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Pump grating-modulation effects in liquid suspensions of microspheres

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Degenerate four-wave mixing is examined for arbitrarily strong pump field interactions using a liquid suspension of Brownian microparticles as the active medium. It is shown that pump-generated interactions act to modulate the field-induced translational particle gratings in a novel way which greatly modifies both the steady-state and the transient properties of such media. Of particular interest is the fact that four-wave mixing in suspensions is radially different for the case of an attractive versus repulsive electrostrictive coupling between the microparticles and the pump radiation.

The macroscopic electrodynamics of liquid suspensions of microparticles has long been of interest to the physics community.[1-3] Of particular interest to us is their use as active media to produce phase-conjugate radiation via degenerate four-wave mixing.[4-6] For media composed of liquid suspensions of microspheres, electrostrictive forces redistribute the particle density in such a way that two orthogonal translational gratings are created. Coherent scattering of pump radiation from these gratings gives rise to the formation of the conjugate wave. A key feature of this process is that translational gratings arising from the interaction of the microparticles with the pump radiation alone play no direct role in phase conjugation. Nevertheless, in this Rapid Communication, we demonstrate that if the pump beams are sufficiently intense, these gratings can vastly alter the four-wave mixing characteristics of the suspension through a nonlinear modulation of the orthogonal gratings. Specifically, the pump-generated grating beats with and modulates the gratings formed by the pump and probe beams to produce two additional gratings that can generate phase-conjugate radiation. This feature of grating electrodynamics gives rise to a rather novel behavior of the four-wave mixing coefficient κ and of the nonequilibrium statistical mechanics of the suspension. Depending on the sign of the particle-field electrostrictive coupling constant, these additional gratings can either emit in or out of phase with respect to the original gratings. Specifically, if the gratings emit out of phase, the four-wave mixing coefficient asymptotically approaches a value that is independent of pump intensity. However, if the gratings emit in phase, the four-wave mixing coefficient asymptotically exhibits a linear dependence on pump intensity and in fact approaches a value that is twice the weak-field form. The transient behavior of the suspension is also significantly modified by the formation of intense pump gratings. Response times for grating formation in the weak-field regime are set by Λ^2/D, where D is the diffusion constant for particles in the suspension, and Λ is the grating spacing. In general, there are two spacings for the orthogonal gratings and therefore two grating response times in this regime.[5] We find, however, that if the pump radiation is sufficiently intense, there is only one grating response time and this is a consequence of the locking, via modulation with the pump grating, of these two additional gratings. Furthermore, if the electrostrictive coupling between the pump and the microparticles is attractive, the gratings that emit conjugate waves are formed on a much shorter time scale than Λ^2/D, even in the limit of an arbitrarily weak probe wave. Alternatively, if the coupling is repulsive, these gratings are created predominantly by particle diffusion, and steady-state conjugate radiation appears on a time scale set by Λ^2/D. We refer to this class of phenomena as pump grating modulation effects.

To understand the origin of pump grating modulation effects, consider the interaction of a collection of identical microspheres, with two intense counterpropagating pump waves, $\mathbf{E}_1\cos(\mathbf{K}\cdot\mathbf{r}-\omega t)$ and $\mathbf{E}_2\cos(\mathbf{K}\cdot\mathbf{r}+\omega t)$, and a weak probe beam, $\boldsymbol{\varepsilon}_p(\mathbf{r},t)=\frac{1}{2}E_p e^{i(Q\cdot\mathbf{r}-\omega t)}+\text{c.c.}$ Then, the electrostrictive coupling between the radiation fields and microparticles is

$$U(\mathbf{r})=-\tfrac{1}{4}\alpha(\omega)\sum_{i\neq j}(\mathbf{E}_i\cdot\mathbf{E}_j^*)\exp[i(\mathbf{K}_i-\mathbf{K}_j)\cdot\mathbf{r}]+\text{c.c.}\,,$$
$$=\tfrac{1}{2}\sum U_{ij}\cos[(\mathbf{K}_i-\mathbf{K}_j)\cdot\mathbf{r}]=U_0\cos(2\mathbf{K}\cdot\mathbf{r})+\delta U(\mathbf{r}). \quad (1)$$

