R}_i(t)$, which is a random phase if the molecular motion is random. Accordingly, the parameter $\vec{K}=\vec{k}-\vec{k}_0$ plays exactly the role of index of modulation.

The mechanism of phase modulation is actually, but tacitly, included in any consistent, dynamic, microscopic formulation of scattering; the initial expressions of Komarov and Fisher and their equivalents contain this. However, the mechanism is obscured and overlooked in the process of averaging over all the molecules from the outset. This brings us to the fundamental thesis of this paper.

The averaging over all molecules from the outset is an unnecessary complication if one admits the fundamental principle underlying all of statistical mechanics[25]: *that in the course of time, the behavior of a single molecule and a pair of molecules is statistically indistinguishable from that of any other single or pair of molecules selected at random.*

Equivalently, the representative ensemble of the coordinates $\vec{R}_i(t)$ of the ith molecule, taken as a stochastic process, is the same as the representative ensemble for $\vec{R}_j(t)$ of the jth molecule in the sense that both ensembles are composed of the same set of representative functions with the same probability measure; for N molecules there are N statistically identical ensembles. It should be possible, therefore, to gain insight into the mechanism of scattering by first focusing attention on a typical molecule and pair of molecules taking due cognizance of their trajectories in a stochastic manner.

B. Radiation from Moving Dipoles

We adopt a conventional model of representing the gas by a distribution of dipoles, each molecule having an induced dipole moment proportional to the incident field at the position of the molecule. The principal electrodynamic distinction between dense and dilute systems rests in the difference between the local field at the molecule and the incident field. For simplicity, this paper is confined to dilute systems in which equating the two fields is a valid procedure, i.e., multiple scattering is negligible. It is also restricted to electrically neutral molecules whose motion is nonrelativistic. The position vector of a typical molecule is taken to be a stochastic process $\vec{R}_i(t, \sigma)$ defined on the Cartesian product set $\{t, \sigma\}$, t being the time and σ a subset of the sample space Σ on which a suitable probability measure $P(\sigma)$ is defined. We assume that all processes are stationary at least to second order, and that the ensemble is so constructed that time and ensemble averages are equivalent.

To determine the radiation field on the ith molecule, one selects a representative function $\vec{R}_i(t, \sigma_m)$ for a given σ_m and computes the field conventionally using the Hertz potential $\vec{Z}_i$, it being understood that the Maxwell field equations map each element of the ensemble $\vec{R}_i(t, \sigma)$ to an element $\vec{Z}_i(\vec{R}, t, \sigma)$ in the ensemble of the radiation field at the position $\vec{R}$. In what follows, therefore, we omit writing σ explicitly, except when emphasis calls for it.

Our purpose now is reduction of the scattered field to a phase-modulated function. Let $\vec{E}_0(\vec{R}, t)$ be the electric vector of the incident field and α the polarizability of the modecule. Then the molecular dipole moment is

$$\vec{P}(\vec{R}, t) = \alpha \vec{E}_0(\vec{R}, t)\delta(\vec{R} - \vec{R}_i(t)), \tag{1}$$

and its radiation field at points $\vec{R} \neq \vec{R}_i$ is determined from the Hertz potential $\vec{Z}_i(\vec{R}, t)$ satisfying the standard field equations, in RMKS,

$$\vec{E}_i(\vec{R}, t) = \nabla \times \nabla \times \vec{Z}_i(\vec{R}, t), \tag{2}$$

$$\vec{H}_i(\vec{R}, t) = \epsilon_0 \frac{\partial}{\partial t} \nabla \times \vec{Z}_i(\vec{R}, t), \tag{3}$$

$$\nabla^2 \vec{Z}_i(\vec{R}, t) - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec{Z}_i(\vec{R}, t) = -\frac{1}{\epsilon_0}\vec{P}_i(\vec{R}, t). \tag{4}$$

The permittivity here is taken to be that of vacuum since the effect of polarization is already accounted for in the induction zone by the very field being computed. Inasmuch as Eq. (1) signifies a moving source, the entire problem must be treated in the time domain. The solution to Eq. (4) is obtained directly via its Green's function, viz.,

$$\vec{Z}_i(\vec{R}, t) = \frac{1}{4\pi\epsilon_0}\int_{-\infty}^{\infty} dt' \int_v d\vec{R}' \frac{\vec{P}_i(\vec{R}', t')}{|\vec{R} - \vec{R}'|} \times \delta\left(t' - t + \frac{1}{c}|\vec{R} - \vec{R}'|\right). \tag{5}$$

After substituting Eq. (1) and carrying out the integration over $\vec{R}'$ subject to the usual far-zone condition, $R \gg R_i$, we reduce Eq. (5) to

$$\vec{Z}_i(\vec{R}, t) = \frac{\alpha}{4\pi\epsilon_0 R}\int_{-\infty}^{\infty} \vec{E}_0(\vec{R}_i(t'), t') \times \delta\left(t' - \frac{1}{c}\hat{R}\cdot R_i(t') - \left(t - \frac{1}{c}R\right)\right) dt', \tag{6}$$

where $\hat{R} = \vec{R}/R$ is the radial unit vector from the origin to the point of observation.

Although one can evaluate the integral (6) by again using the formal property of the δ function (distribution), it is necessary for our purpose first to make a nonlinear transformation of time:

$$\xi = t' - \frac{1}{c}\hat{R}\cdot\vec{R}_i(t'), \qquad d\xi = dt'[1 - \hat{R}\cdot\vec{\beta}_i(t')],$$

where $\vec{\beta}_i = \vec{V}_i/c$, and $\vec{V}_i$ is the velocity of the molecule. We now proceed to make an iterative Taylor expantion of $\vec{R}_i(t')$ about $t' = \xi$ to obtain for the first iteration

$$\vec{R}_i(t') = \vec{R}_i(\xi) - \vec{\beta}_i(\xi)\hat{R}\cdot\vec{R}_i(\xi) + \cdots.$$

A few repetitions show that all terms decrease in ascending powers of β_i, so that $\vec{R}_i(t') = \vec{R}_i(\xi)$ in the nonrelativistic limit $\beta_i \ll 1$. The correction introduced by $\vec{R}_i$ is significant only in the argument of the δ function; it is negligible in the differential dt' consistently with the radiation-zone approximation. With this correction, then, Eq. (6) becomes

$$\vec{Z}_i(\vec{R}, t) = \frac{\alpha}{4\pi\epsilon_0 R}\int_{-\infty}^{\infty} \vec{E}_0\left(\vec{R}_i(\xi), \xi + \frac{1}{c}\hat{R}\cdot\vec{R}_i(\xi)\right) \times \delta\left(\xi - \left(t - \frac{R}{c}\right)\right) d\xi. \tag{7}$$

This integral is simply a statement that the retardation in time depends on the position of the molecule, which is itself a function of this retarded time. It takes an added meaning, however, when the incident field is a uniform, plane, monochromatic wave of the form

$$\vec{E}_0(\vec{R}, t) = \vec{e}E_0 \exp(i\vec{k}_0\cdot\vec{R} - i\omega_0 t), \tag{8}$$

$\vec{e}$ being the fixed polarization vector of the wave. The additional retardation arising from the particle position then appears as a time-dependent phase angle as may be seen by substituting (8) into (7) to get

$$\vec{Z}_i(\vec{R}, t) = \frac{\alpha}{4\pi R\epsilon_0}\vec{e}E_0\Phi_i\left(t - \frac{R}{c}\right), \tag{9}$$

where

$$\Phi_i(t) = \exp(-i\omega_0 t - i\vec{K}\cdot\vec{R}_i(t)), \tag{10}$$

$$\vec{K} = \vec{k}_s - \vec{k}_0; \quad \vec{k}_s = \hat{R}k_0.$$

Here, $\vec{k}_s$ is the wave vector of the scattered field. From here on, the incident field is assumed to be plane and monochromatic. The exponential representation is understood to be an analytic signal, in the sense of Gabor, whose real and imaginary parts are Hilbert-transform pairs.[26] This choice simplifies stochastic aspects of the problem though the actual field is the real part of Φ_i.

The electromagnetic field is now obtained by substituting Eq. (9) into (2) and (3). Carrying out the details and observing that $\omega_0 >> KV_i$ and $|dV_i/dt| << \omega_0 c$, we obtain, for the radiation field,

$$\vec{E}_i(\vec{R}, t) = -\frac{\alpha k_0^2}{4\pi\epsilon_0 R}E_0\hat{R}\times\hat{R}\times\vec{e}\Phi_i\left(t - \frac{R}{c}\right), \tag{11}$$

$$\vec{H}_i(\vec{R}, t) = \frac{\alpha k_0^2 c}{4\pi R}E_0\hat{R}\times\vec{e}\Phi_i\left(t - \frac{R}{c}\right). \tag{12}$$

We have verified that, within the constraints of the radiation zone and nonrelativistic approximation, a moving dipole excited with a monochromatic wave is equivalent to a stationary dipole fixed at the origin but excited with the phase-modulated function $\Phi_i(t)$. Clearly, $\Phi_i(t)$ reduces to $e^{-i\omega_0 t}$, with a fixed phase, when the dipole is static, as to be expected. The problem has been cast in a very lucid form in which translational degrees of freedom of the molecule appear as the information encoded into the phase of scattered field much as the internal degrees of freedom are encoded as amplitude modulation through a time-dependent polarizability in Raman scattering.

In the present microscopic viewpoint, the parameter $\vec{K}$ plays the role of index of modulation whose value to a large measure determines the spectrum of the modulated wave. It also determines the instantaneous frequency of $\Phi_i(t)$ which, by definition, is the temporal derivative of the total phase, i.e.,

$$\omega(t) = \omega_0 + \vec{K}\cdot\vec{V}_i(t). \tag{13}$$

This is exactly the frequency change one would obtain for small velocity if the phenomenon were viewed as a relativistic Doppler effect. It is preferable, however, for logical consistenty, to view it as a consequence of phase modulation. The relativistic Doppler effect is a consequence of invariance of the four-vector $(\vec{k}, i\omega/c)$ under Lorentz transformation of the special relativity of *uniform* motion. Since a molecule in random motion is necessarily accelerated, strictly speaking, special relativity is not tenable. One might argue that between collisions the molecule is in uniform motion; but this argument amounts to a restrictive presupposition on molecular motion whose very nature is to be deduced from observations on the scattered field. Equation (9) shows that it is not necessary to invoke the Lorentz transformation. Inasmuch as their validity is contingent only upon the conditions $V_i/c << 1$ and $|dV_i/dt| << \omega_0 c$ — conditions amply statisfied in molecular motion — Eqs. (9), (11), and (12) include accelerated, randomly moving molecules.

Before passing to the autocorrelation function of the field, we pause to examine the basis of the Fourier space-time transform relation between the scattered field and the density-correlation function. We observe that Fourier transformation, over time, of the general integral solution in Eq. (5) converts it to

$$\vec{Z}'(\vec{R}, \omega) = \frac{1}{4\pi\epsilon_0}\int\frac{\vec{P}'(\vec{R}', \omega)}{|\vec{R} - \vec{R}'|}\exp(ik|\vec{R} - \vec{R}'|)d\vec{R}', \tag{14}$$

where $k = \omega/c$ and the prime on $\vec{Z}$ and $\vec{P}$ in this case only denotes Fourier transform over time. Obviously, this integral is also the general solution of the Helmholtz equation obtained by Fourier transformation of Eq. (4). In particular, when $R \gg R'$ in the radiation zone, Eq. (14) reduces to

$$\vec{Z}'(\vec{R}, \omega) = \frac{e^{ikR}}{4\pi R\epsilon_0}\int P_i'(\vec{R}', \omega)e^{-i\vec{k}\cdot\vec{R}'}d\vec{R}', \tag{15}$$

where $\vec{k} = \hat{R}k$. This integral is properly interpreted as the Fourier space transform of the source field $\vec{P}_i(\vec{R}', t)$. Note, however, that the integration is with respect to spatial coordinates of the source field, which to begin with are independent of time, and that the relationship is valid only for the transforms over time. It is on the basis of this integral only that one can justify the transform relationship between the scattered field and the density-correlation function. In contrast, when $\vec{P}(\vec{R}, t)$ is given by a summation of terms like that in Eq. (1), the general solution for each term is given as

$$\vec{Z}_i(\vec{R}, t) = \frac{\alpha}{4\pi\epsilon_0}\int\frac{\vec{E}_0(\vec{R}_i(t'), t')}{|\vec{R} - \vec{R}_i(t')|} \times\delta\left(t' - t + \frac{1}{c}|\vec{R} - \vec{R}_i(t')|\right)dt'. \tag{16}$$

Under the radiation-zone approximation, $R_i(t') << R$, this integral reduces to (6). There exists no valid mathematical manipulation by which these integrals, (6) or (16), can be reduced to a space transform of the discrete source field for the sole reason that the integrands are implicit functions of local time. This is a matter of impossibility in principle and not one of inability to devise a suitable approximation leading to the desired result. The point is extremely important because approximations through a vague succession of Fourier transformations and inversions, coupled with averaging over time and ensemble, ultimately result in a tacit but serious confusion of correlation functions with probability density functions. Unless the autocorrelation function of the radiation field, which is random, is defined and understood in the strict sense of optical coherence theory and stochastic theory, the very meaning of a spectrum via the Wiener-Khinchin theorem becomes questionable.[27]

C. Autocorrelation of Scattered Field

The problem of finding the autocorrelation function of the scattered field has been reduced to that of finding correlation functions of phase-modulated signals whose theory is well developed. Here we include only those relations needed for our purpose. Throughout the remainder of this paper, we adopt the following notations and conventions.

Where necessary to distinguish between time and ensemble averages, the former is designated by brackets $\langle\cdots\rangle$ and the latter by $E\{\cdots\}$; thus

$$\langle f(t,\sigma)\rangle = \lim_{T\to\infty}\frac{1}{2T}\int_{-T}^{T} f(t,\sigma)dt\,, \tag{17}$$

$$E\{f(t,\sigma)\} = \int_{\Sigma} f(t,\sigma)dP(\sigma). \tag{18}$$

Careful distinctions are drawn among a random process $\vec{\mathrm{R}}_i(t,\sigma)$, its domain set $\{t,\sigma\}$, and its range set $\{\vec{\mathrm{r}}\}$. A probability measure is properly defined only on the sample set Σ or the range set $\{\vec{\mathrm{r}}\}$. Accordingly, the symbolism

$$p(\vec{\mathrm{r}})d\vec{\mathrm{r}} = P\{\vec{\mathrm{R}}_i(t)\in(\vec{\mathrm{r}},\vec{\mathrm{r}}+d\vec{\mathrm{r}}]\}$$

denotes the probability of the semiclosed interval $(\vec{\mathrm{r}},\vec{\mathrm{r}}+d\vec{\mathrm{r}}]$ of the range set defined as the measure of the subset of all σ such that $\vec{\mathrm{R}}_i(t,\sigma)\in(\vec{\mathrm{r}},\vec{\mathrm{r}}+d\vec{\mathrm{r}}]$. The probability of a vector quantity is understood to mean the joint probability of its Cartesian components.

