

FIG. 1. The torque critical field ratio H_θ/H_t versus θ (the angle between H and specimen plane), where H_t corresponds to $\theta = 90^\circ$. The arrow indicates the value H_{C3}/H_{C2} theoretically predicted by Saint-James and de Gennes (reference 5). For further information, consult Tables I and II.

conducting laminar region or sheath centered a distance $X_0 = 0.7682\xi$ below the interface, where ξ is the coherence length. Within this sheath, the local free energy is less than the bulk G-L value. According to their detailed calculations, the sheath will remain superconducting up to a limit $H_{C3} = 1.692H_{C2}$. For the case of a magnetic field applied normal to the interface, they conclude that the superconducting phase nucleation limit will equal H_{C2} . Also, at intermediate angles of applied field, they suggest that this limit is probably a smooth function of angle.

The numerical agreement between the calculated value of H_{C3}/H_{C2} and our observed values

of H_l/H_t is striking. The observed correlation between H_t and H_{C2} is also in harmony with the theory. On the basis of this evidence it is suggested that $H_l = H_{C3}$ and $H_t = H_{C2}$, where H_l and H_t are defined operationally in terms of a torque measurement. In general, it is believed that our observations lend strength to the notion of a superconducting sheath which persists in the interval $H_{C2} < H < 1.692H_{C2}$.

We wish to thank Dr. T. G. Berlincourt for acquainting us with the theory of Saint-James and de Gennes and for suggesting its possible applicability. We are indebted to D. Saint-James and P. G. de Gennes for making available the results of their theoretical investigation prior to publication. We wish to thank R. R. Hargrove for aid with specimen preparation, R. E. Gile for help with the measurements, and E. P. Parry for the chemical analyses.

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

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OBSERVATION OF DIFFUSION BROADENING OF RAYLEIGH SCATTERED LIGHT*

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(Received 10 December 1963)

Light which is Rayleigh scattered by dilute solutions of macromolecules is normally considered to be spectrally identical to the incident or exciting light. Although angular scattering intensity and polarization measurements have been employed for many years in the study of polymers and colloids,¹ the additional information carried by the spectral distribution of scattered light has been inaccessible because of the limited resolu-

tion of traditional spectroscopic apparatus.

We have utilized a cw optical maser in conjunction with optical heterodyne detection techniques to examine the spectrum of Rayleigh scattering with an instrumental resolution of 6 cps, corresponding to an equivalent optical resolving power of approximately 10^{14} . The observed spectrum is found to be broadened, and the broadening has been found to depend both on the size of the scat-

tering center and on the angle of observation.

The important line-broadening effects are determined by the dynamics of the individual scatterers. If the molecules are strongly anisotropic, there will be a rotational variation of polarizability which would, in the absence of the solvent, give rise to a rotational Raman spectrum. Free rotations will be heavily damped by the dense liquid environment, and thermally induced correlations in orientation will therefore be described by a relaxation time τ_R . Benoit² has shown that this relaxation time is related to the rotational diffusion constant D_R by $\tau_R = 1/(6D_R)$. The resultant spectrum should therefore be Lorentzian with a full width at half-maximum intensity given by

$$\Delta\nu_{\text{rot}} = 6D_R/\pi. \quad (1)$$

Linear motion of the particles will also contribute to the observed linewidth. In the absence of the solvent, one would expect a simple Doppler broadening, but the occurrence of collisions with solvent molecules drastically reduces the linewidth. Dicke and Wittke³ have discussed this process for radiating atoms in an atmosphere of inert buffer gas, and showed that the Doppler-broadened Gaussian line will be narrowed by the collisions if the mean free path is much less than the emitted wavelength. Dicke's theory may be taken over directly for scattering with appropriate modification of the expression for the radiation field, and leads to a prediction of a Lorentzian spectrum of width $\Delta\nu = D_L K^2/\pi$, where D_L is the linear diffusion constant and $\vec{K} = \vec{k}_S - \vec{k}_0$ is the vector difference between the incident and scattered wave vectors. Since $|\vec{k}_S| \approx |\vec{k}_0|$, $|K| \approx 2k_0 \sin\theta/2$, whence

$$\Delta\nu_{\text{linear}} = (16\pi D_L/\lambda^2) \sin^2\theta/2. \quad (2)$$

The effects of linear and rotational diffusion on scattering linewidths have also been analyzed by Pecora⁴ who employed the Van Hove⁵ space-time correlation function formalism. Pecora's theoretical treatment leads to expressions identical to our Eqs. (1) and (2).