Here, $U_0\cos(2\mathbf{K}\cdot\mathbf{r})$ is the electrostrictive coupling between the microparticles and the pump beams, $\delta U(\mathbf{r})$ is the coupling between a pump beam, the particles and either the probe or conjugate wave. The coupling between the particles and the probe and conjugate waves is neglected. In Eq. (1), U_{ij} is an electrostrictive coupling constant and $\alpha(\omega)$ is the polarizability of a given microparticle. The grating pattern defined by Eq. (1) orders the microparticles such that in steady state the particle density $n(\mathbf{r})$ is given by the Maxwell-Boltzmann distribution.

If we limit the analysis to situations in which the probe wave is weak, the electrostrictive coupling between the microparticles and the pump and probe waves can be treated with first-order perturbation theory. However, the interaction between the microparticles and the pump waves alone is large and must be treated exactly. Accordingly, we may write the steady-state distribution as, with n_0 the

microparticle density in the absence of radiation,

$$n(\mathbf{r}) = n_0\left[1+2\sum_{l=1}^{\infty}(-1)^l\frac{I_l(U_0/k_BT)}{I_0(U_0/k_BT)}\cos(2l\mathbf{K}\cdot\mathbf{r})\right]\times\left[1-\frac{\delta U(\mathbf{r})}{k_BT}\right], \quad (2)$$

where $I_l(z)$ is the lth order modified Bessel of argument z.[6] The first bracketed term on the right-hand side of Eq. (2) represents spatial gratings of spacing $\Lambda_l = \pi/l|K|$ due to the electrostrictive interaction between the microparticles and the pump radiation alone. The strength of each grating is of order $I_l(U_0/k_BT)/I_0(U_0/k_BT)$, so that gratings of order $l < U_0/k_BT$ are substantially occupied. Note that a single microparticle can reside in more than one grating, a fact that greatly influences the strong-field behavior of these media.

An examination of Eq. (2) reveals that two sets of terms contribute to phase conjugation. These are the terms contributing to only that part of the density distribution which varies spatially as $\mathbf{K}\pm\mathbf{Q}$. The first of these, which we denote by $\delta n_1(\mathbf{r})$, consists of particles which are in the gratings set up by the probe or conjugate wave and one of the pump beams:

$$\begin{aligned}\delta n_1(\mathbf{r}) &= -n_0\frac{\delta U(\mathbf{r})}{k_BT}\\ &= n_0\frac{\alpha(\omega)}{2k_BT}\mathrm{Re}\{\mathbf{E}_1\cdot\mathbf{E}_p^*\exp[i(\mathbf{K}-\mathbf{Q})\cdot\mathbf{r}]+\mathbf{E}_2\cdot\mathbf{E}_p^*\exp[-i(\mathbf{K}+\mathbf{Q})\cdot\mathbf{r}]\\ &\quad+\mathbf{E}_1\cdot\mathbf{E}_c^*\exp[i(\mathbf{K}+\mathbf{Q})\cdot\mathbf{r}]+\mathbf{E}_2\cdot\mathbf{E}_c^*\exp[-i(\mathbf{K}-\mathbf{Q})\cdot\mathbf{r}]\}, \quad (3)\end{aligned}$$

where the conjugate wave $\boldsymbol{\varepsilon}_c(\mathbf{r},t) = \frac{1}{2}\mathbf{E}_c\exp[-i(\mathbf{Q}\cdot\mathbf{r}+\omega t)]+\text{c.c.}$ Equation (3) describes the gratings which exist in the weak pump field regime. At higher pump intensities the $l=1$ term in Eq. (2) introduces the second set of translational gratings which contribute to phase conjugation:

$$\begin{aligned}\delta n_2(\mathbf{r}) &= 2\frac{I_1(U_0/k_BT)}{I_0(U_0/k_BT)}n_0\left\langle\frac{\delta U(\mathbf{r})}{k_BT}\cos(2\mathbf{K}\cdot\mathbf{r})\right\rangle,\\ &= -n_0\frac{I_1(U_0/k_BT)}{I_0(U_0/k_BT)}\frac{\alpha(\omega)}{2k_BT}\mathrm{Re}\{\mathbf{E}_1\mathbf{E}_p^*\exp[-i(\mathbf{K}+\mathbf{Q})\cdot\mathbf{r}]+\mathbf{E}_2\mathbf{E}_p^*\exp[i(\mathbf{K}-\mathbf{Q})\cdot\mathbf{r}]\\ &\quad+\mathbf{E}_1\mathbf{E}_c^*\exp[-i(\mathbf{K}-\mathbf{Q})\cdot\mathbf{r}]+\mathbf{E}_2\mathbf{E}_c^*\exp[i(\mathbf{K}+\mathbf{Q})\cdot\mathbf{r}]\}, \quad (4)\end{aligned}$$

where the angle brackets imply that we extract from the product only those terms which vary spatially as $\mathbf{K}\pm\mathbf{Q}$. Physically, the δn_2 contribution arises from modulation of the weak-field grating (δn_1) with the first-order grating generated by the intense pump waves. As a manifestation of the nonlinear response of the medium, this term is seen to mix the $\mathbf{K}+\mathbf{Q}$ and $\mathbf{K}-\mathbf{Q}$ components of the density distribution.

Associated with each of these two sets of microparticle gratings is a third-order polarization capable of generating phase-conjugate radiation, as well as amplifying the probe beam. If the polarization of the pump waves is parallel with $\mathbf{E}_1=\mathbf{E}_2$, we find for the four-wave mixing coefficient[5] from Eqs. (2)–(4),

$$\begin{aligned}\kappa &= \frac{3f}{2\lambda}\varepsilon_h\left(\frac{\varepsilon_r-1}{\varepsilon_r+2}\right)\frac{U_0}{k_BT}\left[1-\frac{I_1(U_0/k_BT)}{I_0(U_0/k_BT)}\right]\\ &= \kappa_0\left[1-\frac{I_1(U_0/k_BT)}{I_0(U_0/k_BT)}\right]. \quad (5)\end{aligned}$$

In Eq. (5), κ_0 is the four-wave mixing coefficient in the diffusive limit, f is the volume fraction of microspheres, ε_h the dielectric constant of the host fluid at ω, ε_r the ratio of the dielectric constant of the microparticles to ε_h, and λ is the laser wavelength. The bracketed factor corrects for nonlinearity in the presence of arbitrarily strong pump field intensities and gives rise to different behavior depending on the sign of U_0. In particular, if $U_0>0$, $\kappa\rightarrow\kappa_s \equiv 3f/4\lambda\varepsilon_h[(\varepsilon_r-1)/(\varepsilon_r+2)]$, and the four-wave mixing coefficient is independent of pump intensity. On the other hand, if $U_0<0$, then $\kappa\rightarrow 2\kappa_0$, and the four-wave mixing coefficient increases linearly with pump power.