In terms of the probability density on the range set, the expectation of any deterministic function of $\vec{\mathrm{R}}_i(\mathrm{t})$ becomes

$$E\{f(\vec{\mathrm{R}}_i(t,\sigma))\} = \int_{-\infty}^{\infty} f(\vec{\mathrm{r}})p(\vec{\mathrm{r}})d\vec{\mathrm{r}} \tag{19}$$

and its autocorrelation function,

$$\begin{aligned} C_f(t_2,t_1) &= E\{f(\vec{\mathrm{R}}_i(t_2,\sigma))f^*(\vec{\mathrm{R}}_i(t_1,\sigma))\} \\ &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(\vec{\mathrm{r}})f^*(\vec{\mathrm{r}}_0)P_{ii}(\vec{\mathrm{r}},t_2;\vec{\mathrm{r}}_0,t_1)d\vec{\mathrm{r}}_0 d\vec{\mathrm{r}}\,, \end{aligned} \tag{20}$$

where the asterisk denotes complex conjugate, $d\vec{\mathrm{r}} = dxdydz$ as usual, and P_{ii} is the joint probability density,

$$\begin{aligned} &P_{ii}(\vec{\mathrm{r}},t_2;\vec{\mathrm{r}}_0,t_1)d\vec{\mathrm{r}}d\vec{\mathrm{r}}_0 \\ &\quad = P\{\vec{\mathrm{R}}_i(t_2)\in(\vec{\mathrm{r}},\vec{\mathrm{r}}+d\vec{\mathrm{r}}];\vec{\mathrm{R}}_i(t_1)\in(\vec{\mathrm{r}}_0,\vec{\mathrm{r}}_0+d\vec{\mathrm{r}}_0]\}. \end{aligned}$$

It is emphasized that all integrals with probability densities extend over $(-\infty,\infty)$ in the range set by definition of probability. It is not an approximation dictated by physics or a particular geometry. The physics of a situation determine the particular analytical expressions for the probabilities.

To determine the autocorrelation of a phase-modulated function we shall need the following probability densities:

$$p(\vec{\mathrm{r}}_0)d\vec{\mathrm{r}}_0 = P\{\vec{\mathrm{R}}_i(0)\in(\vec{\mathrm{r}}_0,\vec{\mathrm{r}}_0+d\vec{\mathrm{r}}_0]\},$$

$$\begin{aligned} &W_{1j}(\vec{\mathrm{r}},\tau\,|\,\vec{\mathrm{r}}_0)d\vec{\mathrm{r}} \\ &\quad = P\{\vec{\mathrm{R}}_j(\tau)\in(\vec{\mathrm{r}},\vec{\mathrm{r}}+d\vec{\mathrm{r}}]\,|\,\vec{\mathrm{R}}_1(0)\in(\vec{\mathrm{r}}_0,\vec{\mathrm{r}}_0+d\vec{\mathrm{r}}_0]\}, \\ &\qquad j=1,2. \end{aligned}$$

In this notation, the event upon which the probability is conditioned is to the right of the vertical bar. The joint probability densities are now defined as

$$P_{1j}(\vec{\mathrm{r}},\tau;\vec{\mathrm{r}}_0) = p(\vec{\mathrm{r}}_0)W_{1j}(\vec{\mathrm{r}},\tau\,|\,\vec{\mathrm{r}}_0),\quad j=1,2. \tag{21}$$

All probability densities are invariant under translation of time in accordance with the assumption of stationarity. Also, by definition of W_{11} and P_{1j} we have the useful properties

$$W_{11}(\vec{\mathrm{r}},0\,|\,\vec{\mathrm{r}}_0) = \delta(\vec{\mathrm{r}}-\vec{\mathrm{r}}_0), \tag{22}$$

$$P_{1j}(\vec{\mathrm{r}},\tau;\vec{\mathrm{r}}_0) = P_{j1}(\vec{\mathrm{r}}_0,-\tau;\vec{\mathrm{r}}),\quad \tau = t_2 - t_1. \tag{23}$$

We now proceed to calculation of the autocorrelation of the scattered field.

Of the several autocorrelation functions that can be defined for an electromagnetic field,[26] the one most suitable to light scattering is defined as

$$\Gamma(\vec{\mathrm{R}},\tau) = \langle\vec{\mathrm{E}}(\vec{\mathrm{R}},t+\tau)\times\vec{\mathrm{H}}^*(\vec{\mathrm{R}},t)\rangle\cdot\hat{R}\,. \tag{24}$$

From here on, time averages are replaced by equivalent ensemble averages in accordance with the hypothesis of ergodicity. Thus

$$\Gamma(\vec{\mathrm{R}},\tau) = E\{\vec{\mathrm{E}}(\vec{\mathrm{R}},\tau)\times\vec{\mathrm{H}}^*(\vec{\mathrm{R}},0)\cdot\hat{R}\}. \tag{25}$$

This choice of definition is motivated by the fact that the time-averaged total intensity is simply

$$I_{\mathrm{av}}(\vec{\mathrm{R}}) = \Gamma(\vec{\mathrm{R}},0)\,. \tag{26}$$

Moreover, by the Wiener-Khinchin theorem, the spectral function $S(\vec{\mathrm{R}},\omega)$ and $\Gamma(\vec{\mathrm{R}},\tau)$ form the Fourier-transform pair

$$S(\vec{R}, \omega) = \int_{-\infty}^{\infty} \Gamma(\vec{R}, \tau) e^{i\omega\tau} d\tau, \tag{27}$$

$$\Gamma(\vec{R}, \tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} S(\vec{R}, \omega) e^{-i\omega\tau} d\omega. \tag{28}$$

It is seen from Eqs. (26) and (28) that $S(\vec{R}, \omega)$ is indeed the observable quantity in any spectroscopic experiment since

$$I_{av}(\vec{R}) = \frac{1}{2\pi} \int_{-\infty}^{\infty} S(\vec{R}, \omega) d\omega. \tag{29}$$

The total electromagnetic field is the sum of the fields from N molecules,

$$\vec{E}(\vec{R}, t) = \sum_{i=1}^{N} \vec{E}_i(\vec{R}, t), \tag{30}$$

$$\vec{H}(\vec{R}, t) = \sum_{i=1}^{N} \vec{H}_i(\vec{R}, t), \tag{31}$$

each of the partial fields being of the forms (11) and (12). When one substitutes Eqs. (30) and (31) into Eq. (25) and executes the algebraic operations indicated, there results an equation of the form

$$\Gamma(\vec{R}, \tau) = A(\vec{R}) e^{-i\omega_0\tau} \left(\sum_{i=1}^{N} \Gamma_{ii}(\vec{K}, \tau) + \sum_{i=1}^{N} \sum_{j \neq i}^{N} \Gamma_{ij}(\vec{K}, \tau) \right), \tag{32}$$

where

$$\Gamma_{ij}(\vec{K}, \tau) = E\{\exp(-i\vec{K}\cdot\vec{R}_j(\tau) + i\vec{K}\cdot\vec{R}_i(0))\} \tag{33}$$

is the cross-correlation function of the phase-modulated signals from a typical pair of molecules i and j.

It is at this point that we invoke the principle of statistical identity of single and pairs of molecules. Accordingly,

$$\Gamma_{ii}(\vec{K}, \tau) = \Gamma_{11}(\vec{K}, \tau), \quad \text{all } i$$

$$\Gamma_{ij}(\vec{K}, \tau) = \Gamma_{12}(\vec{K}, \tau), \quad \text{all } i \neq j$$

the subscripts refering to molecules 1 and 2 of a typical pair selected at random. Thus the autocorrelation of the field of N statistically identical molecules becomes

$$\Gamma(\vec{R}, \tau) = I_R(R, \theta) e^{-i\omega_0\tau} \times \{\Gamma_{11}(\vec{K}, \tau) + \tfrac{1}{2}(N-1)[\Gamma_{12}(\vec{K}, \tau) + \Gamma_{21}(\vec{K}, \tau)]\}, \tag{34}$$

where

$$I_R(R, \theta) = \frac{N\alpha^2 k_0^4}{(4\pi\epsilon_0 R)^2} c\epsilon_0 E_0^2 \sin^2\theta \tag{35}$$

is the Rayleigh intensity one would obtain if the molecular positions, and therefore the phases, were uncorrelated at $t = 0$ and $t = \tau$; θ is the angle subtended between the incident-field polarization $\vec{e}$ and the direction of observation, $\vec{R}$.

The spectrum is now obtained from the definition (27). However, since Γ_{21} is a correlation function, it has the universal property $\Gamma_{21}(\vec{K}, \tau) = \Gamma_{12}^*(\vec{K}, -\tau)$. Consequently, the spectrum simplifies to

$$S(\vec{R}, \omega) = I_R(R, \theta)[S_{11}(\vec{K}, \Omega) + (N-1)\mathrm{Re}S_{12}(\vec{K}, \Omega)], \tag{36}$$

where $\Omega = \omega - \omega_0$ is the translated frequency and S_{11} and S_{12} are, respectively, the Fourier transforms of Γ_{11} and Γ_{12}; S_{11} is always positive, real function of Ω.

Returning to the definition of the autocorrelation function in Eq. (20) and the form of Γ_{1j} in (33) we observe that, because of the peculiar form of a phase-modulated function, its autocorrelation function is the Fourier integrals

$$\Gamma_{1j}(\vec{K}, \tau) = \iint \exp(-i\vec{K}\cdot\vec{r} + i\vec{K}\cdot\vec{r}_0) P_{1j}(\vec{r}, \tau; \vec{r}_0) d\vec{r} d\vec{r}_0, \quad j = 1, 2. \tag{37}$$

In probability theory, the Fourier transform of a probability density function is its characteristic, or moment generating, function. It is well known in modulation theory[28] that the autocorrelation function of a stationary phase-modulated signal is the characteristic function of the joint probability density of the random phase. Hence, we arrive at the general theorem for scattering of light:

Theorem 1. The autocorrelation of the field scattered by N statistically identical molecules is proportional to the sum of the characteristic functions of the joint probability densities of positions of single and paired particles,

$$\Gamma(\vec{R}, \tau) = I_R(R, \theta) e^{-i\omega_0\tau} \{p_{11}(\vec{K}, \tau; -\vec{K}) + \tfrac{1}{2}(N-1) \times [p_{12}(\vec{K}, \tau; -\vec{K}) + p_{12}^*(\vec{K}, -\tau; -\vec{K})]\}. \tag{38}$$

Further reduction of this relation is not possible without additional restrictions. For the case of a statistically homogeneous process, however, the conditional probability densities depend only on differences $\vec{r} - \vec{r}_0$ in the range set. Using the fact that

$$\int p(\vec{r}_0) d\vec{r}_0 = 1,$$

and the relation (21), one obtains for the homogeneous case

$$\Gamma_{1j}(\vec{K}, \tau) = \int W_{1j}(\vec{\rho}, \tau) e^{-i\vec{K}\cdot\vec{\rho}} d\vec{\rho}, \quad \vec{\rho} = \vec{r} - \vec{r}_0. \tag{39}$$

Equation (38) now reduces to

$$\Gamma(\vec{R}, \tau) = I_R(R, \theta) e^{-i\omega_0\tau} [w_{11}(\vec{K}, \tau) + (N-1)\mathrm{Re}w_{12}(\vec{K}, \tau)]. \tag{40}$$

This equation provides the starting point for analysis of the statistics of a gas. When the system is isotropic as well, then W_{11} and W_{12} depend on absolute differences $|\vec{\rho}|$ and their characteristic functions w_{ij} depend on $|\vec{K}|$ only.

D. Scattering by Gas

The second term in Eq. (40) can be further arranged in a form which is more suitable for analysis and interpretation by introducing two additional stochastic processes defined as

$$\vec{R}_c(t,\sigma)=\tfrac{1}{2}\vec{R}_1(t,\sigma)+\tfrac{1}{2}\vec{R}_2(t,\sigma), \tag{41}$$

$$\vec{R}_0(t,\sigma)=\vec{R}_2(t,\sigma)-\vec{R}_1(t,\sigma), \tag{42}$$

together with the probability density functions

$$W_c(\vec{r},\tau\,|\,\vec{r}_0)d\vec{r} = P\{\vec{R}_c(\tau)\in(\vec{r},\vec{r}+d\vec{r}]\,|\,\vec{R}_c(0)\in(\vec{r}_0,\vec{r}_0+d\vec{r}_0]\},$$

$$W_0(\vec{r},\tau\,|\,\vec{r}_0)d\vec{r} = P\{\vec{R}_0(\tau)\in(\vec{r},\vec{r}+d\vec{r}]\,|\,\vec{R}_0(0)\in(\vec{r}_0,\vec{r}_0+d\vec{r}_0]\},$$

$$G(\vec{r}_0)d\vec{r}_0=P\{\vec{R}_0(t)\in(\vec{r}_0,\vec{r}_0+d\vec{r}_0]\}.$$

The processes $\vec{R}_c$ and $\vec{R}_0$, for a system of particles having identical mass, are recognized as the coordinates of the center of mass of a pair and the reduced coordinates about the center of mass, respectively. In terms of these functions, the second term in Eq. (34) corresponding to the second term of Eq. (40) takes the form

$$\Gamma_{12}(\vec{K},\tau)=E\{\exp(-i\vec{K}\cdot[\vec{R}_c(\tau)-\vec{R}_c(0)+\tfrac{1}{2}\vec{R}_0(\tau) -\tfrac{1}{2}\vec{R}_0(0)+\vec{R}_0(0)])\}. \tag{43}$$

Now, from the standpoint of a typical pair of particles, the chaotic force field due to the remaining $(N-2)$ particles is an external force. By the well-known theorem of classical mechanics on the independence of motion of the center of mass and the reduced motion about the center of mass, the processes $\vec{R}_0(t)$ and $\vec{R}_c(t)$ are statistically independent. Therefore, the expectation of the product of any functions of $\vec{R}_c$ and $\vec{R}_0$ equals the product of the expectations, i.e.,

$$\Gamma_{12}(\vec{K},\tau)=\Gamma_c(\vec{K},\tau)\Gamma_0(\vec{K},\tau), \tag{44}$$

where

$$\Gamma_c(\vec{K},\tau)=E\{\exp(-i\vec{K}\cdot[\vec{R}_c(\tau)-\vec{R}_c(0)])\}, \tag{45}$$

$$\Gamma_0(\vec{K},\tau)=E\{\exp(-\tfrac{1}{2}i\vec{K}\cdot[\vec{R}_0(\tau)-\vec{R}_0(0)]) \times\exp(-i\vec{K}\cdot\vec{R}_0(0))\}, \tag{46}$$

By the same procedure as in the previous section, we have for a statistically homogeneous system

$$\Gamma_c(\vec{K},\tau)=w_c(\vec{K},\tau) \tag{47}$$

and

$$\Gamma_0(\vec{K},\tau)=\int\exp(-\tfrac{1}{2}i\vec{K}\cdot\vec{\rho})W_0(\vec{\rho},\tau) \times\exp(-i\vec{K}\cdot\vec{r}_0)G(\vec{r}_0)d\vec{\rho}\,d\vec{r}_0 = w_0(\tfrac{1}{2}\vec{K},\tau)g(\vec{K}). \tag{48}$$

Equation (43) therefore simplifies to

$$\Gamma_{12}(\vec{K},\tau)=w_c(\vec{K},\tau)w_0(\tfrac{1}{2}\vec{K},\tau)g(\vec{K}). \tag{49}$$

In obtaining this relation, we have also proved that

$$w_{12}(\vec{K},\tau)=w_c(\vec{K},\tau)w_0(\tfrac{1}{2}\vec{K},\tau)g(\vec{K}), \tag{50}$$

which can be seen by comparing (34) and (40) with (49). Alternatively, it could be obtained via a theorem of probability theory, namely, the probability density of sums of independent random variables is the convolution of the probability densities of the summand variables. Hence the characteristic functions, being Fourier integrals, factor into a product.

