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Optical phase conjugation through translational and rotational diffusive rearrangements of liquid-dispersed microparticles

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Optical phase conjugation by degenerate four-wave mixing has been achieved in the cw regime in liquid suspensions of polymer microellipsoids. The results clearly show that particle-number-density gratings and orientational gratings are generated within the suspensions over different ranges of the excitation frequency depending upon the beam polarization configuration and the host-liquid viscosity. The measured parameters are in good agreement with a classical model based on light-induced particle diffusive rearrangements.

Diffusive behavior of microparticle liquid suspensions can give rise to large third-order optical nonlinearities through light-induced rearrangements of the particulate distribution function. This occurs because electrostrictive forces and torques act on individual particles and change their equilibrium number density and average orientation. The case of isotropic-particle dispersions, where only the equilibrium number density is modified via translational diffusion processes, has been extensively studied in recent years using water suspensions of quartz or latex microspheres.[1-7] Such translational effects, however, are independent of the light polarization direction and thus just produce a scalar nonlinearity, with relatively high values of the response time ($\tau \sim 200-400$ ms).

Less work has in contrast been done on anisotropic-particle suspensions, where light-induced reorientating processes can also take place via rotational diffusion. As demonstrated by optical Kerr effect[8] (OKE) and ellipse-rotation[9] measurements, these processes give rise to a macroscopic polarization-sensitive optical nonlinearity, described by the $\chi^{(3)}_{ijkl}$ tensor, which shows considerably shorter response times (2.6 ms). Induced-reorientation experiments have also been performed in the microwave range[10,11] by using a graphite-microrod suspension, thus dramatically demonstrating the broadband nature of such electrostrictive processes. Owing to the severe restraints imposed by microwaves, however, just one-dimensional effects have been observed by a waveguide geometry and with a much larger time constant (20 s).

It has not yet been demonstrated, however, that both translational and orientational processes can be effective at the same time and interact with each other, this being the most distinctive characteristic of anisotropic-particle suspensions. Different kinds of particle spatial arrangements should in fact be generated when both the intensity and the polarization state of light are modulated. In four-wave mixing experiments, for instance, theory[12] predicts that particle orientational gratings should set up alone, or be superimposed upon number-density gratings, depending on the nature of the light fringes. In addition, each grating is expected to evolve with its own response time in the non-steady-state regime and thus be effective over different frequency ranges in ac excitation.

In order to investigate such properties we have performed optical phase conjugation by degenerate four-wave mixing (DFWM) in liquid suspensions of polymer microellipsoids. Translational and orientational nonlinearities have been discriminated by an analysis of the conjugate signal versus the pump chopping frequency using different kinds of beam polarization configurations and varying the host-liquid viscosity. A clear evidence of the onsets of the two effects is observed and the values of the measured parameters are in good agreement with theory.

The liquid suspensions used in this study are similar to the ones characterized in previous works[8,9] and consist of polytetrafluoroethylene (PTFE) particles suspended in water-glycerol host solutions, with a concentration of 10 vol % solids in a monodisperse regime. The particle shape is fairly ellipsoidal and the dimensions are $0.2\times0.2\times0.4$ μm^3 with a 10% standard deviation. The bulk intrinsic birefringence of PTFE ($\Delta n = 0.02$),[9] greatly enhances the particle polarizability anisotropy and hence reorientation effects. Measurements of the optical Kerr effect[8] have shown that the orientational nonlinearity of such suspensions can well be described within the model by Rogovin,[12] that assumes the particle suspension as a statistical ensemble of ellipsoidal, noninteracting, rigid rotators immersed in an environment governed by Brownian-like rotational diffusion. Single microellipsoids are optically characterized by a body-fixed microscopic polarizability tensor $\overleftrightarrow{\alpha}_B$ diagonal and uniaxial with respect to the geometrical principal axes, whose eigenvalues are thus $\alpha_\parallel$, $\alpha_\perp$, and $\alpha_\perp$. The action of light on individual particles is considered through the electromagnetic interaction between the optical field $\mathbf{E}(\mathbf{r},t)$ and the induced dipole $\mathbf{p}(\mathbf{r},t)=\overleftrightarrow{\alpha}_\omega \mathbf{E}(\mathbf{r},t)$, both varying at optical frequencies. Since particles are immersed in a host liquid, electrostrictive torques and forces are opposed by Langevin ones, which tend to wash out the optically formed arrangements of particles. To work out the macroscopic optical behavior of the suspension a statistical calculation is therefore carried out with the thermodynamic average over the ensemble and assuming the Maxwell-Boltzmann distribution for the equilibrium perturbed particle distribution function $n(\mathbf{r},\mathbf{\Omega})$ [where $\mathbf{r}$ and $\mathbf{\Omega}=(\phi,\theta)$ are the particle angular and translational coordinates]. The general expression of the third-order polarizability of the suspension in terms of the microscopic particle parameters is therefore obtained:[12]