In calculations involving intense laser radiation, it is convenient to introduce a saturation intensity I_S defined here by $|U_0|/k_BT \equiv I/I_S$, with I the pump intensity. For 1000-Å ZnSe microspheres suspended in liquid N_2 at 77 K, the saturation intensity at CO_2 wavelengths is 1.59 kW/cm^2. Figure 1 depicts the dependence of the four-wave mixing coefficient on the pump intensity of a suspension of ZnSe microspheres with $f=10^{-2}$ for $U_0>0$ (labeled κ_-) and $U_0<0$ (labeled κ_+). An examination of the κ_- curve reveals that the four-wave mixing coefficient is initially a linear function of pump power, corresponding to the suspension being in the diffusive region. However, once $I/I_S \geq \frac{1}{4}$, grating modulation effects begin to manifest themselves and κ no longer increases linearly with I. Note that the four-wave mixing coefficient for this case peaks when $I/I_S=1.68$. Further increases in pump power first decrease the size of the four-wave mixing coefficient which eventually saturates to κ_s. Fixing our attention on the κ_+ curve, we see that the four-wave mixing coefficient departs from a linear pump intensity dependence when $I/I_S \sim \frac{1}{4}$. It then displays a greater than linear dependence on I, eventually achieving a limiting value of $2\kappa_0$.

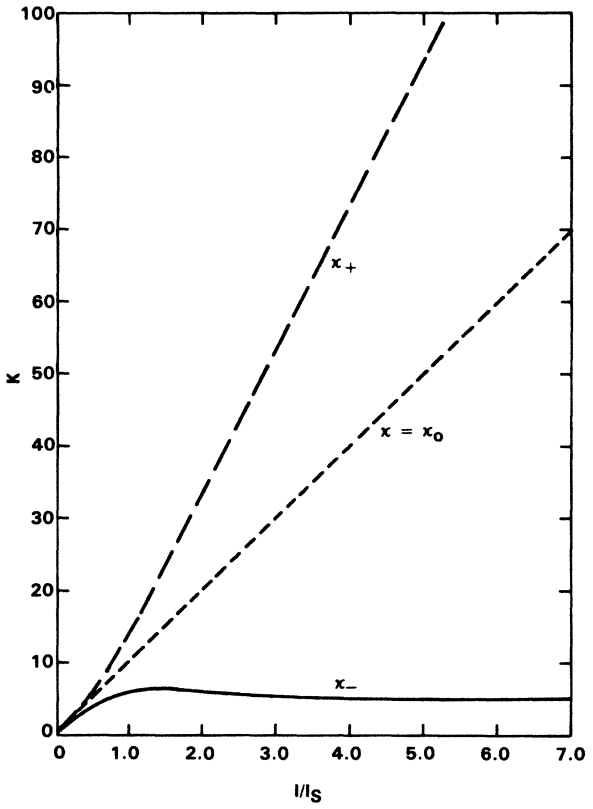

FIG. 1. Four-wave mixing coefficient vs pump intensity for 1000-Å ZnSe microspheres suspended in liquid N_2 at 77 K and irradiated by CO_2 laser beams.

These features of microparticle electrodynamics can be understood as follows. As noted above, the intense pump waves generate a translational grating of the form $\cos(2\mathbf{K}\cdot\mathbf{r})$. Through the nonlinearities of the medium, this grating beats with either of the translational gratings $\cos[(\mathbf{K}+\mathbf{Q})\cdot\mathbf{r}]$ or $\cos[(\mathbf{K}-\mathbf{Q})\cdot\mathbf{r}]$ created by the pump and probe fields to produce a translational grating $\cos[(\mathbf{K}-\mathbf{Q})\cdot\mathbf{r}]$ or $\cos[(\mathbf{K}+\mathbf{Q})\cdot\mathbf{r}]$, respectively, which also emits phase-conjugate radiation. If $U_0>0$, these gratings are out of phase with the initial gratings and the four-wave mixing coefficient decreases in size relative to its weak pump field behavior. Alternately, if $U_0<0$, they are in phase and κ increases relative to its weak-field value, depicted by the dotted curve. In particular, $\kappa_+ \rightarrow 2\kappa_0$ reflects the fact that two sets of translational gratings are now contributing to the emission of phase-conjugate radiation.