It should be noted that Eq. (2) is only valid if the mean free path a is $\ll 1/K$, a condition which is easily satisfied in the visible at all scattering angles for molecular diffusion in liquids. Recently reported observation of the diffusion broadening of Mössbauer emission from macromolecules in liquid environments satisfy the equivalent criterion $a \ll \lambda$ only weakly, and might therefore

be expected to exhibit only partial collision narrowing, consistent with the anomalously large linewidths reported by the authors.⁶

The spectrum of the scattered light will be influenced by thermal convection currents in the solvent as well as by the dynamics of the scattering centers. Although solvent currents may be minimized by thermal and acoustical isolation of the scattering cell, residual currents of 4×10^{-4} cm/sec will produce measurable effects with the resolution employed. Since the scattering centers are carried with the solvent by these currents, the effect on the spectrum should be independent of particle size, and therefore become relatively less important with decreasing particle size. The actual frequency shift $\delta\nu$ produced by a current of velocity v will be

$$\delta\nu_{\text{cur}} = (2/\lambda)v_K \sin\theta/2, \quad (3)$$

where v_K is the component of v in the direction of \vec{K} . Gradients in the current will produce dispersion of $\delta\nu$, and lead to line broadening in addition to frequency shifts. Although the three effects considered here will all contribute simultaneously to the observed linewidth, their effects may be isolated, in principle, through the different angular dependences involved.

Experimental.—We have observed broadening of the Rayleigh scattered light from dilute solutions of monodisperse polystyrene molecules. This material, which has been discussed by Alfrey et al.,⁷ forms a suspension of uniform spheres which should not produce rotational diffusion broadening. The apparatus is shown in Fig. 1. The output beam of a 6328Å He-Ne maser is split at a half-silvered mirror and provides both direct illumination to the sample cell and an optical local oscillator beam for heterodyne detection. A 12-Mc/sec frequency difference is imposed on the two beams by means of acoustical Bragg-reflection modulators which we have previously described.⁸ All optical components are mounted on a massive acoustically isolated iron table.

The 12-Mc/sec heterodyne signal is analyzed with circuitry of approximately 6-cps bandwidth as determined with an auxiliary 12-Mc/sec reference. The beat signal produced by direct combination of the light beams exhibits no broadening beyond the instrumental limit. In order to improve signal-to-noise ratios without interference from long-term optical instabilities, the 1150-cps broad-banded signal is recorded on a 2.5-minute

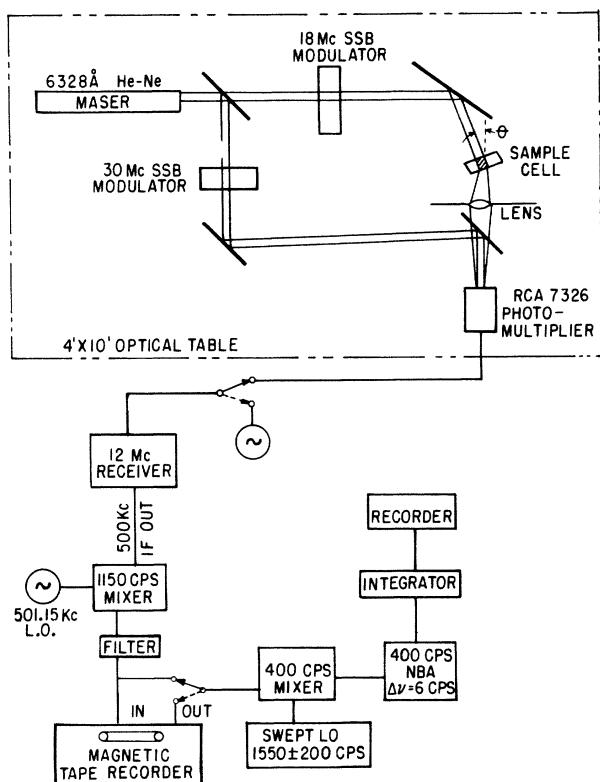


FIG. 1. Experimental arrangement.

magnetic tape loop which is later frequency-scanned at 2.5 cps per minute with a 30-second time constant.

Equation (2) evaluated for spherical particles in water at 20°C with $\lambda = 6328 \text{ \AA}$, and $D_L = kT/6\pi\eta r$ leads to

$$\Delta\nu = \frac{49 \sin^2\theta/2}{r(\mu)}, \quad (4)$$

where $r(\mu)$ is the sphere's radius in microns. The solid curves in Fig. 2 are evaluations of Eq. (4) for particles of diameter 0.088 μ and 0.567 μ . Experimental points are found to lie above the theoretical curves, implying an additional broadening due to nonuniform convection currents. This excess broadening is roughly equal for both samples, in agreement with the above discussion of the assumed current mechanism. Since current effects are relatively unimportant for small samples, linewidth measurements can serve as a useful means of determining the size of molecules smaller than 500 \AA , where traditional light scattering techniques become marginal.

The data points shown in Fig. 2 were selected from a larger number of runs. Occasionally, anomalously large linewidths were found combined