Before proceeding further, we call attention to the limiting property of W_c and W_0 inherent in their definition as conditional probability densities, namely

$$W_i(\vec{r},0\,|\,\vec{r}_0)=\delta(\vec{r}-\vec{r}_0),\quad i=0,c \tag{51a}$$

$$w_i(\vec{K},0)=1. \tag{51b}$$

It follows that

$$w_{12}(\vec{K},0)=g(\vec{K}), \tag{52}$$

which is to be expected since $G(\vec{\rho})$ is precisely $W_{12}(\vec{\rho},0)$ by definition.

The autocorrelation function of the scattered field in (40) now takes the general form, valid for a statistically homogeneous system of particles,

$$\Gamma(\vec{R},\tau)=I_R(R,\theta)e^{-i\omega_0\tau} \times(w_{11}(\vec{K},\tau)+g'(\vec{K})\,\mathrm{Re}[w_c(\vec{K},\tau)w_0(\tfrac{1}{2}\vec{K},\tau)]), \tag{53}$$

where

$$g'(\vec{K})=(N-1)g(\vec{K}). \tag{54}$$

Recalling that the total integrated intensity I_{av} is simply $\Gamma(\vec{R},0)$, we also have from the properties of w_{11}, w_0, and w_c,

$$I_{av}(\vec{R})=I_R(R,\theta)[1+g'(\vec{K})]. \tag{55}$$

To obtain the spectrum, let S_c^r, S_c^i, S_0^r, and S_0^i be the Fourier transforms of the real and imaginary parts of $w_c(\vec{K},\tau)$ and $w_0(\vec{K},\tau)$, respectively. Then the total spectrum, as defined in (36), becomes

$$S(\vec{R},\omega)=I_R(\vec{R},\theta)\{S_{11}(\vec{K},\Omega) +g'(\vec{K})[(S_0^r*S_0^r)(\Omega)-(S_c^i*S_0^i)(\Omega)]\}, \tag{56}$$

where the last terms are convolutions

$$(S_c * S_0)(\Omega) = \int_{-\infty}^{\infty} S_c(\vec{K}, \Omega - \Omega')S_0(\tfrac{1}{2}\vec{K}, \Omega')d\Omega' . \quad (57)$$

Equations (53), (55), and (56) are the principal results of this section on scattering theory. No restrictions have been imposed on the statistics of the particles other than that of homogeneity, i.e., the probability densities are functions of the vector difference $\vec{\rho} = \vec{r} - \vec{r}_0$, which is weaker than isotropy. From here on, it is a problem of statistical theory and mechanics to determine the forms of S_{11}, S_c, and S_0, which we attempt in the next section. However, to consolidate the development here, we state some results which are essential to discussion of the spectrum of a gas. It is shown in the following sections that for a gas $w_c(\vec{K}, \tau)$ and $w_0(\vec{K}, \tau)$ are real so that S_c^i and S_0^i vanish, and that [Eq. (111)]

$$S_0^r(\tfrac{1}{2}\vec{K}, \Omega) = \tfrac{1}{2}\delta(\Omega - \Omega_B) + \tfrac{1}{2}\delta(\Omega + \Omega_B).$$

Under these circumstances, Eq. (56) reduces to

$$S(\vec{R}, \omega) = I_R\{S_{11}(\vec{K}, \Omega) + \tfrac{1}{2}g'(\vec{K}) \times [S_c(\vec{K}, \Omega + \Omega_B) + S_c(\vec{K}, \Omega - \Omega_B)]\} , \quad (58)$$

where the superscript on S_c is deleted since w_c is real. This expression in essence summarizes the general features of the Rayleigh-Brillouin spectrum of gases. Under appropriate conditions determined by $\vec{K}$, when $S_{11}(\vec{K}, \Omega)$ and $S_c(\vec{K}, \Omega)$ are sufficiently narrow and have their peaks at $\Omega = 0$, the first term in (58) would correspond to the undisplaced Rayleigh line while the second and third terms to the symmetrically displaced Brillouin doublet.

Although the forms of S_{11} and S_c are not determined at this point, Eq. (58) together with (55) and the general relations

$$\int S_c(K, \Omega)d\Omega = \int S_{11}(K, \Omega)d\Omega = 1 \quad (59)$$

and

$$2\int S_c(K, \Omega)\Omega^2 d\Omega = \int S_{11}(K, \Omega)\Omega^2 d\Omega , \quad (60)$$

verified in Appendix B, contain several broad conclusions worth emphasizing, especially in light of the qualitative observations enumerated in Sec. II:

(1) The undisplayed Rayleigh line is a manifestation of the statistical trajectory of a typical single particle, while the Brillouin doublet is a manifestation of dynamic interference between typical pairs.

(2) The ratio of total integrated intensities of each of the Brillouin lines to that of the Rayleigh line is $g'(\vec{K})/2$.

(3) Deviations of the total scattered intensity I_{av} in magnitude and dependence on angle, from that predicted by incoherent scattering I_R, is determined solely by the functional dependence of g' on $\vec{K}$.

(4) Existence of a Brillouin doublet in a given gas and deviations from incoherent Rayleigh scattering are concommitant phenomena.

(5) In view of the integral relation (60), in general, the natural width of the Rayleigh line is greater than those of the Brillouin lines at the same viewing angle.

As pointed out by Komarov and Fisher[1] and others,[10] the scientific value of Rayleigh-Brillouin scattering does not lie so much in calculating the spectrum from known or assumed features of the gas, as in the inverse process of deducing properties of the gas from observed spectra. In this respect, one of the valuable conclusions of the present microscopic theory is the fact that $g'(\vec{K})$ is directly measurable from observed spectra at successive angles. However, in actual measurements the relationship of g' to intensities is not as simple as that stated above, but it is corrupted by response of the measuring instrument as discussed in Sec. V.

IV. STATISTICAL THEORY

A. General Background

In the preceding development we have maintained that molecules are statistically identical in that the trajectories of all single molecules and pairs of molecules are described by the same probability densities W_{11} and W_{12}. This hypothesis, however, does not imply that molecules do not interact. On the contrary, it is our imperfect knowledge of the chaotic interaction among molecules that necessitates probabilistic analysis in the first place. Each molecule moves in accordance with the total force field due to the remaining $(N-1)$ molecules, and by statistical identity we mean that, as a stochastic process, the force field experienced by one molecule is the same as that by any other molecule in the sense that the representative ensembles are composed of the same functions with the same probability measure. Each member function of the ensemble is understood to be a deterministic function of $\{t, \sigma\}$; the randomness arises in the selection of a particular function corresponding to a subset σ with probability $P(\sigma)$. The classical equations of motion for a single particle are viewed as linear operations mapping every member function $\vec{R}_i(t, \sigma)$ of this ensemble to a member function $\vec{F}_i(t, \sigma)$ in the ensemble representing the force field. If each member function $\vec{R}_i$ is differentiable and integrable, the differential and integral operators we will write are understood in the ordinary sense.

Our central problem now is as follows: Given the linear operator equation

$$\mathcal{L}_t[\vec{R}_i(t,\sigma)] = \vec{F}(t,\sigma),$$

we wish to find the probability densities for $\vec{R}_i(t,\sigma)$. We approach this problem through solution of recently derived partial differential equations for probability densities of a general class of stochastic processes. We first state these relations as background material.

Theorem 2. Let $\vec{R}(t,\sigma) = (X_1(t,\sigma),\ldots,X_n(t,\sigma))$ be a Cartesian vector stochastic process in the space of continuous differentiable functions, and let $\vec{r} = (x_1,\ldots,x_n)$ be its range set. Then, if the process is stationary, the conditional probability density

$$W(\vec{r},\tau|\vec{r}_0)d\vec{r}d\vec{r}_0 = P\{\vec{R}(\tau)\in(\vec{r},\vec{r}+d\vec{r}]|\vec{R}(0)\in(\vec{r}_0,\vec{r}_0+d\vec{r}_0]\}$$

satisfies the set of equations provided the first m derivatives are statistically independent of $\vec{R}(t,\sigma)$ at simultaneous time.

$$\frac{\partial W}{\partial\tau} = \frac{\partial}{\partial x_i}v_iW, \tag{61}$$

$$\frac{\partial^2 W}{\partial\tau^2} = \frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}u_{ij}W - \frac{\partial}{\partial x_i}a_iW, \tag{62}$$

where

$$v_i = E\{\dot{X}_i(\tau)|\vec{R}(\tau)=\vec{r};\vec{R}(0)=\vec{r}_0\},$$

$$u_{ij} = E\{\dot{X}_i(\tau)\dot{X}_j(\tau)|\vec{R}(\tau)=\vec{r};\ \vec{R}(0)=\vec{r}_0\},$$

$$a_i = E\{\ddot{X}_i(\tau)|\vec{R}(\tau)=\vec{r};\ \vec{R}(0)=\vec{r}_0\}$$

are conditional expectations of derivatives of $X_i(\tau)$ given $\vec{R}(t)$ at $t=\tau$ and $t=0$.

In the expressions for the conditional expectations the dot denotes temporal derivative and the abridged notation $\vec{R}=\vec{r}$ is understood as $\vec{R}$ lying in the semiclosed interval $(\vec{r},\vec{r}+d\vec{r}]$; repeated indices are summed from 1 to n. It should be emphasized that conditional expectations may in general be functions of $\vec{r}$, $\vec{r}_0$, and τ, even when the marginal expectations are not. For brevity, the symbol $E_c\{\cdots\}$ is used henceforth to denote the conditional expectation defined above.

Three important corrollaries of this theorem are essential to the development that follows. They are:

Corollary 2.1. Conditional expectation and temporal differentiation are commutative operations,

$$\frac{\partial^m}{\partial\tau^m}E_c\{X_i\} = E_c\left\{\frac{\partial^m X_i}{\partial t^m}\right\},$$

Corollary 2.2. If $\dot{\vec{R}}(t,\sigma)$ and $\vec{R}(t,\sigma)$ are statistically independent, then the conditional probability density of $\dot{\vec{R}}(\tau)$ given $\vec{R}(\tau)$ and $\vec{R}(0)$ is of the general form

$$P\{\dot{\vec{R}}(\tau)=\vec{\xi}|\vec{R}(\tau)=\vec{r};\ \vec{R}(0)=\vec{r}_0\} = f(\vec{\xi}-\vec{v})d\vec{\xi},$$

where $f(\vec{\xi})$ is the marginal probability density of $\dot{\vec{R}}(t)$ and $\vec{v}(\tau) = E_c\{\dot{\vec{R}}(\tau)\}$ is the conditional expectation defined in Theorem 2.

Corollary 2.3. If $\dot{X}_i(t,\sigma)$ and $X_i(t,\sigma)$ are statistically independent at simultaneous instants, and if there exists a Hamiltonian function relating the $6N$ stochastic processes $\dot{X}_i$ and X_i, then the *marginal* probability density of any $\dot{X}_i$ is Gaussian independently of the potential function in the Hamiltonian; that is

$$P\{\dot{X}_i(t)=\xi\} = f_0(\xi)d\xi$$

$$= (m/2\pi k_BT)^{1/2}\exp(-m\xi^2/2k_BT).$$

This theorem has been derived for a general class of stochastic processes whose only restriction is that each member function $\vec{R}(t,\sigma)$ of the ensemble be continuous and differentiable in t. Its proof and implications are discussed elsewhere[29]; here, we reduce it to the particulars of a homogeneous, isotropic gas. In Corollary 2.3, it should be noted that f_0 is the probability density of a Cartesian component of the velocity of any single molecule. It should not be confused with the Maxwell distribution function, whose conventional significance is that of being the fractional number of molecules whose velocities lie within a certain interval. It can be shown,[29] by the hypothesis of statistical identity and Corollary 2.3, that if $N(\vec{v},t,\sigma)$ is a stochastic process such that $Nd\vec{v}$ is the number of molecules whose velocities at time t lie in the interval $(\vec{v},\vec{v}+d\vec{v}]$, then the expectation value of $N(\vec{v},t,\sigma)$ is the conventional Maxwell function.

The power of this theorem lies in the fact that the probability density is determined as a solution of a partial differential equation once its moments $\vec{v}$, u_{ij}, and $\vec{a}$ are specified. It is motivated by the viewpoint that in a physical system the role of an ensemble is no more than that of an abstract representation of the system, and what distinguishes one ensemble, or sample set $\{\sigma\}$, from others similarly composed is precisely its probability measure, which must be so endowed with particular properties as to give an accurate, though probabilistic, description of a set of events (or measurements on the system) *sequenced in time*. Probability and statistical theory provides only the discipline and logical structure, but it does not provide an *apriori* probability measure;

the only conditions that probability theory imposes on the measure are those stated in its three well-known axioms.[30] Indeed, in any statistical representation or analysis of a real-world system, the central problem is that of judicious assignment of a realistic probability measure, and the latter is realistic when it leads to agreement with observation through the logical framework of the theory. One effective way of specifying a measure is to specify its moments. In a mechanical system, the moments $\vec{v}$, u_{ij}, and $\vec{a}$ are determined from the particular differential equations which every member $\vec{R}(t, \sigma)$ of the ensemble must satisfy, i.e., the classical equations of motion.

When writing a differential equation of motion, however, one is immediatley faced with the related questions of scale of the time intervals Δt and the meaning of collision. In the final sense, collision is really just another conceptual model for the interaction between two particles wherein momentum and energy are exchanged. However short the duration of this exchange may be, a collision is a force that the molecule experiences, and hence should not be separated from the total chaotic force field though it is convenient to do so sometimes. When the time scale is sufficiently short, and granted that the force of interaction between colliding molecules depends on their spatial separation, what we call a collision becomes a gradually unfolding process which is continuous in time. On the other hand, when collisions are viewed separately from the total force field, one invariably reduces the process to a discontinuous one whose limiting form, on time intervals much longer than the duration of the discontinuous steps, is inevitably an irreversible relaxation or diffusion. Much detail is then lost. For example, the diffusion equations of Chapman-Kolmogorov and Focker-Planck describe the continuous long-term limit of what is a discontinuous Markov process in the short term.[31,32]

Typically, the probability densities obtained from such equations satisfy the Smoluchowski relation,[31]

$$W(\vec{r}, t\,|\,\vec{r}_0, t_0) = \int W(\vec{r}, t\,|\,\vec{r}_1, t_1) W(\vec{r}_1, t_1, |\,\vec{r}_0, t_0)\, d\vec{r}_0,$$

provided $t_0 \leqslant t_1 < t$. This is the continuous limit of the one-step Markov process, which is based on the crucial property of "independent increments." That is, the process in the interval $[t_0, t_1]$ is statistically independent of the process in $(t_1, t]$, regardless of choice of t_1. The obvious question is how small can the time intervals be before this one-step independence breaks down. The theorem stated above, when applied to a mechanical system, states that the value of $\vec{R}$ at $t + \Delta t$ is linearly dependent on $\dot{\vec{R}}$ at t. More specifically, the coordinates at $t + \Delta t$ and the momentum at t are statistically dependent, though they are independent at the same instant, t.

