ently badly missing. It is in this energy range that detailed information can be obtained on the balance between the contributions to the optical-model potential of the attractive and repulsive components of the nucleon-nucleon interaction. The Dirac-Hartree model could be tested in some detail, since it makes definite predictions on the spin-orbit potential.[4] The latter depends only very weakly on energy and can thus essentially be taken over from Refs. 4 and 6. It will be advisable to perform the analysis of these data with a relativistic optical-model equation, which is best adapted to the Dirac-Hartree theoretical model. Such relativistic wave equations have already been used by Arnold, Clark, and Mercer,[19] in conjunction with phenomenological potentials wells $U_0(r)$ and $U_e(r)$. These were fitted to the available data which correspond to energies larger than 500 MeV.

After the submission of the first version of the present Letter, a paper by Arnold and Clark[20] appeared in which a relativistic optical-model potential is constructed at low energy. These authors also use a σ- and ω-exchange interaction. However, they adopt a folding prescription rather than a self-consistent theory; hence, they use densities as input. Moreover, they do not discuss the value and the shape of the potential at intermediate energy.

We gratefully thank R. Brockmann for having kindly set us detailed results of the calculation described in Ref. 6, and B. C. Clark for a useful correspondence. We acknowledge a stimulating discussion with G. E. Brown.

[1]A. E. S. Green, F. Riewe, M. L. Nack, and L. D. Miller, in *The Nuclear Many-Body Problem*, edited by F. Calogero and C. Ciofi degli Atti, (Editrice Compositori, Bologna, 1973), p. 415, and references therein.
[2]L. D. Miller and A. E. S. Green, Phys. Rev. C 5, 241 (1972).
[3]L. D. Miller, Phys. Rev. C 14, 706 (1976), and references therein.
[4]R. Brockmann and W. Weise, Phys. Rev. C 16, 1282 (1977).
[5]R. Brockmann and W. Weise, Phys. Lett. 69B, 167 (1977).
[6]R. Brockmann, Phys. Rev. C 18, 1510 (1978).
[7]A. E. S. Green, see Ref. 1, p. 771.
[8]J. P. Jeukenne, A. Lejeune, and C. Mahaux, Phys. Rep. 25, 83 (1976).
[9]J. D. Walecka, Ann. Phys. (N.Y.) 83, 491 (1974).
[10]K. Erkelenz, K. Holinde, and R. Machleidt, as quoted in Ref. 6.
[11]W. T. H. Van Oers and H. Haw, Phys. Lett. 45B, 227 (1973).
[12]J. P. Jeukenne, A. Lejeune, and C. Mahaux, Phys. Rev. C 16, 80 (1977).
[13]G. Duhamel, unpublished.
[14]M. Jaminon, C. Mahaux, and P. Rochus, unpublished.
[15]L. R. B. Elton, Nucl. Phys. 89, 69 (1966).
[16]J. P. Jeukenne, A. Lejeune, and C. Mahaux, in *Nuclear Self-Consistent Fields*, edited by G. Ripka and M. Porneuf (North-Holland, Amsterdam, 1975), p. 155.
[17]R. Humphreys, Nucl. Phys. A182, 580 (1972).
[18]W. D. Myers, Nucl. Phys. A204, 465 (1973).
[19]L. G. Arnold, B. C. Clark, and R. L. Mercer, Phys. Rev. C 19, 917 (1979).
[20]L. G. Arnold and B. C. Clark, Phys. Lett. 84B, 46 (1979).

Anticorrelations in Light Scattered by Nonspherical Particles

W. G. Griffin
Cavendish Laboratory, Cambridge University, Cambridge CB3 0HE, United Kingdom

and

P. N. Pusey[(a)]
Royal Signals and Radar Establishment, Malvern WR14 3PS, United Kingdom
(Received 23 July 1979)

We describe both the theory and first experimental realization of a new light-scattering method for studying nonspherical particles in dilute solution. It is based on measuring the cross correlation of signals from two spatially separated detectors each of which receives light from the same *small number* of scatterers. Possible reasons for observed differences between experiment and theory are discussed.