Next, we examine the transient dynamics for this system. We shall assume that the pump wave fields remain constant in intensity throughout the experiment and that the pump wave gratings have already been formed when, at time $t=0$, the weak probe field is switched on. Then the initial particle density is

$$n(\mathbf{r},0)=n_0\exp[-(U_0/k_BT)\cos(2\mathbf{K}\cdot\mathbf{r})]/I_0(U_0/k_BT) \ .$$

The subsequent evolution of the particle density $n(\mathbf{r},t)$ is governed by the Planck-Nernst equation[5]

$$\frac{\partial}{\partial t}n(\mathbf{r},t)=D\nabla\cdot\left[\nabla n(\mathbf{r},t)-\frac{\mathbf{F}(\mathbf{r})}{k_BT}n(\mathbf{r},t)\right] , \tag{6}$$

where $\mathbf{F}(\mathbf{r})=-\nabla U(\mathbf{r})$ is the electrostrictive force acting on a particle at position $\mathbf{r}$ in the suspension. It is convenient to transform Eq. (6) by introducing a new quantity, $\eta(\mathbf{r},t)$ of order $\delta U(\mathbf{r})/k_BT$:

$$n(\mathbf{r},t)\equiv n(\mathbf{r},0)\left[1+\eta(\mathbf{r},t)-\frac{\delta U(\mathbf{r})}{k_BT}\right] . \tag{7}$$

Setting $\mathbf{F}(\mathbf{r})=\mathbf{F}_0(\mathbf{r})+\delta\mathbf{F}(\mathbf{r})$, with $\mathbf{F}_0(\mathbf{r})=-\nabla U_0(\mathbf{r})$ and $\delta\mathbf{F}(\mathbf{r})=-\nabla\delta U(\mathbf{r})$, we have to first order in small quantities

$$\frac{\partial}{\partial t}\eta(\mathbf{r},t)=D\left[\nabla^2\eta(\mathbf{r},t)+\frac{\mathbf{F}_0(\mathbf{r})}{k_BT}\cdot\nabla\eta(\mathbf{r},t)\right] , \tag{8}$$

with $\eta(\mathbf{r},t=0)=\delta U(\mathbf{r})/k_BT$ and $\eta(\mathbf{r},t\rightarrow\infty)=0$. Equation (8) can be solved numerically by decomposing the particle density into grating functions[6,7]

$$\eta(\mathbf{r},t)=\sum_{l=-\infty}^{\infty} m_l(t)\cos\{[(2l+1)\mathbf{K}+\mathbf{Q}]\cdot\mathbf{r}\}$$
$$\equiv\sum_{l=-\infty}^{\infty} m_l(t)\,|\,(2l+1)\mathbf{K}+\mathbf{Q}\rangle \ , \tag{9}$$

with the boundary conditions $m_0(0)=\langle\mathbf{K}+\mathbf{Q}\,|\,\delta U(\mathbf{r})/k_BT\rangle$, $m_{-1}(0)=\langle\mathbf{K}-\mathbf{Q}\,|\,\delta U(\mathbf{r})/k_BT\rangle$, and $m_l(0)=0$ otherwise. At long times $m_l(t)$ approaches zero for all l.

At intermediate times, the gratings of order $l\sim U_0/k_BT$ are significantly populated and may influence the electro-