B. Constraints

To reduce Theorem 2 to a form suitable for a mechanical system, with $\vec{R}$ being the three-dimensional coordinates of a typical molecule, we need to impose only one requirement, namely, that the probability densities must be independent of the choice of reference frame. Because of the form of Eqs. (61) and (62), rotational invariance under orthogonal transformations is assured if the conditional moments u_{ij} are components of a tensor and v_i and a_i are components of vectors. This implies that $\vec{v}$ and $\vec{a}$ have fixed orientation independently of the reference frame. If $\vec{v}$ is a vector, then it follows, from Corollary 2.2, that u_{ij} is a tensor. However, since the derivatives $\partial/\partial x_i$ refer to the components of $\vec{r}$ and not $\vec{r} - \vec{r}_0$, reduction of the moments to components of tensors assures rotational invariance only but not translational. For complete independence from choice of reference frame, the system must be invariant under translation as well, thereby requiring the probability densities to be functions of $\vec{\rho} = \vec{r} - \vec{r}_0$. That is, the process must be homogeneous. This condition is satisfied if the moments, in addition to being functions of τ, are at most functions of the difference $\vec{\rho} = \vec{r} - \vec{r}_0$. We summarize the foregoing as follows:

Theorem 3. The necessary and sufficient conditions for the probability density $W(\vec{r}, \tau\,|\,\vec{r}_0)$ of the stochastic process $\vec{R}(t, \sigma)$ to be invariant under orthogonal rotation and translation of reference frame is that the conditional moments $\vec{a}$ and $\vec{v}$ be vectors which are functions of $\vec{\rho} = \vec{r} - \vec{r}_0$ and $\tau = t_2 - t_1$.

The condition of isotropy, $W = W(|\vec{\rho}|)$, while not necessary for invariance, is motivated from empirical consideration. In addition to invariance under transformation, one requires the probabilities describing a fluid to be independent of any direction even in a particular reference frame. Obviously, isotropy presupposes statistical homogeneity.

On the basis of the foregoing discussion, the following constraints are taken as sufficient for description of a statistically isotropic fluid:

(1) The conditional expectations of velocities and accelerations are fixed in space and directed along the line, $\vec{\rho} = \vec{r} - \vec{r}_0$, joining the initial and final positions.

(2) Statistical behavior of a single particle and the center of mass of a pair of particles is isotropic in the laboratory frame.

The first constraint appears to be related to Chandrasekhar's concept[31] of "probability aftereffect." If one accepts an interpretation of expected value as the "most probable value," then, in the case of a single particle, the physical significance of a radially directed $\vec{\mathrm{v}}$ is the tendency of the particle, which has moved from $\vec{\mathrm{r}}_0$ to $\vec{\mathrm{r}}$ in the interval $[0, \tau]$, to continue to move in the direction $\vec{\mathrm{r}} - \vec{\mathrm{r}}_0$. However, it should not be surmized that the actual path from $\vec{\mathrm{r}}_0$ to $\vec{\mathrm{r}}$ is a straight line. Moreover, that the conditional expectation of velocity has a fixed direction does not in any way imply the random process $\vec{\mathrm{R}}(t, \sigma)$ to have preferred direction.

It seems worthwhile to comment here on alternative constraints which one might adopt to achieve invariance. Because of the independence of orthogonal components of the equations of motion in classical mechanics, it seems plausible to require the orthogonal components $X_i(t, \sigma)$ to be statistically independent. This condition coupled with homogeneity, but not isotropy, was therefore pursued to its logical consequences, resulting in some severe conditions on the moments and the probability density of velocity, as required by Theorem 2. The results, not included here for brevity, were found to be reasonable in that a physical interpretation could be given to each of the subsidiary conclusions and conditions. However, the hypothesis fails in one critical respect in that the scattered light spectrum to which it leads becomes negative for some combinations of parameters, notably the vector $\vec{\mathrm{K}}$ defined in Sec. III, which clearly contradicts the mathematically established fact that the spectrum of a stochastic process is always positive.

Statistical independence of orthogonal components and isotropy, on the other hand, are in general incompatible conditions. Both conditions are simultaneously satisfied if, and only if, the orthogonal components are independent Gaussian processes. Thus, were we to impose both conditions, we would severely restrict the theory. In what follows, therefore, we assume the two constraints listed above, and, motivated by Theorem 3, as sufficient conditions for analysis of an isotropic fluid. The remaining properties, to be derived next, result from mechnaical laws. It should be noted, however, in the limit of long time intervals, τ, when events at $t + \tau$ become statistically independent of those at t, isotropy coupled with independence is consistent with limiting Gaussian forms.

C. Probability of a Single Particle

In this section we obtain the particular form of the partial differential equations resulting from the constraints of Sec. IV B. In order to simplify the first term of Eq. (62), it is necessary to revert to the general integral definition of the moments u_{ij}, viz.,

$$\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j} u_{ij} W_{11} = \int \xi_i \xi_j \frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j} W_{11} f(\vec{\xi}, \tau \,|\, \vec{\mathrm{r}}, \vec{\mathrm{r}}_0)\, d\vec{\xi}\,, \tag{63}$$

where in abbreviated notation

$$f(\vec{\xi}, \tau \,|\, \vec{\mathrm{r}}; \vec{\mathrm{r}}_0) d\vec{\xi} = P\{\dot{\vec{\mathrm{R}}}(\tau) = \vec{\xi} \,|\, \vec{\mathrm{R}}(\tau) = \vec{\mathrm{r}}; \vec{\mathrm{R}}(0) = \vec{\mathrm{r}}_0\}$$

is the conditional probability density (cpd) of the velocity. For the particular case on hand, however, f is the displaced Gaussian density by Corollaries 2.2 and 2.3, and W_{11} is a function of ρ only. Also, ξ_i and ξ_j in the integrand are strictly parameters of integration, and the indices are summed from 1 to 3.

The key to simplifying this term is the following identity, valid for any constant vector $\vec{\mathrm{q}}$, and a differentiable function ϕ of the radial coordinate,

$$q_i q_j \frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j} \phi(\rho) = |\hat{\rho}\cdot\vec{\mathrm{q}}\,|^2 \frac{d^2\phi}{d\rho^2} + \frac{1}{\rho}\,|\hat{\rho}\times\vec{q}\,|^2 \frac{d\phi}{d\rho}, \tag{64}$$

where $\hat{\rho}$ is the unit radial vector. With this identity and the Gaussian form of f, Eq. (63) reduces to

$$\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j} u_{ij} W_{11} = \frac{\partial^2 W_{11}}{\partial\rho^2}\int |\hat{\rho}\cdot\vec{\xi}\,|^2 f_0(\vec{\xi} - \vec{\mathrm{v}})\, d\vec{\xi} + \frac{1}{\rho}\frac{\partial W_{11}}{\partial\rho}\int |\hat{\rho}\times\vec{\xi}\,|^2 f_0(\vec{\xi} - \vec{\mathrm{v}})\, d\vec{\xi}\,. \tag{65}$$

To perform the indicated integration, it is convenient to select one of the ξ axes parallel to $\hat{\rho}$ and to make the substitution $\vec{\xi}' = \vec{\xi} - \vec{\mathrm{v}}$. The first integral, then, becomes the mean square of a Cartesian component of $\vec{\mathrm{R}}$. After carrying out the details, and using the fact that $\vec{\mathrm{v}}$ is radial, we find

$$\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j} u_{ij} W_{11} = (\tfrac{1}{3}u_M^2 + v^2)\frac{\partial^2 W_{11}}{\partial\rho^2} + \tfrac{2}{3}u_M^2 \frac{1}{\rho}\frac{\partial W_{11}}{\partial\rho}\,, \tag{66}$$

where

$$u_M^2 = 3k_B T/m \tag{67}$$

is the mean square speed resulting from the Gaussian form of f_0. The terms multiplied by u_M^2 in (66) are recognized as the radial part of the Laplace operator, ∇^2. Thus, substitution of Eq. (66) into (62) gives the intermediate form

$$\tfrac{1}{3}u_M^2 \nabla^2 W_{11} + v^2 \frac{\partial^2 W_{11}}{\partial\rho^2} - \nabla\cdot\vec{\mathrm{a}} W_{11} = \frac{\partial^2 W_{11}}{\partial\tau^2}\,. \tag{68}$$

Our next task is to express the conditional mean acceleration $\vec{\mathrm{a}}$ in terms of $\vec{\mathrm{v}}$, using Corollary 2.1 and Eq. (61). To this end, we introduce the logarithmic derivative defined by

$$\frac{1}{v}\frac{\partial v}{\partial \tau} = h(\tau), \tag{69}$$

which plays a fundamental role in the statistics of the system. In terms of this function, and by Corollary 2.1, we have

$$\nabla\cdot\vec{a}\,W_{11} = h(\tau)\nabla\cdot\vec{v}\,W_{11}. \tag{70}$$

Substituting Eq. (61) into (70) and the result into (68), we obtain the final desired form:

$$\tfrac{1}{3}u_M^2\nabla^2 W_{11} + v^2\frac{\partial^2 W_{11}}{\partial \rho^2} = \frac{\partial^2 W_{11}}{\partial \tau^2} - h(\tau)\frac{\partial W_{11}}{\partial \tau}. \tag{71}$$

Equation (71) is the principal relation governing the cpd of position of a single particle. It is evident from the definition (69) that $v(\tau)$ and $h(\tau)$ are related as

$$v(\tau) = b\exp\left[\int_0^\tau h(t)\,dt\right], \tag{72}$$

where b is an arbitrary constant.

So far no mechanical principles have been invoked except the Hamiltonian relation implied in the Gaussian form of $f(\vec{\xi}-\vec{v})$ as stated in Corollaries 2.2 and 2.3. However, the Gaussian form affects only the particular value of u_M but not the form of Eq. (71). It is also evident that, through W_{11}, the second-order statistics of a single particle is completely characterized by the one function $h(\tau)$, the logarithmic derivative of the conditional mean velocity. The problem of statistical analysis, therefore, devolves to that of deducing the form of this function, a task which is far from being trivial. At this writing, no attempt has been made at determining $h(\tau)$ from mechanical principles, but we will deduce some useful asymptotic properties by considering the equations of motion next.

With the viewpoint that collisions are an inseparable part of the total stochastic force field, and faced with imperfect knowledge of the temporal evolution of this force, the only equation of motion one can write, without major presuppositions, is simply

$$m\ddot{\vec{R}}_1(t,\sigma) = \vec{F}_1(t,\sigma), \tag{73}$$

where

$$\vec{F}_1(t,\sigma) = \sum_{j=2}^{N}\vec{f}_{1j}(\vec{R}_1,\vec{R}_j). \tag{74}$$

The conventional concept of collisions can be included by replacing the summation in Eq. (74) with a random time sequence (Poisson sequence) of δ functionals with random amplitudes. The total force here is a stochastic one because each of the $\vec{R}_j(t,\sigma)$ is a stochastic process inasmuch as the remaining $N-1$ particles, comprising the environment, are also in unknown chaotic motion. Moreover, Eq. (73) as it stands is nonlinear, since the desired function $\vec{R}_1$ appears nonlinearly in the force term. However, we have seen that for statistical description of the system, it is not essential that an explicit solution $\vec{R}_1$ be found in the ordinary sense. All that we require are conditional expectations of the derivatives at given values of $\vec{R}_1$ at $t=\tau$ and $t=0$. As far as determining these expected values is concerned, the problem is a linear one. We need only keep two points in mind.

First, the expectation of the sum of random variables is the sum of the expectations of the summand. Second, each member function $\vec{R}(t,\sigma)$ of the ensemble is a deterministic function, the differential equation being a mapping from one ensemble to another. Every member function must, therefore, satisfy all relations implied in the differential equation, the most important one being the energy relation. Thus, through the usual steps of classical mechanics, we find that in the interval $[0,\tau]$ every member function $\vec{R}_1(t,\sigma)$ satisfying Eq. (73) must also satisfy the relation

$$\tfrac{1}{2}m\dot{\vec{R}}_1^{\,2}(\tau,\sigma) = \tfrac{1}{2}m\dot{\vec{R}}_1^{\,2}(0,\sigma) + \epsilon_1(\tau,\sigma), \tag{75}$$

where

$$\epsilon_1(\tau,\sigma) = \sum_{j=2}^{N}\int_0^\tau \vec{f}_{1j}\cdot\dot{\vec{R}}_j\,dt \tag{76}$$

is recognized as the net energy gain of a single particle from the environment of the remaining $N-1$ particles. The relation among the conditional expected values follows readily from Eq. (75) as

$$E_c\{\dot{\vec{R}}_1^{\,2}(\tau,\sigma)\} = E_c\{\dot{\vec{R}}_1^{\,2}(0,\sigma)\} + \frac{2}{m}\bar{\epsilon}_1(\tau), \tag{77}$$

where $\bar{\epsilon}_1$ is the conditional expected value of the net energy gain in the interval $[0,\tau]$.

Now we compare Eq. (77) to the independent relation for the conditional expectation of squared speed as obtained from the known density $f_0(\vec{\xi}-\vec{v})$. We find

$$\sum_{i=1}^{3}u_i^2(\tau) = u_M^2 + v^2(\tau). \tag{78}$$

As inherent in the definition of conditional probability, and by virtue of independence of coordinates and velocities (momenta) at simultaneous time, all conditional expectations of velocity at $\tau=0$ necessarily reduce to the corresponding marginal ones. Hence, it is known that

$$E_c\{\dot{\vec{R}}_1^{\,2}(0,\sigma)\} = E\{\dot{\vec{R}}_1^{\,2}(0,\sigma)\} = u_M^2. \tag{79}$$

Since the left-hand sides of Eqs. (77) and (78) are identical, it follows that

$$v^2(\tau) = \frac{2}{m}\bar{\epsilon}_1(\tau). \tag{80}$$

Thus the conditional mean velocity, and therefore $h(\tau)$, defined in Eq. (69), is identified with the conditional mean change in energy. In fact, $2h(\tau)$ is also the logarithmic derivative of $\bar{\epsilon}_1(\tau)$. It must be emphasized that $\bar{\epsilon}_1(\tau)$ cannot vanish identically for all τ; otherwise, Eq. (61) leads to inconsistency. However, by definition of $\epsilon_1(\tau,\sigma)$, it is evident that both $\bar{\epsilon}_1$ and v vanish at $\tau = 0$. Moreover, since it is necessary that as τ increases the particle statistics become independent of conditions at $\tau = 0$, the conditional expectations must tend to the marginal ones in the limit $\tau \to \infty$. Consequently, since the marginal expectation of velocity must vanish, $\bar{\epsilon}_1$ and v must vanish in this limit; otherwise, the particle would have a net drift over a long period of time. To summarize,

$$\bar{\epsilon}_1(\tau) \geqslant 0 , \tag{81a}$$

$$v(0) = 0 , \tag{81b}$$

$$v(\infty) = 0 . \tag{81c}$$

The conditions (81) necessarily imply the following asymptotic behavior for the logarithmic derivative $h(\tau)$:

$$h(\tau) \to \frac{1}{\tau}, \quad \tau \to 0 \tag{82a}$$

$$h(\tau) \to -\zeta, \quad \tau \to \infty \tag{82b}$$

as may be verified by referring to Eq. (72); ζ is a constant which has the significance of some characteristic reciprocal-time or frequency.