We report an experiment which essentially observes the rotational Brownian motion of a succession of *single*, nonspherical macromolecules. A dilute solution of tobacco mosaic virus (TMV), a rod-shaped particle of length about 300 nm and diameter of about 15 nm, was illuminated by las-

er light and the outputs of two detectors placed in the same plane at scattering angles $\theta_1 = 90°$ and $\theta_2 = -90°$ (Fig. 1) were cross correlated (i.e., their product, with variable time delay, was time averaged). With a strongly focused laser beam, where the scattering volume contained, on average, only about one particle, a small but unambiguous *anti*correlation was observed [i.e., the value of the cross-correlation coefficient at zero delay time was *less* than its value at later times (Fig. 1)].

This observation has a simple qualitative explanation: If, for example, at some instant the particle lies in the scattering plane and its long axis bisects the angle θ_1 between the beam and detector 1 (Fig. 1), there is virtually no phase shift in the light scattered by different parts of the particle into this detector which therefore receives a strong signal [Eq. (2) with $\varphi = 90°$]. However, for a particle in this orientation, there is an optical path difference of about one wavelength between the light scattered from either end of the particle into detector 2 which, due to destructive interference, [Eq. (2) with $\varphi = 0°$]. Clearly, then, strong anticorrelations exist for certain particle orientations. The theory (see below) shows that

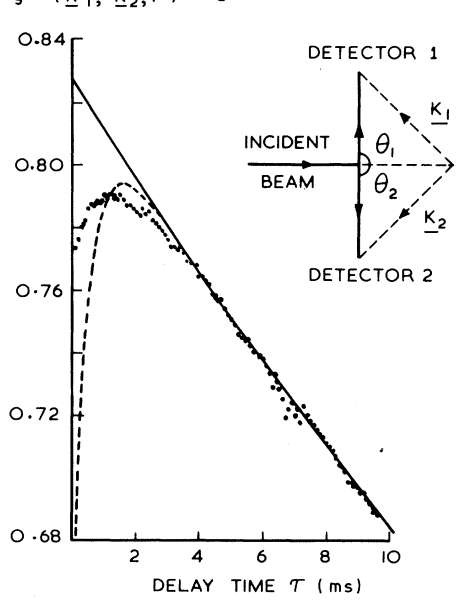

FIG. 1. Upper right: Plan view of deployment of detectors with relevant scattering angles and vectors. Lower left: Time-dependent part of normalized intensity cross-correlation function vs delay time τ. Points, experimental results; solid line, translational (number fluctuation) part of correlation function; dotted line, full theoretical prediction.

a small effect survives the full average over orientation as the particle executes its rotational Brownian motion.

In general, the variation with scattering angle (and/or light) wavelength of the magnitude and sign of this cross-correlation coefficient should be a sensitive indicator of particle size and shape while its temporal rate of decay will provide a measure of the rotational diffusion coefficient.

This experiment falls into a third, relatively new, category of light-scattering methods which provide characterization of particles in dilute solution. The first method, so-called conventional light scattering, measures the angular variation (due to intraparticle interference) of the average scattered intensity from which the radius of gyration can be deduced. The second method, intensity fluctuation spectroscopy[1] (IFS), measures the normalized temporal autocorrelation function of the intensity of the fluctuating diffraction/interference pattern arising from the scattering of coherent light by many particles in Brownian motion. This provides translational and rotational diffusion coefficients. The third, new, method is IFS with a scattering volume V small enough to contain only a small number $\langle M \rangle$ of scatterers.[2] Then a new term, of relative magnitude $\langle M \rangle^{-1}$, enters the intensity correlation function. For spherical particles this term is associated with fluctuations in the instantaneous particle number M as particles diffuse in and out of V[2-4]; for nonspherical particles it depends also on orientational and configurational motions.[4,5] Since the amplitude of the electric field of light scattered by a large number of particles is a complex Gaussian random variable, method 2 is often referred to as *Gaussian* IFS whereas method 3 is *non-Gaussian* IFS.[4]

The experiment reported here appears to be one of the first performed in the non-Gaussian regime on nonspherical particles involving more than one detector. However, some of the principles underlying the experiment have been discussed recently by Kam,[5] albeit from a somewhat different point of view.