$$\mathbf{P}^{(3)}(\mathbf{r},t)=n_0\frac{\alpha_s^2(\omega)}{2kT}[\bar{E}^{\,2}(\mathbf{r},t)-\langle\langle \bar{E}^{\,2}(\mathbf{r},t)\rangle\rangle]\mathbf{E}(\mathbf{r},t)+n_0\frac{\beta^2(\omega)}{18kT}\overline{\langle(\mathbf{E}\cdot\overleftrightarrow{\mathbf{K}}\cdot\mathbf{E})\overleftrightarrow{\mathbf{K}}\cdot\mathbf{E}(\mathbf{r},t)\rangle}\ , \tag{1}$$

where $\overleftrightarrow{\mathbf{K}}(\mathbf{\Omega})$ is the orientation matrix, n_0 is the unperturbed distribution function, $\beta=\alpha_{\parallel}-\alpha_{\perp}$ and $\alpha_s=\frac{1}{3}(\alpha_{\parallel}+2\alpha_{\perp})$, the angular brackets imply a spatial average over the entire volume of the suspension as well as an average over the orientation angles, and the bars imply an average over many optical periods, required because of the particle inertia. Equation (1) clearly shows that translational effects are involved in the scalar coefficient of $\mathbf{E}(\mathbf{r},t)$ in the first term, whereas rotational effects are represented by the tensorial transformation in the second term and the two processes are not coupled at the third order.

By specifying the frequencies and the wave vectors of the fields in Eq. (1) detailed predictions of nonlinear effects can be obtained. Specifically, in the case of phase conjugation by DFWM, the perturbed distribution function of the microparticles under the influence of the light gratings can be obtained and related to the specific values of the conversion coefficients κ_T and κ_R, where the subscripts T and R refer to the translational and orientational gratings, respectively, which determine the conjugation efficiency $\eta=\tan^2(\kappa L)$ (L is the beam-interaction length). It is worth pointing out that, because of the noncoupling in Eq. (1), the contributions of the two gratings, when present, add coherently in generating conjugated waves. The effective conversion coefficient is thus

$$\kappa=\kappa_T+\kappa_R\ . \tag{2}$$

The transient behavior of the particle arrangement can be studied by a nonequilibrium statistical treatment and solving the Plank-Nerst equation for the perturbed distribution function. In the case of a transient steplike light excitation, the induced distribution-function changes Δn show the exponential, low-pass form[12]

$$\Delta n(\mathbf{r},\Omega,t)=\Delta n_T(\mathbf{r},\mathbf{\Omega},\infty)[1-\exp(-t/\tau_T)]+\Delta n_R(\mathbf{r},\mathbf{\Omega},\infty)[1-\exp(-t/\tau_R)]\ , \tag{3}$$

where the time constants τ_T and τ_R depend upon the particle geometrical parameters and are proportional to the host-liquid viscosity.

A standard ring-type geometry was used for the DFWM experimental setup,[7] with the 514-nm, 2-W TEM_{00} output of an Ar^+ laser and a probe-to-pump intensity ratio of 0.05. The pump and probe beams were focused down to a 50-μm-diam spot into a 1-mm-thick optical cell filled with the PTFE suspension and the estimated coarse and fine grating periods were, respectively, 4 and 0.25 μm. A mechanical chopper was placed in the optical path of the grating-writing pump beam so as to allow a lock-in detection technique and versus-frequency measurements.