Interestingly, with the asymptotic form (82b), Eq. (69) reduces to the homogeneous Langevin equation

$$\frac{d\vec{v}}{d\tau} + \zeta\vec{v} = 0 , \tag{83}$$

whose validity is known to be restricted to time scales encompasing many collisions in the conventional sense. Also in this limit, v^2 as defined in Eq. (72) becomes negligible so that the asymptotic form of Eq. (71), the principal equation for W_{11}, tends to the conventional damped wave equation, viz.,

$$\tfrac{1}{3} u_M^2 \nabla^2 W_{11} = \frac{\partial^2 W_{11}}{\partial \tau^2} + \zeta \frac{\partial W_{11}}{\partial \tau} . \tag{84}$$

On a coarser time scale, and when ζ is sufficiently large such that

$$\left| \frac{\partial W_{11}}{\partial \tau} \right| \gg \frac{1}{\zeta} \left| \frac{\partial^2 W_{11}}{\partial \tau^2} \right| , \tag{85}$$

the damped wave equation is further approximated by the ordinary diffusion equation

$$\frac{1}{3} \frac{u_M^2}{\zeta} \nabla^2 W_{11} = \frac{\partial W_{11}}{\partial \tau} . \tag{86}$$

If ζ is interpreted as a collision frequency, then the ratio $u_M^2/3\zeta$ is identical to the celebrated Einstein relation for the diffusion constant,

$$D = \frac{u_M^2}{3\zeta} = \frac{k_B T}{m\zeta} , \tag{87}$$

as can be seen from Eq. (67). It is indeed remarkable that Einstein predicted this relation from purely statistical considerations of the idealized random-walk model of Brownian motion. It is now well known that if a stochastic process satisfies the inhomogeneous Langevin equation its conditional probability density is governed by a diffusion equation.[31]

D. Probability of Pair of Particles

In this section, we obtain the equations for the cpd of the center-of-mass coordinates $\vec{R}_c(t,\sigma)$, and that of the reduced coordinates $\vec{R}_0(t,\sigma)$. Statistics of the center of mass is similar to that of a single particle, but that of the reduced coordinates deserves special attention.

1. *cpd of Center of Mass*

The procedure for deriving the partial differential equation for W_c is virtually the same as that for W_{11}. In the latter, the cpd of velocity was needed, but in this case the cpd for the velocity of center of mass, $f_c(\vec{\xi} - \vec{v}_c)$, is not necessarily Gaussian. To determine f_c from the known Gaussian marginal densities of each of the particles of the pair, one needs the joint probability density of the velocities $\dot{\vec{R}}_1(t,\sigma)$ and $\dot{\vec{R}}_2(t,\sigma)$, which is not known. This circumstance, however, does not create any difficulty since the form of f_c, as it was emphasized in connection with Eq. (71) for the single particle, does not affect the form of the partial differential equation, but it only determines the numerical value of the marginal expectation of the square of velocity at $\tau = 0$. The latter can be deduced alternately from the energy relation. Thus, through exactly the same steps as in the previous section, we find

$$\tfrac{1}{3} u_{c0}^2 \nabla^2 W_c + v_c^2 \frac{\partial^2 W_c}{\partial \rho^2} = \frac{\partial^2 W_c}{\partial \tau^2} - h_c(\tau) \frac{\partial W_c}{\partial \tau} . \tag{88}$$

To relate u_{c0}, v_c, and h_c to the corresponding quantities of a single particle, we refer to the equation of motion of the center of mass:

$$2m\ddot{\vec{R}}_c(t,\sigma) = \vec{F}_2(t,\sigma) + \vec{F}_1(t,\sigma) , \tag{89}$$

where $\vec{F}_1(t,\sigma)$ and $\vec{F}_2(t,\sigma)$ are defined as in Eq. (74). Note, however, that even though they annul each other, the terms $\vec{f}_{12}$ and $\vec{f}_{21}$ are included in the total forces to preserve statistical identity of $\vec{F}_1$ and $\vec{F}_2$. Since statistical identity of two stochastic processes means precisely equality of their probability measures and moments, the expectation of the force on the center of mass is twice that on a single particle; and since the mass is also doubled, it follows that

$$E_c\{\ddot{\vec{R}}_c(\tau,\sigma)\}=E_c\{\ddot{\vec{R}}_1(\tau,\sigma)\}\;. \tag{90}$$

By Corollary 2.1, Eq. (90) implies that the conditional expectation of velocity of the center of mass is equal to that of the single particle, $\vec{v}_c=\vec{v}$, which in turn implies equality of the logarithmic derivatives $h_c(\tau)$ and $h(\tau)$.

Next, we determine u_{c0} from the energy relation which is obtained in a way similar to that used for Eq. (77). However, the expectation of net energy gain in this case is twice that of a single particle as evident from Eq. (89). Thus

$$E_c\{\dot{\vec{R}}_c^2(\tau,\sigma)\}=E_c\{\dot{\vec{R}}_c^2(0,\sigma)\}+\frac{2}{m}\epsilon_1(\tau)\,. \tag{91}$$

Note that the expectation of energy gain, as related to v in Eq. (80), is in agreement with the equality $\vec{v}_c=\vec{v}$ deduced above. Now, from the generic form of f_c, given by Corollary 2.2, we have the independent relation

$$u_c^2(\tau)=\int\xi^2 f_c(\vec{\xi}-\vec{v}_c)d\vec{\xi}\;,$$

which reduces to

$$u_c^2(\tau)=u_{c0}^2+v^2(\tau)\,, \tag{92}$$

where u_{c0}^2 is the second moment of the unknown density $f_c(\vec{\xi})$. Comparing Eqs. (91) and (92), and recalling that conditional expectations reduce to marginal ones at $\tau=0$, we obtain

$$u_{c0}^2=E\{\dot{\vec{R}}_c^2(0,\sigma)\}\;. \tag{93}$$

By the principle of equipartition of energy, which must be satisfied by the marginal expectations at $\tau=0$, the total energy of the pair must divide equally between the two degrees of freedom, associated with the center of mass and the reduced coordinates, so that

$$mu_{c0}^2=\tfrac{1}{2}mu_M^2\;, \tag{94}$$

where u_M is given in Eq. (67). With the foregoing relationships, Eq. (88) takes the final form

$$\tfrac{1}{6}u_M^2\nabla^2W_c+v^2\frac{\partial^2W_c}{\partial\rho^2}=\frac{\partial^2W_c}{\partial\tau^2}-h(\tau)\frac{\partial W_c}{\partial\tau^2}\;. \tag{95}$$

Comparison of Eqs. (71) and (95) shows that W_c and W_{11} are governed by virtually the same equation, the difference being the factor of $\frac{1}{2}$ in the first terms.

2. *cpd of Reduced Coordinates*

The statistics of reduced motion about the center of mass is significantly different from that of the center of mass of a single particle. By its definition in Eq. (42), $\vec{R}_0(t,\sigma)$ satisfies the equation of motion,

$$m\ddot{\vec{R}}_0(t,\sigma)=\vec{F}_2(t,\sigma)-\vec{F}_1(t,\sigma)\,. \tag{96}$$

Again, to preserve statistical identity of $\vec{F}_2$ and $\vec{F}_1$, the interaction terms $\vec{f}_{12}$ and $\vec{f}_{21}$ are not isolated as they would be in deterministic analysis of reduced motion. Now, since the total force is the difference between statistically identical processes, it follows that

$$E_c\{\ddot{\vec{R}}_0(\tau,\sigma)\}=\vec{0}\,. \tag{97}$$

By Corollary 2.1, the vanishing conditional mean acceleration necessarily implies that the conditional expectation of velocity is a constant, $\vec{v}_0$. It is shown in Theorem 4, Appendix A, that this constant must be the conditional root-mean-square value of $\dot{\vec{R}}_0(\tau,\sigma)$, i.e.,

$$v_0^2=u_0^2=E_c\{\dot{\vec{R}}_0^2(\tau,\sigma)\}\;, \tag{98}$$

and that the conditional probability density of the reduced velocity $\dot{\vec{R}}_0$ must be

$$P\{\dot{\vec{R}}_0(\tau,\sigma)=\vec{\xi}\,|\,\vec{R}_0(\tau,\sigma)=\vec{r};\vec{R}_0(0,\sigma)=\vec{r}_0\}=\delta(\vec{\xi}-\vec{v}_0)d\xi\,. \tag{99}$$

We are now in a position to simplify the first term of Eq. (62). For this purpose, it is more convenient to use an alternative form of the identity (64) namely,

$$q_i\,q_j\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}\phi=\sum_{i=1}^{3}q_i^2\nabla^2\phi-\vec{q}\times\nabla\cdot\vec{q}\times\nabla\phi\,, \tag{100}$$

where the operator ∇ is understood in its Cartesian form. With the integral form of the moments u_{ij} as given in Eq. (63), and the particular form of the velocity cpd in Eq. (99), we find

$$\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}u_{ij}W_0=v_0^2\nabla^2W_0-\vec{v}_0\times\nabla\cdot\vec{v}_0\times\nabla W_0\,. \tag{101}$$

Since $\vec{v}_0$ is radial and W_0 is a function of ρ only, the second term in Eq. (101) vanishes. This condition, together with (97), reduces Eq. (62) to

$$v_0^2\nabla^2W_0=\frac{\partial^2W_0}{\partial\tau^2}\;, \tag{102}$$

which is the desired equation governing the cpd of the reduced coordinates.

The value of v_0 is determined from the velocity cpd in Eq. (99) and the energy relation. Since v_0 is constant, it has the same value at $t=\tau$ and $t=0$;

that is

$$v_0^2 = E_c\{\dot{\vec{R}}_0^2(\tau, \sigma)\} = E_c\{\dot{\vec{R}}_0^2(0, \sigma)\} . \tag{103}$$

Alternatively, this relation is also obtained by direct integration of Eq. (96), as was done for the single particle in obtaining Eqs. (91)–(93), and noting that in this case the expectation of net energy gain vanishes, being a difference of statistically identical processes. Since at $\tau = 0$ conditional expectations reduce to marginal ones, the right-hand member of Eq. (103) must satisfy the principle of equipartition of energy, that is

$$\tfrac{1}{4} m v_0^2 = \tfrac{1}{2} m u_M^2 . \tag{104}$$

Consequently, Eq. (102) reduces to the final form

$$2u_M^2 \nabla^2 W_0 = \frac{\partial^2 W_0}{\partial \tau^2} , \tag{105}$$

where u_M is given in Eq. (67). Equation (105), which is recognized as a wave equation, is independent of the form of intermolecular forces. As evident, it is largely a consequence of statistical principles. Note also that it is not an approximation, as in the case of Eq. (84).

It is interesting to compare the energy relation of the center of mass in Eq. (91) to that of the reduced coordinates in Eq. (103). These relations show that, as far as expectation values are concerned, the net gain of energy in the interval $[0, \tau]$ due to interaction of the pair with the N-2 energy particles as an environment is manifested entirely in the motion of the center of mass, the reduced motion about the center of mass remaining unaffected. In this sense, the forces of the N-2 particles are equivalent to an "external" force. This interpretation, however, refers to expectation values (in a classical sense), and its physical significance must be accepted in the context of repeated trials. That is, in repeated observations at $t = t_i$ and $t = t_i + \tau$, $i = 1, 2, \ldots,$ the two sets of measurements differing by the interval τ would yield the same average values for the energy in the center-of-mass frame. There is no implication, however, that the motion about the center of mass is free of force at all time.

In summary, we have found from a set of hypotheses and theorems, together with the laws of classical mechanics, that the conditional probability density of the separation between a pair of particles is governed *exactly* by a wave equation. The resulting solution, however, need not be a physical wave such as density or pressure wave. It is a wave in abstract probability space indicating that the probability of a particular separation undulates in time. The principal equations governing the conditional probability densities of the positions of a single particle and the center of mass of a pair are Eqs. (71) and (95). The time scale on which these equations describe the processes is dependent solely on the detail included in the logarithmic derivative, $h(\tau)$, of the conditional expectation of velocity. As mentioned earlier, at this writing, no attempt has been made at a detailed analysis of $h(\tau)$. Accordingly, the significance of its asymptotic value ζ, Eq. (82), and whether it can be properly interpreted as a collision frequency remain unsettled. Nevertheless, we consider the damped wave equation (84) as an approximation which is intermediate between the coarse description provided by the diffusion equation (86), and the fine-scale description provided by the as yet unknown form of Eqs. (71) and (95). Exact solution of the damped wave equation leads to surprisingly close agreement with experimental data as we consider next.

V. APPLICATION TO LIGHT SCATTERING

In the following sections, particular solutions are obtained for the various terms of the natural spectrum given in the general form in Eq. (58). For convenience of reference, "natural spectrum" designates the spectrum prior to being altered by intervening instruments, while "modified spectrum" refers to what is actually observed. The effect of instruments is considered in Sec. V B, after which theoretical and experimental results are compared in Sec. V C.

A. Natural Spectrum

Our interest here is mainly in calculating the characteristic functions of probability densities, all of which are constrained to the initial conditions,

$$w(\vec{K}, 0) = 1 , \tag{106a}$$

$$\frac{\partial}{\partial \tau} w(\vec{K}, 0) = 0 , \tag{106b}$$

where w stands for w_{11}, w_c, or w_0 in the first condition, (106a), which follows readily from the properties (22) and (51), while the conditions (106b) in the case of w_{11} and w_c follow from Eq. (61) and the fact that $\vec{v}(0) = 0$; however, in the case of w_0, the condition follows from the radial orientation of $\vec{v}_0$.

Equation (105), which is an exact one for $W_0(\rho, \tau)$, is considered first. By Fourier transformation of this equation, one obtains, for the characteristic function $w_0(K, \tau)$,

$$\frac{\partial^2}{\partial \tau^2} w_0(K, \tau) + 2u_M^2 K^2 w_0(K, \tau) = 0 . \tag{107}$$

The particular solution of this equation subject to the initial conditions (106) is found to be

$$w_0(K,\tau)=\cos(\sqrt{2}\,Ku_M\tau)\,. \tag{108}$$

It is recalled that in Eq. (56), the spectrum is related to $w_0(\frac{1}{2}K,\tau)$ which is, by Eq. (108),

$$w_0(\tfrac{1}{2}K,\tau)=\cos(\Omega_B\tau)\,, \tag{109}$$

where

$$\Omega_B=(1/\sqrt{2})Ku_M\,. \tag{110}$$

Next, the spectrum term S_0^r is found from its definition as the Fourier transform of the real part of w_0 over τ. Thus, from Eq. (109), one obtains

$$S_0^r(K,\tau)=\tfrac{1}{2}\delta(\Omega-\Omega_B)+\tfrac{1}{2}\delta(\Omega+\Omega_B)\,, \tag{111}$$

which justifies Eq. (58) and the inferences drawn therefrom at the end of Sec. III D. As discussed there, Ω_B is identified as the angular frequency of the Brillouin doublet. From its definition (110) and that of u_M in (67), this frequency is

$$\Omega_B=K\left(\frac{3k_BT}{2m}\right)^{1/2}. \tag{112}$$

This expression is used later when experimental data are compared to theoretical calculations.