We consider a large volume V_S of sample containing a large number N of noninteracing particles and assume that the scattered light originates from a small volume V defined by an illumination profile $b(\vec{r})$, $\vec{r}$ being the position vector. The instantaneous amplitude of the scattered field can then be written

$$E(\vec{K}, t) \propto \sum_{i=1}^{N} a_i(\vec{K}, t) b(\vec{r}_i(t)) \exp[i\vec{K} \cdot \vec{r}_i(t)], \quad (1)$$

where $\vec{K}$ is the usual scattering vector (Ref. 1, p. 26) and, for a rod-shaped particle of length L and radius $\ll\lambda$, the light wavelength, the orientational factor $a(\vec{K},t)$ is (Ref. 1, p. 166)

$$a(\vec{K},t)=\frac{1}{L}\int_{-L/2}^{L/2}\exp[iKx\cos\varphi(t)]dx, \tag{2}$$

where $\varphi(t)$ is the instantaneous angle at time t between $\vec{K}$ and the long axis of the rod. The instantaneous position of the center of mass of the particle is $\vec{r}_i(t)$ and we have assumed the illuminating intensity to vary negligibly over distance L for all $\vec{r}_i$ and φ (see below for discussion of this assumption). With the assumption that $V^{1/3}\gg K^{-1}$ and that orientational and translational motions are not coupled, it can, following previous treatments,[2,4,6] be shown that the normalized intensity *auto*correlation function is

$$g^{(2)}(K,\tau)\equiv\langle I(K,0)I(K,\tau)\rangle/\langle I(K)\rangle^2 =1+\beta[g^{(1)}(K,\tau)]^2+g_{\mathrm{NG}}{}^{R}(K,\tau)g_{\mathrm{NG}}{}^{T}(\tau). \tag{3}$$

Here the intensity $I(K,t)\equiv|E(K,t)|^2$, τ is the correlation delay time, and β is a constant of order 1. For a rod-shaped particle the normalized field correlation function is (Ref. 1, p. 179)

$$g^{(1)}(K,\tau)=B_0(KL)\exp(-D_TK^2\tau)+B_1(KL)\exp[-(D_TK^2+6D_R)\tau]+\cdots, \tag{4}$$

where B_0, B_1, etc., are calculable numerical coefficients, and D_T and D_R are, respectively, the translational and rotational diffusion coefficients. $g_{\mathrm{NG}}{}^{R}(K,\tau)$ is the normalized orientational part of the non-Gaussian term and $g_{\mathrm{NG}}{}^{T}(\tau)$ is its translational or number-fluctuation part which, for a "three-dimensional Gaussian" scattering volume[4,6,7] (see below) of radius σ, takes the form

$$g_{\mathrm{NG}}{}^{T}(\tau)=\langle M\rangle^{-1}[1+(4D_T\tau/\sigma^2)]^{-3/2}, \tag{5}$$

where the average number of particles in the scattering volume is given by $\langle M\rangle=NV/V_S$ and $V=(\pi\sigma^2)^{3/2}$. In the case of *cross* correlation with two spatially separated detectors the second, interference term in Eq. (3) is absent and, in the third term,

$$g_{\mathrm{NG}}{}^{R}(\vec{K}_1,\vec{K}_2,\tau) =\langle a^2(\vec{K}_1,0)a^2(\vec{K}_2,\tau)\rangle/\langle a^2(K_1)\rangle\langle a^2(K_2)\rangle. \tag{6}$$