Measurements of the conjugate beam intensity versus the pump intensity are shown in Fig. 1 for a 10 vol % suspension of PTFE ellipsoids in water and with all the pump and probe waves linearly polarized and parallel to each other (we will define this configuration with $\uparrow\uparrow\uparrow$). The pump chopping frequency was 20 Hz. The circles are the measured data, while the solid line represents the polynomial best fit obtained with a first and a third power term. This shows that the typical cubic power dependence of the conjugate signal in the weak-field limit is verified and is superimposed on a linear dependence due to the scattered light. Theory[12] predicts that in these polarization conditions both the particle-number-density grating and the orientational grating set up in the suspension. A higher particle concentration and a preferred alignment along the polarization direction should therefore coexist in the bright fringe areas, and the phase conjugated signal should arise from both gratings. However, the chopping period used in these measurements (0.05 s) was considerably shorter than the formation time of the number-density grating, which can be estimated at 0.45 s.[12] It can thus be assumed that only the orientational grating contributes to the data of Fig. 1. The measured conjugation efficiency was $\eta=0.022$ for a pump power density of 50 $\mathrm{kW/cm^2}$ and it corresponds to $\chi^{(3)}_{1111}=(1.3\pm0.7)\times10^{-8}$ esu units. This value of the diagonal elements of the $\chi^{(3)}$ tensor compares well with the one of $\chi^{(3)}_{1221}=(1.7\pm0.7)\times10^{-8}$ esu previously obtained from the ellipse-rotation effect[9] (in isotropic media it should be[13] $\chi^{(3)}_{1111}=\frac{4}{3}\chi^{(3)}_{1221}$).

In order to verify the orientational nature of the signal, measurements of the conjugate beam intensity versus the chopping frequency have been carried out in the same suspension and polarization configuration as above and are reported in Fig. 2 (circles). The data show the expected low-pass behavior with two 20-dB/decade slopes in accordance with Eq. (3) (note that the conjugate signal is proportional to the square of the induced Δn). The two

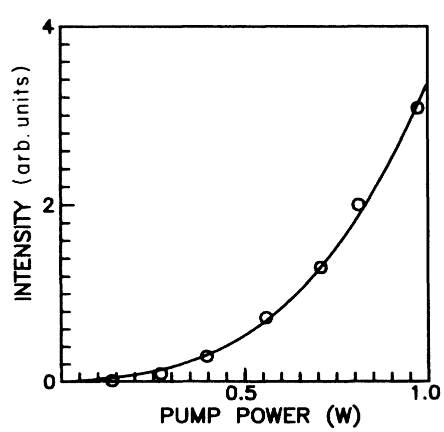

FIG. 1. Conjugate beam intensity as a function of the pump power for a suspension of PTFE microellipsoids in water. All beam polarization vectors are parallel.

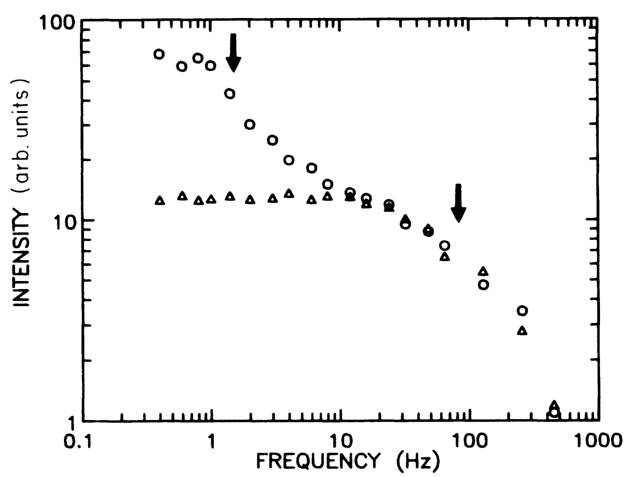

FIG. 2. Frequency response of the phase-conjugation signal for a PTFE suspension in water. Circles and triangles represent the data recorded in the ↑↑↑ and in the ↑→↑ polarization configurations, respectively (see text). The arrows in the graph indicate the cutoff frequencies.

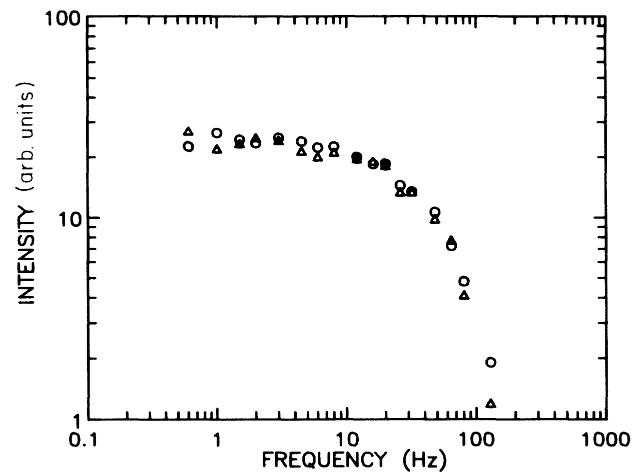

FIG. 3. Frequency response of the phase-conjugation signal for a PTFE suspension in a glycerol-water host solution. Circles and triangles refer to the ↑↑↑ and the ↑→↑ configurations, respectively (see text).