We turn now to w_{11} and w_c which are treated concurrently owing to the similarity of their equations. As mentioned at the end of Sec. IV, exact solution of Eqs. (71) and (95) cannot be obtained at this time since the form of $h(\tau)$ is not known; only its asymptotic properties were determined. Hence for a preliminary appraisal of theory against experiment, we consider Eq. (84) which, after Fourier transformation, becomes

$$\frac{\partial^2}{\partial\tau^2}w_{11}(K,\tau)+\zeta\frac{\partial}{\partial\tau}w_{11}(K,\tau)+\tfrac{1}{3}u_M^2K^2w_{11}(K,\tau)=0\,. \tag{113}$$

The Laplace-transform method is most convenient for solving this equation since the spectral function is obtained in the process by simply setting the image parameter s equal to $i\Omega$. After transforming Eq. (113), subject to the initial conditions (106), and solving the resulting algebraic equation for the Laplace transform of w_{11}, one obtains

$$\bar{w}_{11}(K,s)=\frac{s+\zeta}{s^2+\zeta s+\frac{2}{3}\Omega_B^2}\,. \tag{114}$$

Inversion of $\bar{w}_{11}$ gives

$$w_{11}(K,\tau)=e^{-\zeta\tau/2}\left(\cosh\Omega_0\tau+\frac{\zeta}{2\Omega_0}\sinh\Omega_0\tau\right)\,, \tag{115}$$

where

$$\Omega_0^2=\tfrac{1}{4}\zeta^2-\tfrac{2}{3}\Omega_B^2\,. \tag{116}$$

While the time domain solution $w_{11}(K,\tau)$ is not needed to obtain the spectrum, it will prove useful later when we examine effects of instrumental response. The spectrum $S_{11}(K,\Omega)$, however, is obtained from the relation

$$S_{11}(K,\Omega)=\mathrm{Re}\,\bar{w}_{11}(K,i\Omega)\,, \tag{117}$$

implied by its definition. Thus, from Eq. (114),

$$S_{11}(K,\Omega)=\frac{2}{3}\,\frac{\zeta\Omega_B^2}{(\frac{2}{3}\Omega_B^2-\Omega^2)^2+\zeta^2\Omega^2}\,. \tag{118}$$

To obtain $w_c(K,\tau)$ we observe that the asymptotic form of Eq. (95) is, correspondingly,

$$\frac{\partial^2}{\partial\tau^2}w_c(K,\Omega)+\zeta\frac{\partial}{\partial t}w_c(K,\tau)+\tfrac{1}{6}u_M^2K^2w_c(K,\tau)=0\,, \tag{119}$$

which differs from Eq. (113) by the factor of $\frac{1}{2}$ multiplying u_M^2. Equivalently, this factor can be associated with K, so that by inspection one obtains

$$w_c(K,\tau)=w_{11}((1/\sqrt{2})K,\tau) \tag{120}$$

and

$$S_c(K,\Omega)=S_{11}((1/\sqrt{2})K,\Omega)\,. \tag{121}$$

By Eq. (121), the complete spectrum in Eq. (58) now takes the particular form

$$S(\vec{\mathrm{R}},\omega)=I_R[S_{11}(K,\Omega)+\tfrac{1}{2}g'(K)\{S_{11}((1/\sqrt{2})K,\Omega-\Omega_B)+S_{11}((1/\sqrt{2})K,\Omega+\Omega_B)\}]\,, \tag{122}$$

and the corresponding autocorrelation function takes the form

$$\Gamma(\vec{\mathrm{R}},\tau)=I_Re^{i\omega_0\tau}[w_{11}(K,\tau)+g'(K)w_{11}((1/\sqrt{2})K,\tau)\cos(\Omega_B\tau)]\,. \tag{123}$$

It is convenient, for graphical presentation, to define the dimensionless frequencies

$$\nu=\Omega/\Omega_B\,, \tag{124}$$

$$\beta=\Omega_B/\zeta=Ku_M/\sqrt{2}\zeta \tag{125}$$

and the normalized spectrum

$$S_0(\nu,\beta)=(3\zeta/I_R)S(\vec{\mathrm{R}},\omega)\,. \tag{126}$$

In terms of these dimensionless frequencies the normalized spectrum is

$$S_0(\nu,\beta)=S_R(\nu,\beta)+\tfrac{1}{2}g'(K)[S_B^+(\nu,\beta)+S_B^-(\nu,\beta)]\,, \tag{127}$$

where S_R and $S_B^\pm$ are the normalized versions of the terms in Eq. (122), and which, by Eq. (118), are

$$S_R(\nu,\beta)=\frac{2}{\beta^2(\frac{2}{3}-\nu^2)^2+\nu^2}\,, \tag{128}$$

$$S_B^\pm(\nu,\beta)=\frac{1}{\beta^2[\frac{1}{3}-(\nu\pm1)^2]^2+(\nu\pm1)^2}\,. \tag{129}$$

The parameter β as defined in Eq. (125) is determined by K, which in turn is determined by the

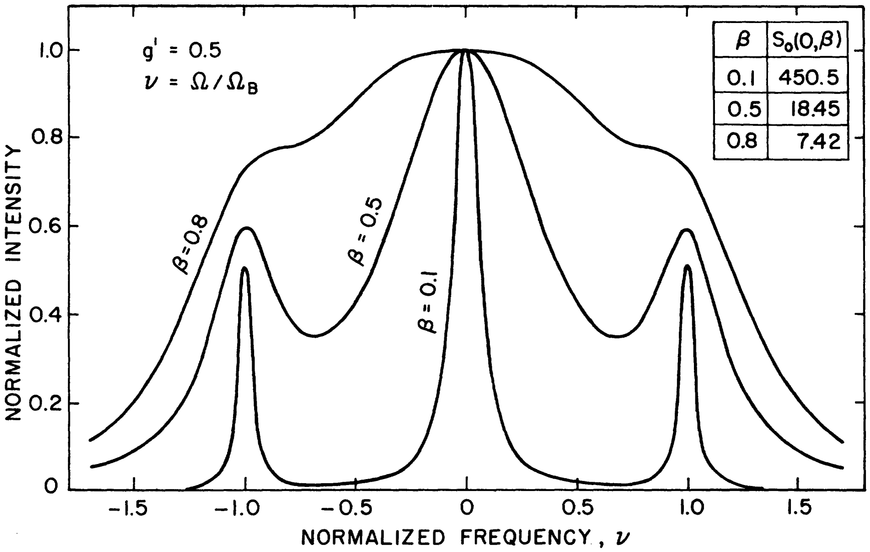

FIG. 1. Typical spectra calculated from Eq. (127) at $g'(K) = 0.5$. The ordinate is normalized to the value of $S_0(0,\beta)$.

viewing angle from $K = 2k_0 \sin(\frac{1}{2}\psi)$; for a particular value of K, both β and $g'(K)$ are fixed. Interestingly, β is similar to the reciprocal of y, the parameter employed by Yip and others[2-6,10] in kinetic calculations of the molecular density-correlation function. While in these treatments y is the sole parameter characterizing the shape of the spectrum, here we find that both β and $g'(K)$ significantly affect the shape. In the context of modulation theory, β is the index of modulation.

Typical spectra for several fixed values of β and g' are shown in Figs. 1 and 2, where all curves have been scaled such that $S_0(0,\beta) = 1$. It is evident that when β is less than 0.5, the spectrum exhibits the behavior predicted by hydrodynamic theory, and when β is of order 1, kinetic behavior is discerned. In particular, when β is equal to or less than 0.1, the peaks of the composite spectrum virtually coincide with those of the individual terms S_R and $S_B^{\pm}$, namely at $\nu = -1, 0, +1$. Under such condition, meaningful ratios of peak intensities and linewidths can be defined. From Eqs. (128) and (129), we find the ratio of each of the displaced peaks to the center peak to be $g'(K)/2$, and the dimensionless full linewidths at half-amplitude to be

$$\Delta\nu_R = \frac{1}{\beta}\left\{\tfrac{4}{3}\beta^2 - 1 + \left[\left(\tfrac{4}{3}\beta^2 - 1\right)^2 + \tfrac{16}{9}\beta^4\right]^{1/2}\right\}^{1/2}, \quad (130)$$

$$\Delta\nu_B = \frac{1}{\beta}\left\{\tfrac{2}{3}\beta^2 - 1 + \left[\left(\tfrac{2}{3}\beta^2 - 1\right)^2 + \tfrac{4}{9}\beta^4\right]^{1/2}\right\}^{1/2}. \quad (131)$$

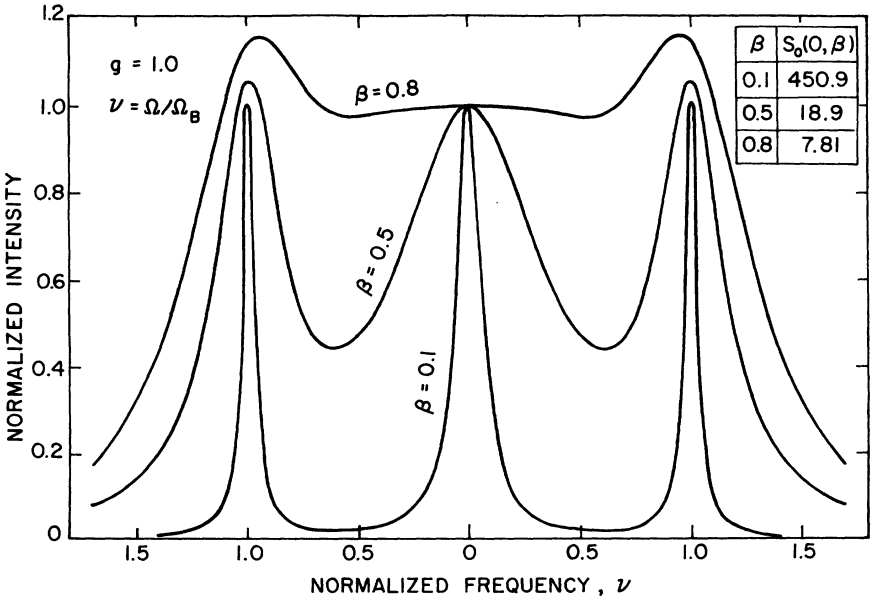

FIG. 2. Typical spectra showing the effect of increased value of $g'(K)$. Ordinate normalized to the value of $S_0(0,\beta)$.

However, with β less than 0.1, Eqs. (130) and (131) are approximated by the leading terms of their expansions, namely

$$\Delta\nu_R = \tfrac{4}{3}\beta, \tag{132}$$

$$\Delta\nu_B = \tfrac{2}{3}\beta. \tag{133}$$

The natural width of the Rayleigh line is therefore approximately twice that of each of the Brillouin lines, which agrees with the general property conveyed by the integral relation (60). It is worthwhile to estimate these linewidths. For typical values of $\beta = 0.1$ and Brillouin frequency $f_B = 100$ MHz, the Rayleigh and Brillouin linewidths are 13.3 MHz and 6.7 MHz, respectively. These widths are comparable to typical bandwidths of spectrum analyzers, so that the effect of the latter must be taken into account.

B. Modified Spectrum

Typically, the scattered light is collected onto a photomultiplier tube through a spectrum analyzer having a narrow bandwidth centered about the translated frequency Ω_s. The situation is that of linearly transforming an input stochastic process to an output process. It is well known that if the system is time-invariant and the input is stationary, then the input and output spectra are related via the system response function $H(\Omega,\Omega_s)$ as[33]

$$S_m(\Omega,\Omega_s) = |H(\Omega,\Omega_s)|^2 S(\Omega), \tag{134}$$

where all frequencies are translated, $\Omega = \omega - \omega_0$ and $\Omega_s = \omega_s - \omega_0$. In this case, the linear system is the spectrum analyzer and $|H(\Omega,\Omega_s)|^2$ is commonly referred to as the *instrumental profile*.

The photomultiplier tube, at the output of the analyzer, responds to the total integrated intensity, and, because its response is comparatively broad-band, its output current pulse rate is proportional to

$$I_m(\Omega_s) = \int_{-\infty}^{\infty} |H(\Omega,\Omega_s)|^2 S(\Omega)\,d\Omega. \tag{135}$$

Operationally, one slowly varies the frequency Ω_s and measures the integrated intensity of that portion of the input spectrum that falls within the narrow pass band of the spectrometer determined by $|H(\Omega,\Omega_s)|^2$.

Analytic forms of $H(\Omega,\Omega_s)$ are usually not known so that one must rely either on assumed approximations or on numerical integration using measured profiles. In recent experiments, Clark[12] employs the latter. Here, however, for the purpose of a preliminary appraisal of theory, and to hold the computations to manageable proportions, we use the Lorentzian approximate form

$$|H_L(\Omega,\Omega_s)|^2 = \frac{\Omega_1}{(\Omega-\Omega_s)^2+\Omega_1^2}, \tag{136}$$

where Ω_1 is the half-width at half-amplitude. Since $|H_L|^2$ is a function of the difference $\Omega - \Omega_s$, the integral (135) becomes in essence a convolution integral which can be evaluated analytically. Rather than evaluating it by the method of residues in the complex plane, we take advantage of results in the previous section. We note that

$$\frac{2\Omega_1}{\Omega_s^2+\Omega_1^2} = \int_{-\infty}^{\infty} \exp(-i\Omega_s\tau - \Omega_1|\tau|)\,d\tau,$$

so that the convolution of the Lorenzian function with $S(\vec{R},\Omega)$ is equivalent to the Fourier transform of the product of $e^{-\Omega_1|\tau|}$ and the inverse of $S(\vec{R},\Omega)$ which is $\Gamma(\vec{R},\tau)$ in Eq. (123). For example, to find the convolution of the first term S_{11} in Eq. (122), one replaces $i\Omega$ with $i\Omega_s + \Omega_1$ in Eqs. (117) and (118). With similar procedure for the remaining terms, we find, after dividing all frequencies by Ω_B and replacing ν_s by ν,

$$I_m(\nu,\beta) = I_1(\nu,\beta) + \tfrac{1}{2}g'(K)[I_2^+(\nu,\beta) + I_2^-(\nu,\beta)], \tag{137}$$

where

$$I_1(\nu,\beta) = \frac{U\nu^2 + bc_1}{(c_1-\nu^2)^2 + (U+b)\nu^2}, \tag{138}$$

$$I_2^{\pm}(\nu,\beta) = \frac{U(\nu\pm1)^2 + bc_2}{[c_2 - (\nu\pm1)^2]^2 + (U+b)(\nu\pm1)^2}. \tag{139}$$

The other symbols are

$$U = \Omega_1/\Omega_B, \qquad b = 1/\beta + U,$$

$$c_1 = \tfrac{2}{3} + U^2 + (1/\beta)U, \qquad c_2 = \tfrac{1}{3} + U^2 + (1/\beta)U.$$

As to be expected, Eqs. (138) and (139) reduce to the natural spectrum when the finite instrumental width U vanishes. However, the case of greater importance is when the instrumental width exceeds the natural linewidth, i.e., when $U \gg \beta$. Equivalently, when U is finite and β tends to zero then the three components of the observed spectra virtually become scaled replicas of the instrumental profile. Typical modified and natural spectra, I_m and S_0, are shown in Fig. 3.