Evaluation of Eq. (6) follows similar lines to Pecora's original derivation of Eq. (4) (Ref. 1, p. 177) and involves tedious but straightforward algebra. The exponential factors in the a's [Eq. (2)] are expanded in terms of spherical harmonics and spherical Bessel functions j_n [see Eq. (4.31) of Brink and Satchler[8]]. The transition probability density for rotational Brownian motion is also written in terms of spherical harmonics (Ref. 1, p. 121). Addition theorems for spherical harmonics (Ref. 8, p. 146) are then used to perform the angular integrals and to obtain the final result

$$\langle a^2(\vec{K}_1,0)a^2(\vec{K}_2,\tau)\rangle=\sum_{l\ \mathrm{even}}(2l+1)P_l(\cos\Phi)\exp[-l(l+1)D_R\tau]\sum_{\substack{p,p'\\ \mathrm{even}}}\sum_{\substack{q,q'\\ \mathrm{even}}}(i)^{p+q-p'-q'}(2p+1)(2p'+1)(2q+1) \times(2q'+1)I_p(K_1)I_{p'}(K_1)I_q(K_2)I_{q'}(K_2)\begin{pmatrix}l&p&p'\\0&0&0\end{pmatrix}^2\begin{pmatrix}l&q&q'\\0&0&0\end{pmatrix}^2, \tag{7}$$

where

$$I_p(K)=\frac{2}{KL}\int_0^{KL/2}j_p(y)dy,$$

P_l is a Legendre polynomial, Φ is the angle between $\vec{K}_1$ and $\vec{K}_2$ and the relevant 3-j symbols are tabulated in Ref. 8 (p. 35). Combination of Eq. (7) with the result (Ref. 1, p. 167)

$$\langle a^2(K)\rangle=\frac{2}{KL}\int_0^{KL}\frac{\sin y}{y}dy+\left(\frac{2\sin(KL/2)}{KL}\right)^2 \tag{8}$$

gives $g_{\mathrm{NG}}{}^{R}(\vec{K}_1,\vec{K}_2,\tau)$.

The sample was prepared in 50-millimolar phosphate buffer (pH 7) by filtration through a Millipore filter (pore size 0.22 μm) into a clean Pyrex cell of cross section 1 cm×1 mm. The beam, of power about 8 mW, from a He-Ne laser ($\lambda=633$ nm) was expanded to fill a microscope objective of numerical aperture 0.25 which focused it into the cell. Two similar objectives at 90° either side of the cell cast images (magnification about 30 ×) of the focal region onto 25-μm circular apertures in front of two photomultiplier tubes (PMT's) which operated in the photon-counting mode. The auto- and cross-correlation functions were computed by a digital correlator. The PMT-

aperture combinations were mounted on x-y-z micropositioning devices. These were adjusted until the non-Gaussian parts of the individual *auto*-correlation functions [the last term in Eq. (3)] took on maximum values, implying smallest $\langle M\rangle$ and V [Eq. (5)] and hence a good imaging of the focal region. One detector was then adjusted for maximum cross correlation. With a large scattering volume which contained many particles, measurements were also made of the field correlation function $g^{(1)}(K,\tau)$ [Eqs. (3) and (4)] to check the TMV parameters against previous measurements; all measurements were made at 21 ± 1 °C.