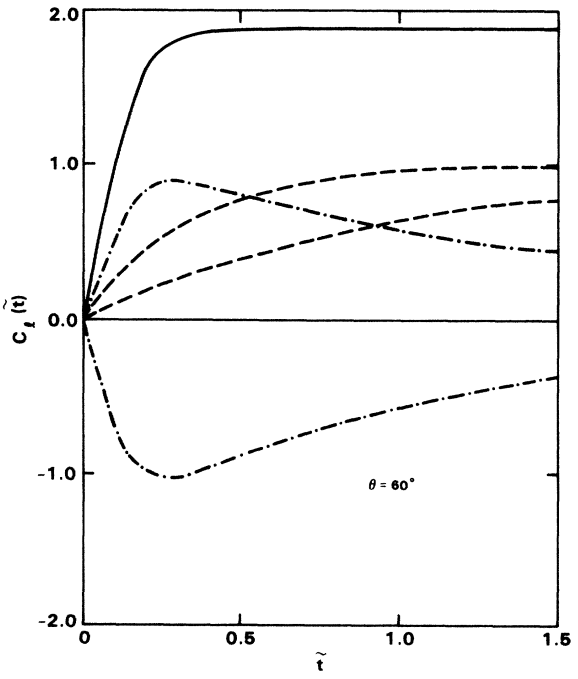

FIG. 2. Transient behavior of the $|\mathbf{K}\pm\mathbf{Q}\rangle$ gratings for the cases $U_0/k_BT=-5$, $U_0/k_BT=+5$ compared to the diffusive limit.

dynamic characteristics of the suspension. In practice we obtain the time-dependent density response for the system by first solving the eigenvalue problem associated with $\eta(\mathbf{r},t)$ and then using Eq. (7).

To study the novel transient behavior arising from pump grating modulation we examine the evolution of the grating components $[C_l(t)=\langle(2l+1)\mathbf{K}+\mathbf{Q}\,|\,n(\mathbf{r},t)\rangle]$, both in presence of strong pump fields and in the diffusive limit. Figure 2 depicts the evolution of the orthogonal gratings $l=0(\mathbf{K}+\mathbf{Q})$ and $l=-1(\mathbf{K}-\mathbf{Q})$ for $I/I_s=5.0$ and a pump-probe angle of 60° as a function of $\tilde{t}=t/\tau_D$, where $\tau_D=(DK^2)^{-1}$ is the time scale set by diffusion. In the diffusive limit, the figure shows two distinct grating formation times proportional to the squares of the corresponding grating spacings (upper dashed curve $l=0$, lower dashed curve $l=-1$). The strong-field behavior is shown by the solid curves (superimposed on the scale of the figure) for $U_0=-5k_BT$ and by the dashed-dotted curves for $U_0=5k_BT$ (upper curve $l=0$, lower curve $l=-1$). The saturation limits of these curves are in correspondence with the curves of Fig. 1 evaluated at $I/I_s=5.0$.

Differences between the dashed curves and the remaining curves of Fig. 2 arise from pump grating modulation. These differences include a locking together of the time response for the $\mathbf{K}+\mathbf{Q}$ and $\mathbf{K}-\mathbf{Q}$ gratings, dependence on the sign of U_0,[8] and a response time component, on a scale set by $\tau_D(I_s/I)$, which can be much faster than that required for diffusive motion over distances comparable to the grating spacing.

Rapid response to the weak probe signal may be understood physically by considering the strong pump limit $(I/I_s\gg1)$. In this limit the eigenfunctions of Eq. (8) approach the Hermite-Gaussian functions with eigenvalues

$$\lambda_n=-(\sin^2\theta+4n\,|U_0|/k_BT)/\tau_D\ , \tag{10}$$

independent of the sign of U_0. The lowest eigenvalue λ_0 describes diffusive motion in the direction perpendicular to the pump propagation and is responsible for the long-time approach to steady state for the $U_0>0$ curves of Fig. 2. In the strong pump limit, particles tend to be localized near their potential energy minima and $n(\mathbf{r},0)$ can be approximated as a periodic set of Gaussian density peaks of width $\sigma=\Lambda/2\pi(k_BT/|U_0|)^{1/2}$, where $\Lambda=\pi/|\mathbf{K}|$.[6] The inverse time for particles to diffuse over this much shorter distance is $D/\sigma^2=4(|U_0|/k_BT)DK^2$ which is comparable to the time scale of the rapid resonse set by λ_1. Although this simple argument ignores the proper weighting by the eigenvector components, which is included in Fig. 2, it does serve to suggest a mechanism for the rapid response even under those conditions where the probe field is too weak for particle drift motion to be significant.

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[8]For experiments on a given suspension, it may be possible to reverse the sign of U_0 by altering the polarization or by inserting a phase delay of π in one of the pump waves.