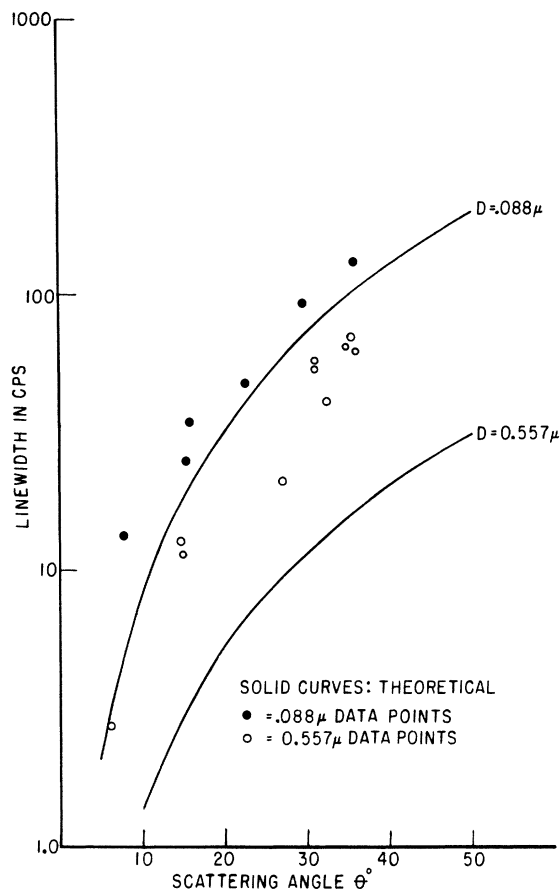


FIG. 2. Theoretical and experimental values of Rayleigh scattering linewidths.

with significant displacements of the line center. This was interpreted as resulting from abnormally large convection currents present when insufficient time had been permitted for the establishment of thermal equilibrium. It was also found that samples of 0.088 μ polystyrene kept longer than about one month gave linewidths less than the prediction based on the linear diffusion theory. It is assumed that this narrowing is associated with a tendency for the molecules to form into larger aggregates over long periods of time. This interpretation is supported by observed modifications in the angular scattering functions of these samples with aging.

We wish to thank Dr. J. W. Vanderhoff of the Dow Chemical Company who provided the polystyrene samples used in this experiment, and Mr. L. Gampel of our laboratory who has carried out an independent check of particle sizes by measuring angular scattering functions. We are particularly indebted to Professor R. Bersohn of the Columbia Department of Chemistry who first

proposed this problem to us and with whom we have had many helpful conversations during the course of the work.

*Work supported by the National Science Foundation under Grant No. NSF-GP 438, the Army Research Office-Durham under Grant No. DA-ARO(D)-31-124-G380, and the Joint Services (U. S. Army, U. S. Air Force Office of Scientific Research, and U. S. Office of Naval Research).

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RESONANCES IN MULTICHANNEL SYSTEMS

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(Received 25 October 1963)

In a recent note to this journal,¹ Oakes and Yang have suggested that the positions of the resonance poles associated with the spin-3/2 baryon decuplet raise serious objections to the currently popular schemes of unitary symmetry. They have pointed out that in the $I=1, S=-1$ channel the Y_1^* resonance must occur as a pole on the sheet obtained by passing through that portion of the unitarity cut which lies between the $\pi\Sigma$ and $\bar{K}N$ thresholds (see Fig. 1). Since the limit of perfect unitary symmetry would seem to require that the Y_1^* appear on the physical sheet (i.e., that it be bound), they argue that the resonance must change sheets three times as the symmetry-breaking interaction is turned off. This could occur, for instance, by having the Y_1^* pole pass consecutively through the $\pi\Lambda$ threshold, the cut between the $\pi\Sigma$ and $\bar{K}N$ thresholds, and the $\pi\Lambda$ threshold. Thus for some strength of the symmetry-breaking interaction, this pole would appear on a sheet far removed from the physical one and would consequently be difficult to observe as a scattering resonance. This behavior would strongly suggest that there may be unobservable poles which will "appear" as gaps in the higher SU_3 multiplets.

Crucial to the above argument is the assumption that it is possible to continuously and unambigu-

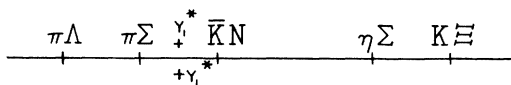


FIG. 1. Thresholds of the $I=1, S=-1$ channel.

ously identify a pole (or more accurately, a pair of poles) with a given resonance in the transition from the physical world to the limit of unitary symmetry. We shall attempt to demonstrate here that in a multichannel problem such as they consider, this identification is generally not possible.

For conciseness we choose to analyze this problem in terms of a nonrelativistic, two-channel, S -wave scattering amplitude. The generalization to include the effects of spin, additional channels, and relativistic kinematics is entirely straightforward. It will be convenient to introduce here the K matrix

$$K = \begin{pmatrix} K_{11} & K_{12} \\ K_{12} & K_{22} \end{pmatrix},$$

which is related to the scattering amplitude T by the matrix equation

$$K = (1 + iT\rho)^{-1}T, \tag{1}$$

where

$$\rho = \begin{pmatrix} E^{1/2} & 0 \\ 0 & (E - M^2)^{1/2} \end{pmatrix}$$

and M^2 is the threshold of the second channel. The advantage obtained by the introduction of K follows from the fact that it does not possess the unitarity cut.

It is entirely straightforward to invert (1) to obtain the elements of T as a function of K . Thus

$$T_{11}\Delta = K_{11}[1 - i(E - M^2)^{1/2}K_{22}] + i(E - M^2)^{1/2}K^2,$$

$$T_{22}\Delta = K_{22}[1 - iE^{1/2}K_1] + iE^{1/2}K^2,$$