To analyze the large-scattering-volume results it was assumed that the virus was 300 nm long with $D_R = 318\ s^{-1}$.[9] The data were then fitted with Eq. (4), values of B_0 and B_1 being obtained from Ref. 1, p. 181. This gave $D_T = 3.14\times10^{-8}$ cm^2/s (corrected to 20 °C) which is within the range found by other authors.[10]

Results of the small-scattering-volume cross-correlation measurements are shown in Fig. 1, where four experiments, each of duration about 10^3 s, have been averaged. As expected from the earlier discussion these results clearly represent the product of a growing term [$g_{NG}{}^R$ in Eq. (3)], with time constant of order $D_R{}^{-1}$, and a decaying term [$g_{NG}{}^T$ in Eq. (3)]. The optical arrangement described above provides a scattering volume which is smeared by diffraction and, for simplicity, we assume the illumination profile to be $b(\vec{R}) = \exp(-|\vec{R}|^2/\sigma^2)$, where $\vec{R}$ is measured from the center of the scattering volume (i.e., a "3D Gaussian" profile[4,7]). It was found that the longer-time part of the observed correlation function could be reasonably well fitted (the solid line in Fig. 1) by Eq. (5) with $\sigma = 1$ μm (implying $V \approx 6$ μm^3) and $\langle M\rangle = 1.21$.

Equations (7) and (8) were evaluated for $D_R = 318\ s^{-1}$ and $KL = 5.6$ ($L = 300$ nm, $\lambda = 476$ nm in the solution and $\theta = 90°$). With $l = 0$ (the τ-independent term), four terms of the quadruple sum in Eq. (7) were enough to give almost perfect agreement with $\langle a^2(K_1)\rangle\langle a^2(K_2)\rangle$ calculated from Eq. (8). Five $l = 2$ terms were evaluated, the negative value of this contribution arising from the fact that $P_2(\cos 90) = -0.5$. The $l = 4$ terms gave a small, positive, rapidly decaying contribution, not shown in Fig. 1. The dashed line in Fig. 1 is the theoretical prediction for the third term in Eq. (3), the product of $g_{NG}{}^R(\vec{K}_1,K_2,\tau)$ (evaluation just described) and $g_{NG}{}^T(\tau)$, Eq. (5) with values of $\langle M\rangle$, D_T, and σ given above.

The data clearly show qualitatively the features predicted by the theory, namely, an anticorrelation decaying in about 1 ms. However, quantitative agreement was not found. The most likely explanation of the marked reduction, observed experimentally, of the amplitude of the anticorrelation is significant variation of the illuminating intensity over a single particle ($\sigma \approx 1$ μm compared with $L \approx 0.3$ μm). This will prevent total destructive interference (on which the magnitude of the anticorrelation depends crucially) from occuring in the light scattered by a particle, whatever its orientation. Attempts to incorporate this effect into the theory lead to discouraging complications. The more promising approach, use of a larger scattering volume (larger σ), will place more stringent requirements on equipment alignment and sample cleanliness (since more dilute samples will have to be used and the passage of just a single large dust particle through the scattering volume could seriously distort the measured correlation function). However this approach, which should be possible in a carefully designed experiment, has the advantage of giving a greater separation between the time scales of the rotational and translational contributions (since $g_{NG}{}^T$ depends on σ, whereas $g_{NG}{}^R$ does not).

In conclusion, we have demonstrated the feasibility of a new, two-detector, non-Gaussian light-scattering method for characterizing nonspherical particles in solution. Significant difficulties remain with both theory and experiment and further detailed work will be necessary to determine whether experiments of this type can actually fulfill their undoubted potential.

We thank Dr. P. J. G. Butler for the kind gift of the TMV, Dr. M. C. A. Griffin for assistance with sample, preparation, and Dr. R. J. A. Tough for checking the derivation of Eq. (7).

---

[a]Corresponding author to whom reprint requests should be sent.

[1]B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976).

[2]D. W. Schaefer and B. J. Berne, Phys. Rev. Lett. 28, 475 (1972).

[3]M. Weissman, H. Schindler, and G. Feher, Proc. Nat. Acad. Sci. USA 73, 2776 (1976).

[4]P. N. Pusey, in *Photon Correlation Spectroscopy and Velocimetry*, edited by H. Z. Cummins and E. R. Pike (Plenum, New York, 1977).

[5]Z. Kam, Macromolecules 10, 927 (1977).

[6]P. N. Pusey, to be published.