C. Comparison with Experimental Results

An important test of the preceding theory is provided by the expression for the Brillouin frequency Ω_B. When the instrumental profile is sufficiently narrow so that overlap is negligible, the maxima of the composite spectrum, I_m, coincide with those of the component terms I_1 and $I_2^{\pm}$. In such cases the observed Brillouin doublet occurs at the normalized frequencies $\nu = \pm1$, in actual frequency at $\pm\Omega_B/2\pi$. Otherwise, when the three components overlap, one must find the roots of

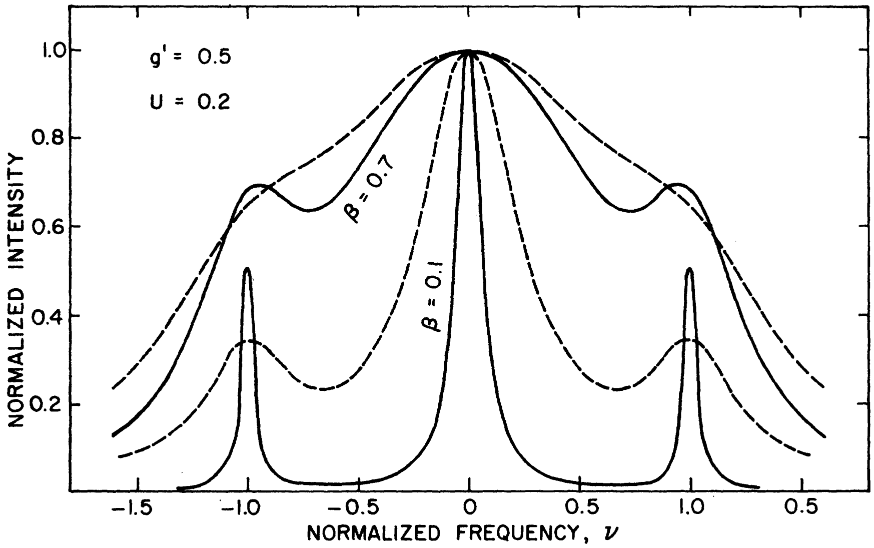

FIG. 3. Effects of a Lorentzian instrumental profile: solid curves are natural spectra, $S_0(\nu,\beta)$; dashed curves are the corresponding modified spectra, $S_m(\nu,\beta)$, the instrumental half-width being $U = 0.2$.

$\partial I_m/\partial\nu = 0$, which is a tedious task.

It is convenient for computation to express the molecular mass m in Eq. (112), in terms of the gram-molecular-weight M and the Avogadro number N_0, and the wave vector $\vec{K}$ in terms of wavelength λ_0. The Brillouin frequency is then given by

$$f_B = \frac{1}{\lambda_0}\left[\frac{6k_BTN_0}{M}\right]^{1/2}\sin(\tfrac{1}{2}\psi)\,, \qquad (140)$$

where ψ is the viewing angle. Using this expression, we calculate frequencies for several gases on which measurements were made by Greytak and Benedek[13] and Clark.[12]

The calculated and measured Brillouin frequencies are compared in Table I. As is evident, agreement between theory and experiment is excellent. A curious trend, however, is also discerned in that the calculated frequencies are lower than the measured ones in monoatomic gases, while the converse appears to hold in polyatomic gases. At this stage of both theory and experiment, it is not certain how much of this trend is a result of experimental discrepancy, arising from instability of lasers and spectrum analyzers, or that of theoretical representation of a complicated molecule as a simple nonrotating dipole. These calculations, however, demonstrate that the microscopic formulation of scattering and the statistical theory of the preceding sections are well founded and point in the right direction.

The next items to be compared are the spectra of Xe and CO_2 at an angle of 169.4° corresponding to the kinetic regime. For this comparison both parameters, β and g', are needed. However, since β depends on ζ whose theoretical significance—other than that of being some characteristic frequency—has not been established, and since at this writing an analytic form of g' has not been determined, a numerical method was employed to evaluate these parameters for best fit of theoretical curves to experimental data in the sense of least rms error.

Experimental data points were read from photo-

TABLE I. Comparison of calculated and measured Brillouin frequencies.

Gas	Molecular weight (g)	Temperature (K)	Calculated frequency (MHz)	Measured frequency (MHz)
He	4.003	295[a]	279.91	288.5[a]
Ar	39.94	301	89.51	93.0 ± 2
Xe	131.30	298.5	49.16	50.8 ± 2
N_2	28.016	301	106.87	100.5 ± 2
CO_2	44.01	297.9	84.83	81.5 ± 1.2
CH_4	16.032	297.7	140.51	129.0 ± 4

[a] Data from Ref. 12. All others from Ref. 13. Laser wavelength, 632.8 nm; $\psi = 10.6°$.

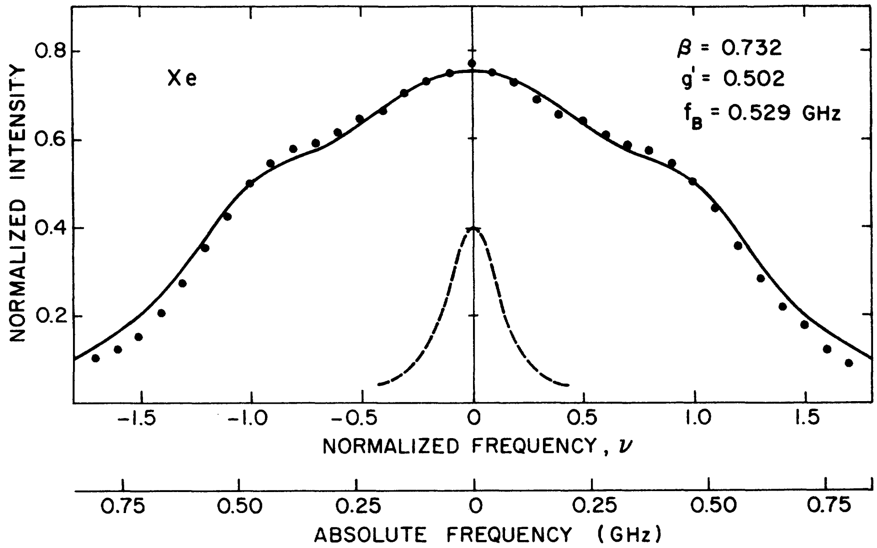

FIG. 4. Comparison of theoretical spectra (solid curve) as calculated from Eq. (137), against experimental data of Ref. 13 for Xe at 780 mm Hg. Normalized instrumental half-width, $U = 0.144$.

graphic enlargements of Fig. 2 in Ref. 13 after the abscissa, given in absolute frequency scale, was normalized to ν using values of f_B calculated from Eq. (140). The ratio of the measured ordinate at $\nu = +1$ to that at $\nu = 0$, together with a fixed value of β, was then used to compute g' from the theoretical ratio $I_m(1)/I_m(0)$ provided by Eq. (137). This constrains the calculated curves always to pass through the datum point at $\nu = 1$. With g' thus fixed for each β, the modified spectrum $I_m(\nu, \beta)$ was calculated as function of ν for a succession of values of β, until the least rms error was found.

The best fit of the theoretical curves to experimental data is obtained with $\beta = 0.732$ and $g' = 0.502$ for Xe, and $\beta = 0.91$ and $g' = 0.508$ for CO_2. As is evident in Figs. 4 and 5, agreement between theory and experiment is remarkably good. A slight discrepancy near the skirts of the spectra is primarily due to the Lorentzian approximation of the instrumental profile, which is known to fall off less steeply than the measured ones.[34] The effect of this approximation, which is most pronounced near the skirts, is also discerned in the theoretical curves of Fig. 3.

It is interesting to evaluate ζ from the relation, $\zeta = \Omega_B/\beta$, using the calculated values of β. With $\Omega_B = 3.33 \times 10^9$ sec^{-1} in Xe and $\Omega_B = 5.74 \times 10^9$ sec^{-1} in CO_2, as obtained from Eq. (140) with $\psi = 169.4°$, we find the corresponding values of ζ to be 4.55×10^9 sec^{-1} and 6.30×10^9 sec^{-1}, respectively. In Table II, these values of ζ are compared to collision frequencies as calculated from the kinetic theory[35] of elastic-sphere molecules and another based on the Boltzman theory.[36] While of the same order of magnitude, the values of ζ are somewhat lower than the elastic-sphere collision frequencies. It remains a question for further theoretical and experimental exploration to as-

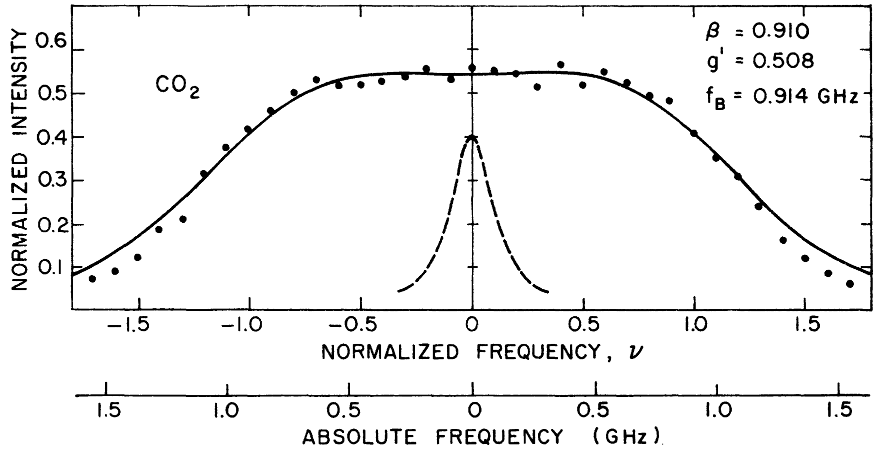

FIG. 5. Comparison of theoretical spectra (solid curve) as calculated from Eq. (137) against experimental data of Ref. 13 for CO_2 at 750 mm Hg. Normalized instrumental half-width, $U = 0.112$.

certain whether or not ζ—which is the long-term asymptotic value of the logarithmic derivative defined in Eq. (69)—is indeed a collision rate in the conventional sense.

Turning to $g'(K)$, we notice its value is virtually the same in both gases. We recall that $g(K)$ is the characteristic function of $G(\vec{r})$, the latter being the probability density of $\vec{R}_0(t,\sigma)$ which is the separation between a typical pair, and there are $N(N-1)/2$ stochastic processes $\vec{R}_0(t,\sigma)$ with identical probability densities $G(\vec{r})$. It can be shown, by the hypothesis of statistical identity, that the quantity

$$m(\vec{r})d\vec{r} = \tfrac{1}{2}N(N-1)G(\vec{r})d\vec{r}$$

is the density of the *expectation value* of the number of pairs whose separation lies in $(\vec{r},\vec{r}+d\vec{r}]$. As evident from its definition in Eq. (54), $g'(K)$ is $2/N$ times the Fourier transform of this mean density. While data and computations on two gases do not constitute sufficiently conclusive evidence, the results here suggest that the analytic form of g' may depend far more on statistical principles than on particular intermolecular forces.

For an additional test, the preceeding computational procedure was applied to the modified spectrum resulting from solution of the diffusion equation, (86). In this case, the three components of the pure spectrum are Lorentzian in shape. The minimum rms error occurs when $\beta = 0.745$ and $g' = 0.522$, for Xe, and the corresponding spectrum is as shown in Fig. 6. Theory and experiment do not agree in this case, indicating that the diffusion equation is not as good an approximation to the general equations (71) and (95), as the damped wave equation (84). Obviously, the latter describes events separated by shorter time intervals.

TABLE II. Comparison of ζ to collision frequency.

Gas	Pressure (mm Hg)	ζ (10^9 sec^{-1})	Collision Frequency (10^9 sec^{-1})	
CO_2	750	6.30	8.82 [a]	6.09 [b]
Xe	780	4.55	6.05 [a]	...

[a] Data from Ref. 35. Elastic-sphere values corrected to given pressure and temperature of 25°C.

[b] Data from Ref. 36. Corrected to same conditions.

VI. DISCUSSION

A striking outcome of the preceeding microscopic theory is the possibility of existence of new spectral lines which heretofore have not been observed. Equations (128) and (129) show that as β increases beyond unity, each of the three spectral components begins to show maxima at its outer extremes while the maximum corresponding to small β diminishes to a minimum. A typical natural spectrum for $\beta = 5.0$ is shown in Fig. 7 wherein the peaks $B1$ and $B2$ represent the split Brillouin terms, and R the split Rayleigh term. As it can be verified from Eqs. (128) and (129), the individual peaks occur at the normalized frequencies,

$$\nu_{RM} = \pm\left[\tfrac{2}{3} - 1/2\beta^2\right]^{1/2},$$

$$\nu_{BM} = \pm\left[\tfrac{1}{3} - 1/2\beta^2\right]^{1/2} \pm 1,$$

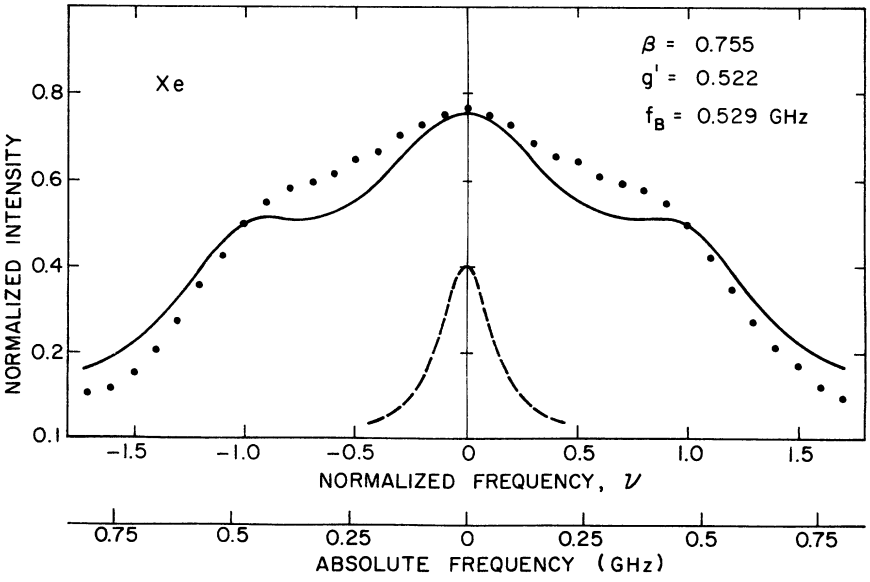

FIG. 6. Comparison of theoretical spectra as calculated from diffusion equation for Xe as in Fig. 4.

and the critical point of transition where these frequencies become real are $\beta \geqslant 0.866$ for the Rayleigh term, and $\beta \geqslant 1.22$ for the Brillouin term. In the extreme cases of very large β, say $\beta > 10$, the frequencies of the maxima of the composite spectrum approach $\nu = \pm 0.816$, ± 0.423, ± 1.577, indicated by vertical bars in Fig. 7.

