Optical Nonlinearity of a Colloidal “Non-Ideal Gas” of Nano-Suspensions

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Abstract: We show that many-body effects in stabilized nano-suspensions can have a profound effect on their optical nonlinearity. The nonlinear properties of these colloids can range from polynomial to exponential depending on their composition and chemistry.

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Light-matter interactions via radiation forces play nowadays a crucial and central role in several areas of physics, chemistry and biology. One such example is the rich interdisciplinary field of optical traps or tweezers. High intensity nonlinear interactions in colloidal nano-suspensions such as self-focusing and four-wave mixing were also considered in the seminal work of Ashkin et al [1]. In these early pioneering studies, the optical nonlinearity of colloidal systems was assumed a priori to be of the Kerr type [1]. Quite recently however, two independent theoretical works have indicated that the nonlinear response of such nano-colloids should instead involve an exponential or Boltzmann distribution-consistent with thermodynamics [2,3]. In a subsequent attempt, a hard sphere model for particle-particle interactions was proposed in order to provide nonlinearity saturation and thus prevent optical beam collapse [4]. However the saturation effects resulting from this type of interactions are only important at exceedingly high filling factors.

Yet recent experimental data obtained at the University of St. Andrews suggest that colloidal systems can exhibit a “Kerr-like” behavior at filling factors of about 0.1%. In this paper we provide for the first time a theoretical explanation for these new experimental results. By taking into account the composition and chemistry of stable colloidal suspensions we develop from statistical physics an equation of state of such “non-ideal gases”. We note that typically such nano-colloids are stabilized using electrostatic or entropic forces. Here we focus our attention on the most common electrostatic component that was prevalent in the experiments under examination. By considering the Gouy-Chapman double layer, the electrostatic interaction potential between two identical nano-particles suspended in an aqueous solution is given by:

$$U(r) = \frac{e^2 Q^2}{4\pi\epsilon_o\epsilon_r} \left(\frac{e^{\kappa a}}{1 + \kappa a} \right)^2 \frac{e^{-\kappa r}}{r} \quad . \quad (1)$$

where e is the electron charge, Q is the number of charges per sphere, ϵ_o is the free space permittivity and ϵ_r the liquid relative permittivity. In Eq.(1) a is the particle radius, r is the center to center distance between two particles and κ^{-1} is the Debye-Huckel screening length associated with the ionic chemical concentration of the solvent [5]. Next we treat the nano-suspension as a non-ideal “van der Waals” gas where the equation of state can be expressed in terms of a virial expansion:

$$\frac{p}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \dots \quad . \quad (2)$$

Here p is the pressure of this gas, k_B is the Boltzmann constant, T is the temperature, ρ is the particle density and B_2, B_3 are the second and third virial coefficients respectively. Note that retaining only the first term in this series is equivalent to the Boltzmann exponential factor previously considered [2]. Here we consider the dominant effect of the second virial coefficient in this expansion. Starting from the grand canonical ensemble one can show that the

second virial coefficient is given by $B_2(T) = -2\pi \int_0^\infty (e^{-U(r)/k_B T} - 1) r^2 dr$ [6]. Eq.(2) can then be used to obtain the

Helmholtz free energy and the chemical potential of the system. From Fick's law one can obtain a general form of the Smoluchowski equation [2] from where one can obtain the nonlinear evolution equation of an optical beam propagating in an interacting colloidal nano-suspension. This is given by the two coupled equations:

$$i \frac{\partial \varphi}{\partial z} + \frac{1}{2k_0 n_b} \nabla_{\perp}^2 \varphi + k_0 (n_p - n_b) f \varphi = 0 \quad (3.a)$$

$$\frac{\alpha}{4k_b T} (|\varphi|^2 - |\varphi_0|^2) = \ln(f/f_0) + 2(B_2/V_p) f_0 (f/f_0 - 1) \quad (3.b)$$

where φ is the optical field amplitude, z is the propagation distance, k_0 is the free space wave number, n_p, n_b are the particle and background refractive indices respectively, f is the volume filling factor and V_p is the particle volume.

To demonstrate the difference between the ideal and the non-ideal gas limits, let us consider an aqueous suspension of polystyrene nano particles of radius 50 nm, refractive index $n_p = 1.56$ and initial concentration $\rho_0 = 2 \times 10^{18} \text{ m}^{-3}$. The refractive index and acidity of water are taken to be $n_b = 1.33$ and pH=8 respectively while the wavelength of the optical beam is taken to be as in the experiment $\lambda = 1090 \text{ nm}$.

Figure 1. (a) depicts the normalized optical intensity as a function of the particle relative filling factors (f/f_0) for two different cases.

Fig.1 (a) Normalized Intensity versus filling factor-Eq.3 (b) - when $B_2/V_p = 300$. The blue curve represents the case of an “ideal gas” while the red line stands for the “non-ideal gas” case. (b) Collapse of a propagating optical beam conveying 0.7 Watts under exponential nonlinearities. (c) The dynamics of this same beam when many-body effects are accounted for. At this same power level the collapse is arrested, indicating a “softened” nonlinearity.

The blue line represents the “ideal gas” case while the red line represents the case where the second virial coefficient is taken into account. It is evident that at filling factors of about 0.3% many-body effects lead to a linear as opposed to an exponential nonlinear response which explains the recent experimental data under consideration. Figure 1 (b) shows the propagation of an optical beam of full wave half maximum $FWHM = 3.4 \mu\text{m}$ at a power level of 0.7 Watts when the system is treated as an ideal gas. The dynamics of the same beam under imperfect gas conditions is shown in Fig.1 (c). It is very clear that the nonlinearity in the second case is “softer” as indicated by the weaker self focusing effects.

In conclusion, we have developed a theory of the optical nonlinearity of stabilized nano-suspensions that can extrapolate between the Kerr and exponential limits depending on composition and chemistry of the soft-condensed matter system, thereby unifying previous theories. In the talk we shall further elucidate the theory and its experimental consequences.

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