[7]D. W. Schaefer, Science 180, 1293 (1973).
[8]D. M. Brink and G. R. Satchler, *Angular Momentum* (Oxford Univ. Press, Oxford, 1968).
[9]J. Newman and H. L. Swinney, Biopolymers 15, 301 (1976).
[10]H. Z. Cummins, in *Photon Correlation and Light Beating Spectroscopy*, edited by H. Z. Cummins and E. R. Pike (Plenum, New York, 1974).

Experimental Evidence for Interference Effect in *K*-Shell–Vacancy Sharing

R. Schuch and G. Nolte
Physikalisches Institut der Universität Heidelberg, D-6900 Heidelberg, Federal Republic of Germany

and

H. Schmidt-Böcking and W. Lichtenberg
Institut für Kernphysik der Universität Frankfurt, D-6000 Frankfurt, Federal Republic of Germany

(Received 31 May 1979)

The impact-parameter dependence of K-shell–vacancy sharing has been investigated with collisions of H-like S (S^{15+}) on Ar. An oscillation of the vacany-sharing ratio with impact parameter has been found which is due to the interference of components of the vacancy-sharing amplitude on incoming and outgoing parts of the collision.

In this note we present experimental evidence of an oscillatory structure in the impact-parameter dependence of the ratio of K-x-ray intensities measured with H-like S(15+) on Ar. This structure is interpreted as interference of contributions to the $2p\sigma$-$1s\sigma$ radial coupling amplitude from the incoming and outgoing parts of the collision. This is the first time that such an interference effect in the transition amplitude between atomic inner shells has been observed in energetic heavy-ion–atom collisions.

It is well established[1] that in nearly symmetric heavy-ion–atom collisions the K shell of the heavier collision partner is predominantly excited by $2p\sigma$-$1s\sigma$ radial coupling. In the theoretical calculations[2-5] of this $2p\sigma$-$1s\sigma$ coupling, the so-called K-shell–vacancy sharing, two approaches have been used: *ab initio* calculations and semiempirical formulations based on a simplified model of Demkov.[6] Such a semiempirical formulation[1] can well describe the ratio of total cross sections for K-shell excitation in heavy and light collision partners. Also the observed dependence of the vacancy-sharing ratio on impact parameter[7] was described reasonably well by the semiempirical formulation[3] of Briggs.

For the case where a K vacancy is already present on the incoming part of the collision, the $2p\sigma$-$1s\sigma$ radial coupling may occur on the incoming part as well as on the outgoing part of the collision. These two couplings have a certain phase relation for a fixed trajectory which gives an interference term in the transition amplitude. The phase difference between the two couplings is changed by varying the impact parameter b and an oscillatory structure in the b dependence of the vacancy-sharing ratio should be observed. Such an interference effect has been predicted by Briggs[3] both in a semiempirical formulation and in an *ab initio* calculation for O on Ne for this so-called two-passage vacancy sharing.

The experimental evidence of such an interference structure observed in the present work is a strong evidence for the existence of a definite phase relation between the coupling on incoming and outgoing parts of swift heavy-ion collisions. The interference structure provides a powerful tool for studying quasimolecular wave functions and dynamical couplings for the theoretical models of the $2p\sigma$-$1s\sigma$ vacancy-sharing process.

For an experimental test of this two-passage vacancy-sharing process a 32-MeV H-like S-beam (S^{15+}) was prepared by poststripping and selecting charge state 15+ by the switching magnet at the model EN tandem Van de Graaff accelerator of the Max-Planck-Institut für Kernphysik in Heidelberg. After being collimated to a size of 1 mm^2 with an angular divergency 0.01°, the beam hit a well-localized ($\lesssim$2-mm) windowless Ar gas target of about 0.05 μg/cm^2 thickness to keep charge exchange below 10%. The particles scattered in the angular region from 0.06° to 0.4° were detected simultaneously by a position-sensitive parallel-plate avalanche detector[8]