Splitting of the lines is a high-frequency phenomenon related to events in short time intervals in the limit $\tau \rightarrow 0$. It is typical of random phase or frequency modulation with large modulation index,[28] this being a ratio of the mean deviation in frequency to the mean rate of this deviation, which is essentially the significance of β. That the present theory can predict this effect is largely a consequence of proper formulation of the radiation field and the fact that the probability densities were determined on a time scale shorter than the mean period between collisions. If the motion of a particle were described as a limiting form of a zero-order Markov process, resulting in the Langevin equation of motion over a time mesh Δt encompassing many collisions, then W_{11} would have been governed by a diffusion equation. In that case, both the Rayleigh and the Brillouin line shapes would have been Lorentzian, negating the possibility for existence of high-frequency peaks.

This conclusion of splitting lines, however, should be treated with extreme caution. Because it occurs at relatively high frequency, and therefore is related to events as $\tau \rightarrow 0$, conditions might easily fall at the borderline of the long-time asymptotic behavior of the logarithmic derivative $h(\tau)$. We recall that it is precisely the asymptotic behavior of $h(\tau)$ that leads to the damped-wave approximation of the general equations (71) and (95). Yet, when one considers the other extreme as $\tau \rightarrow 0$, solutions to the short-time asymptotic form of Eq. (71) turn out to involve Bessel functions, again raising the possibility of spectral peaks at the high-frequency end.

It should be interesting to verify this effect experimentally. To estimate the conditions for its existence, consider collision frequency as a rough estimate of ξ. It is necessary that the collision frequency be maintained sufficiently high to ensure asymptotic validity of the damped-wave approximation. To increase β at the expense of diminished collision frequency (ξ), through reduced pressure, would defeat this condition. It appears that helium under atmospheric pressure offers the desired combination of a large β at moderate collision frequency, when viewed from an angle of 170°. Under these conditions, Ω_B is 18.96×10^9 $\sec^{-1}$ as calculated from Eq. (140) with the laser wavelength being 632.8 nm. Assuming a collision frequency of 6.0×10^9 $\sec^{-1}$, we find β is equal to 3.16. At this value of β, the split Rayleigh lines would be well resolved at approximately 2.4 GHz, while the split Brillouin lines would be too close to it to be observed, depending on the instrumental profile.

Among several refinements that could be incorporated into the theory are effects of internal and rotational degrees of freedom of the molecule. It must be emphasized, however, that the internal degrees cannot affect the phase of the scattered field in any appreciable way if the formulation is to be consistent with the assumption that the molecule is much smaller than the wavelength, which is the condition justifying its representation as

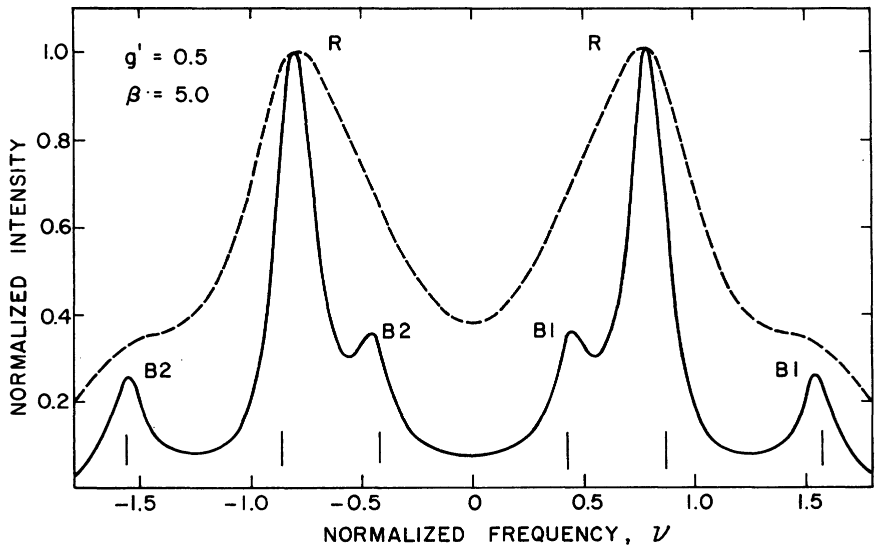

FIG. 7. Typical theoretical natural spectra at high values of β. The dashed curves represent the convolution of the actual spectrum (solid) with a Lorenzian instrumental profile.

a dipole. A time-dependent polarizability is the only classical mechanism by which internal structure of the molecule can logically be connected to the scattered field which, as is well known, forms the theoretical basis for classical interpretation of Raman scattering. Since the frequencies of Raman spectra are an order of magnitude higher than those encountered in Rayleigh scattering, the internal structure of the molecule is not expected to modify the latter. Rotation of the molecule, however, could have an effect which is readily included through the use of a time-dependent, tensor polarizability. Since rotation of the molecule is expected to be slower than internal electronic processes, slight modification of the Rayleigh spectrum is theoretically possible. Effects of the tensor nature of polarizability would be manifested as depolarization of the scattered field.

Another factor which was not considered is the fact that not all the molecules within a region scatter simultaneously. Since the incident beam intersects a segment of the region, only those molecules which happen to be in the incident field contribute to scattering. Strictly speaking, all the results of the preceding sections are contingent upon the probability that a particular molecule and pair of interfering molecules lie within the illuminated region.

A third aspect which deserves attention is the effect of finite boundaries, which would seem to present itself as a straightforward boundary-value problem. However, although the partial differential equations (71), (95), and (105) are invariant under translation, the solutions, when constrained to boundary conditions, would not be. Hence, the conditional probability densities would no longer be functions of the difference $\vec{r}-\vec{r}_0$, which necessitates using the general form of Theorem 1 in terms of joint probability densities.

VII. CONCLUSIONS

We have evolved a consistent microscopic theory of Rayleigh scattering in its simplest form, which provides a basis to account for the observed effects from a unified set of principles. It has also been demonstrated that the Rayleigh spectrum is a manifestation of external degrees of freedom of the molecule, these being the information encoded into the phase of the scattered field. The theory divides the effects into two parts: one related to the statistical trajectory of a typical single molecule causing the undisplaced Rayleigh line, and the other related to interference between pairs causing the Brillouin doublet. Both the Rayleigh and the Brillouin lines are described by propagating waves, the latter in exact sense and the former as an approximation to the general description provided by solutions of Eq. (71). In a microscopic viewpoint, however, these waves represent conditional probability densities propagating in the abstract space which is the range set of the random trajectories. It would be worthwhile to find a connection between these waves and the acoustic waves of hydrodynamic theory.

The same parameter $g'(K)$ that determines the intensity of the Brillouin doublet can also explain the deviation, if any, of the total integrated intensity from that predicted by incoherent scattering. Measurement of ratios of the Brillouin intensity to the Rayleigh intensity as a function of angle would provide needed information on the analytic form of $g'(K)$.

Agreement of theory with experiment was achieved through complete departure from conventional methods of kinetic theory, especially in its viewpoint of collisions, and through proper formulation of the radiation field in terms of moving sources. The present theory is based on the major hypothesis of statistical indistinguishability of single particles and pairs of particles and the well-developed theorems of probability theory. Departure from kinetic theory consisted in this hypothesis and the use of a new set of equations for differentiable stochastic processes, extending the time scale to intervals shorter than a collision period. The remaining restrictions to small volume and spherically symmetric molecules have bearing only on the radiation aspect of the theory, while restriction to dilute systems affects both the radiation aspects, through inequality of the local and incident fields, and the statistical aspects, possibly, through the interaction potential. If particular forms of interaction potential affect the statistics, they are expected to do so only through the logarithmic derivative $h(\tau)$ of the conditional expectation of velocity or energy. Except for the possible dependence of $h(\tau)$ on specific forms of interaction, all other results, especially the Brillouin frequencies, are independent of this potential. Since this function holds a key to statistical features of the aggregate, through Eqs. (71) and (95), determining its analytical form poses an important problem for further investigation.

The problem of interparticle interactions was approached from classical theoretical standpoints largely for the sake of maintaining over-all logical consistency with classical treatment of the radiation aspect of light scattering. In treating the particle statistics from the standpoint of the axiomatic theory of probability, however, we have also arrived at the surprising result that the principles of classical Newtonian mechanics imposed as constraints on the classical theory of probability lead to a wave description of the probabilities of trajectories of randomly interacting particles. This indicates that a wave-mechanical description of particle interactions is not peculiar to quantum mechanics alone. Although the philosophical and pragmatic implications of this finding are beyond the scope of this paper, they remain as most interesting and fundamental questions deserving of further serious attention.

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APPENDIX A: A THEOREM

Theorem 4. If the conditional expectation of the continuous, differentiable process $\dot{\vec{R}}(t,\sigma)$ is a constant, radial vector $\vec{v}$, then its conditional probability density is

$$P\{\dot{\vec{R}}(t)=\vec{\xi}\,|\,\vec{R}(\tau)=\vec{r};\vec{R}(0)=\vec{r}_0\}=\delta(\vec{\xi}-\vec{v})d\vec{\xi}\,,$$

whose second moment is $|\vec{v}|^2$.

Proof. Since the components v_i, $i=1,2,3$, are constant, differentiation of Eq. (61) yields

$$\frac{\partial^2}{\partial\tau^2}W=-v_i\frac{\partial}{\partial x_j}\frac{\partial W}{\partial\tau}\,. \tag{A1}$$

Using Eq. (61) again gives

$$\frac{\partial^2 W}{\partial\tau^2}=v_i v_j\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}W\,. \tag{A2}$$

Subtracting Eq. (A2) from (62) gives

$$\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}(u_{ij}-v_i v_j)W=0\,, \tag{A3}$$

where

$$u_{ij}-v_i v_j=\int(\xi_i\xi_j-v_i v_j)f(\vec{\xi}-\vec{v})d\vec{\xi}\,, \tag{A4}$$

and $f(\vec{\xi}-\vec{v})$ is the unknown conditional probability density of $\dot{\vec{R}}(t,\sigma)$. The integral (A4) is independent of τ, so that if any solutions of (A3) exist, they are not functions of τ. But this contradicts the hypothesis that $W(\rho,\tau)$ is a function of τ. The only condition under which Eq. (A3) is valid and $W=W(\rho,\tau)$ is if each coefficient vanishes, i.e.,

$$u_{ij}-v_i v_j=0\,,\quad i,j=1,2,3\,.$$

In particular, the variance of $\dot{\vec{R}}(t,\sigma)$ is

$$\sum u_{ii}^2-|\vec{v}|^2=0\,.$$

By a well-known theorem of probability theory, the probability density of a random variable whose variance vanishes is a δ distribution localized at the expected value.

APPENDIX B: DERIVATION OF EQ. (57)

Equation (60) follows from the Wiener-Khintchin theorem. If $C(\tau)$ is an autocorrelation function with spectrum $S(\Omega)$, then

$$C(\tau)=\frac{1}{2\pi}\int e^{-i\Omega\tau}S(\Omega)d\Omega\,, \tag{B1}$$

from which one obtains

$$\frac{\partial^2}{\partial\tau^2}C(0)=-\frac{1}{2\pi}\int\Omega^2 S(\Omega)d\Omega\,. \tag{B2}$$

In particular, if $S_\alpha(K,\Omega)$ stands for S_{11} or S_c and $w_\alpha(K,\tau)$ for w_{11} or w_c, then

$$-\frac{\partial^2}{\partial\tau^2}w_\alpha(K,0)=\frac{1}{2\pi}\int\Omega^2 S_\alpha(K,\Omega)d\Omega\,. \tag{B3}$$

Noting that at $\tau=0$ both $\vec{a}$ and $\vec{v}$ vanish in Eq. (68), one obtains after Fourier transformation of this equation

$$\frac{\partial^2}{\partial\tau^2}w_{11}(K,0)=-\tfrac{1}{3}K^2u_M^2 w_{11}(K,0)\,. \tag{B4}$$

Similarly, by the development of Sec. IV D,

$$\frac{\partial^2}{\partial\tau^2}w_c(K,0)=-\tfrac{1}{6}K^2u_M w_c(K,0)\,. \tag{B5}$$

Since $w_c(K,0)=1$ and $w_{11}(K,0)=1$, Eq. (60) follows by combining (B3), (B4), and (B5).

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Variational Calculation of the Electron-Gas Correlation Energy*

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The ground-state correlation energy of the electron gas is calculated in the region of intermediate densities using the variational method of Becker, Broyles, and Dunn for two trial wave functions. Each trial function is taken to be a product of two factors, one factor being the ground-state wave function for the ideal gas of spin-1/2 particles and the other being a product of pair functions in the relative coordinates of the electrons. In one trial function a single pair function is used; in the other, the pair functions between parallel and antiparallel spins are allowed to differ. The pair functions are parametrized and approximations to the energy minimized. The three-particle correlation functions appearing in the kinetic energy are replaced by either the Kirkwood superposition approximation (KSA) or the convolution approximation (CA) to give two approximate energy functionals for each wave function. The ideal-gas N-particle probability density is approximated by a Boltzmann factor with an effective pair potential. This effective potential is obtained by inverting the hypernetted chain equation for the known pair-correlation function of the ideal Fermi gas. The pair-correlation functions for the interacting system are then calculated by means of the hypernetted-chain equation. The CA correlation energies join smoothly with both the high- and low-density expansions. The CA and KSA correlation energies differ by less than 4% everywhere in the intermediate-density region. The pair-correlation functions exhibit generally reasonable physical behavior.

I. INTRODUCTION

Since the pioneering work of Wigner[1] many studies have been devoted to the problem of calculating the ground-state correlation energy of the electron gas. The correlation energy is defined by

$$\epsilon_c = \epsilon - \epsilon_{\rm HF}\,, \tag{1.1}$$

where ϵ is the ground-state energy per electron and $\epsilon_{\rm HF}$ is the familiar Hartree-Fock approximation to ϵ given by[1,2]

$$\epsilon_{\rm HF} = \epsilon_I + \epsilon_x\,, \tag{1.2}$$

with

$$\epsilon_I = \tfrac{3}{5}\epsilon_F\,, \quad \epsilon_x = -3e^2 k_F/4\pi\,,$$

where $\epsilon_F = \hbar^2 k_F^2/2m$, $k_F = (3\pi^2\rho)^{1/3}$, and ρ denotes the mean density of electrons. In conventional units one has

$$\epsilon_{\rm HF} = 2.21/r_s^2 - 0.916/r_s \ {\rm Ry}\,,$$