points at -6 dB are approximately at 80 and 1.5 Hz, respectively (the two arrows in the graph). The 80-Hz point gives a value of the grating time constant $\tau \sim 2.1 \pm 0.3$ ms, which is in reasonable good agreement with the one obtained from the OKE measurements[8] $\tau = 2.6 \pm 0.2$ ms and with the theoretical value of the rotational-diffusion time[12] $\tau_R = 2.7$ ms. The slope in the high-frequency side of the graph can thus be attributed to the cutoff of reorientating effects. Accordingly, the low-frequency slope can be interpreted as due to the cutoff of the translational effects, even though the 1.5-Hz point gives a value for the time constant of the number-density grating $\tau_T = 110 \pm 40$ ms, which does not agree with the theoretical one[12] previously mentioned, $\tau_T = 450$ ms. This disagreement, however, may be due to the great difficulties in using lock-in techniques at very low frequency because of large signal fluctuations caused by the slow thermal convection.

The above interpretation is dramatically verified by just rotating the "writing"-pump beam polarization vector to the direction orthogonal to the probe and the second pump beam polarization direction (↑→↑). In this configuration number-density gratings cannot in fact be generated within the suspension, as no intensity fringes are produced by two orthogonally polarized beams. In contrast, polarization fringes set up and give rise to a particular orientational grating that is expected to generate a conjugate beam linearly polarized perpendicular to the probe polarization vector.[12] The predicted conjugate beam polarization direction has been verified experimentally[14] and the signal intensity versus frequency is reported by triangles in Fig. 2. It is clearly shown that the low-frequency (translational) cutoff has disappeared, as expected, and the frequency response of the suspension is flat from the minimum recorded value (0.4 Hz) up to the orientational cutoff, which does not show any appreciable changes. It should be noted that the two sets of data in Fig. 2 are not plotted in the same absolute scale, as the orientational conjugate signal in the ↑↑↑ configuration was 3.3 times larger than the one in the ↑→↑ configuration, in accordance with the predictions concerning polarization-dependent conjugate field amplitude.[14] Triangles have therefore been multiplied by such a numerical factor in order to compare the two curves more easily.

Versus-frequency measurements also give physical insight into the steady-state characteristics of the optical nonlinearity, and that is the dominating role of translational effects in the low-frequency range. The signal in fact increases by approximately a factor of 6 over the orientational background. This is due to the relatively low anisotropic component of particle polarizability $\beta(\omega)$ with respect to the isotropic one, $\alpha_s(\omega)$. An experimental value of $\kappa_R/\kappa_T = 0.34 \pm 0.04$ is derived and it is in satisfactory agreement with the theoretical value[12] of 0.42, as evaluated using the microscopic parameters of present PTFE microellipsoids.

Finally, measurements with a PTFE suspension in a 30 vol % glycerol-in-water solution have been performed in order to extend the study to different values of the host-liquid viscosity and refractive index. Circles and triangles in Fig. 3 refer to the data recorded in the ↑→↑ and ↑↑↑ configurations, respectively. The orientational cutoff point has now shifted to 35 ± 5 Hz, in agreement with the value of 30 Hz expected from the 2.6 times larger viscosity of the glycerol-water solution compared with the one of pure water. Translational effects are not visible even in the ↑↑↑ polarization configuration, and it is mainly due to the matching between the average refractive index of the PTFE particles (1.376) and the one of the host solution (1.378). This matching in fact decreases by approximately a factor of 6 the Rayleigh-Gans scattering cross section of the suspension and consequently the translational nonlinear processes, because of the proportionality between these two effects.[2] Such a decreasing factor, in addition to the shift in the cutoff towards the lower frequencies, accounts for the lack of translational effects in the range under consideration, whereas it does not appreciably affect the rotational nonlinearity.[9] This, besides the different time constants, is one of the most striking differences between translational and orientational particle gratings, as also predicted by the diffusive models.

In conclusion, we have demonstrated that both translational and orientational light-induced particle gratings set up in liquid suspensions of anisotropic dielectric microparticles through diffusive rearrangements. Scalar and tensorial third-order optical nonlinearities are therefore generated with different time responses and both contribute to optical phase conjugation in DFWM experiments. The results show that the steady state and especially the dynamic properties of light-induced diffusive processes can be experimentally controlled, and are well described by a simple classical model.

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