Ultratransparent glass-ceramics: the structure factor and the quenching of the Rayleigh scattering.

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Abstract

Glass-ceramics with nanocrystals present a transparency higher than that expected from the theory of Rayleigh scattering. This ultra-transparency is attributed to the spatial correlation of the nanoparticles. The structure factor is calculated for a simple model system, the random sequential addition of equal spheres, at different volume filling factor. The spatial correlation given by the constraint that particles cannot superimpose produces a diffraction peak with a low \( S(q) \) in its low-\( q \) tail, which is relevant for light scattering. The physical mechanism producing high transparency in glass-ceramics is demonstrated to be the low density fluctuation in the number of scatterers.

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Glass-ceramics with nanometric size of the crystals are of great interest for photonics, since they combine the spectroscopic properties of crystals with the mechanical properties of glasses [1, 2, 3, 4, 5]. Many glass-ceramics, in particular those obtained from oxyfluoride glasses, have shown a transparency similar to that of glasses, much higher than that expected from the theory of Rayleigh scattering [2, 3]. Recently, Edgar et al. measured the optical extinction coefficient for fluorozirconate glasses containing a volume fraction of about 0.2 of barium chloride nanoparticles, finding that the glass ceramics are about a factor of six more transparent than predicted by the Rayleigh scattering theory, based on estimates of particle sizes from X-ray diffraction and electron microscopy measurements [6]. They modelled the electric response of the material within a discrete dipole approximation, which accounts for the particle-particle interaction. However, they did not succeed in reproducing the observed quenching of the attenuation. In our opinion the dipole-induced-dipole effects are not crucial for the scattering intensity. The particles, in a first approximation, can be considered independent and excited by a homogeneous external field. The main effect is related to their spatial arrangement and the consequent interference pattern of the scattered field. Tick suggested that the low attenuation is related to this effect, but quantitative calculation are lacking. Hopper treated the case of a spinodal decomposition and Hendy found a \( q^8 \sim \lambda^{-8} \) dependence of the Rayleigh cross section in the low \( q \) limit, \( q \) being the wavevector of the light \( (q = 2\pi/\lambda) \) [8].

In the absence of any spatial correlation the scattering attenuation is given by

\[
\alpha = \sum_i \sigma_i, \quad (1)
\]

where the sum in on all the particles in the volume unit and \( \sigma_i \) is the cross section of Mie scattering of the \( i \)-th particle. If the interaction among particles is neglected, i.e. each particle is considered as surrounded by a homogeneous medium, and if all particles are equal, Eq (1) reduces to \( \alpha = \rho_N \sigma \), where \( \rho_N \) is the particle density. Furthermore, if the size of the particle is much smaller than the wavelength of the light, Rayleigh scattering occurs. The cross section for Rayleigh scattering by a not absorbing spherical particle of radius \( R \) and refractive index \( n_p \), embedded in a not absorbing medium of refractive index \( n_m \), is given by [9]:

\[
\sigma_{Ray} = \frac{8}{3} \pi k^4 R^6 \left( \frac{m^2}{m^2 + 2} \right), \quad (2)
\]
where \( m = n_p/n_m \), \( k = 2\pi/\lambda = 2\pi n_m/\lambda_0 \) is the wave vector of the light of wavelength \( \lambda \) in the medium and \( \lambda_0 \) in vacuum.

In the presence of spatial correlation, interference effects occur and the total scattered field at any angle (\( \theta \)) of scattering, or at any exchanged wavevector \( q = (4\pi/\lambda) \sin(\theta/2) \), is the sum of all individual fields. For \( N \) equal particles excited by a plane wave, the individual scattered fields are given by:

\[
E_i(q) = E_0(q) \exp(\imath qr_i),
\]

and the scattered intensity is given by:

\[
E(q)^2 = N E_0(q)^2 S(q),
\]

where \( S(q) \) is the structure factor of the system:

\[
S(q) = \left| \sum_i \exp(\imath qr_i) \right|^2 / N.
\]

We will show that any spatial correlation lowers significantly \( S(q) \) at the small \( q \)-values with respect to the value \( S(q) = 1 \) of the uncorrelated system. The attenuation of the light will depend on the scattering at all angles (0 < \( \theta < \pi \)) or \( q \)-values (0 < \( q < 4\pi/\lambda \)). Furthermore, we will show that for small \( q \)-values, i.e. the ones which are relevant to Rayleigh scattering, the structure factor is nearly constant, i.e. \( S(q) \approx S(q = 0) = S_0 \). Therefore the attenuation, in the presence of a particle correlation measured by \( S(q) \) is well approximated by \( \alpha_c = \rho_N \sigma_{Ray} S_0 \).

An unavoidable correlation among equal spherical hard particles is given by the impossibility of interpenetration. Interestingly, this effect may enforce non-trivial spatial correlations even on length-scales larger than \( 2R \). A simple process yielding three dimensional systems subjected only to such hard-sphere constraint is given by the random sequential addition (RSA) \[10\]. In such process, the \( n \)-th particle is placed randomly within a cubic box with periodic boundary condition only if it finds the space left free from the previous \( n - 1 \) particles. The correlation among the particles increases when the filling factor \( \phi = 4/3\pi R^3 \rho_N \), where \( R \) is the particle radius, grows. For \( \phi = 0 \), there is no spatial correlation, while the maximum filling factor for RSA in 3-D is \( \phi_{sat} \approx 0.3828 \) \[10\].

Figure 1 shows the calculated \( S(q) \) for various values of \( \phi \), obtained by averaging over 30 realizations of the RSA process with \( N = 10000 \) particles. As \( \phi \) increases, a diffraction
peak, located at \( q_p \approx 2\pi/2R \) becomes more and more well defined. The radial distribution function \( g(r) \) (not shown here) is zero for \( r < 2R \) and presents a single peak at \( r_p \gtrsim 2R \).

The radial correlation decays very fast with \( r \) for \( r \geq 2R \) for any \( \phi \), similarly to the case near \( \phi_{\text{sat}} \) (\( \phi = 0.3812 \)), described by Torquato et al. [10].

*Figure 1 around here*

The quenching of the \( S(q) \) in the low-\( q \) region is shown in more detail in the inset of Fig. 1. When plotted as a function of \( q^2 \), the parabolic behavior \[ S(q) = S_0 + aq^2 \] (6) appears as a straight line. Here \( S_0 \) is the low-\( q \) limit, being \( q_{\text{min}} = 2\pi/L \), where \( L \) is the edge of the cubic box, the minimum \( q \)-value accessible in the calculations. The fitted \( S_0 \) values are reported in Fig. 2, together with the value found near the saturation density [10].

A quantitative prediction can be obtained by studying the simplest form for \( g(r) \) which takes into account both the hard-sphere constraint and some possible correlation over a length-scale \( \xi \),

\[
g(r) = \begin{cases} 0 & r < 2R \\ 1 + Ae^{-r/\xi} & r > 2R. \end{cases}
\] (7)

In fact with that choice one finds:

\[ S_0 = 1 - 8\phi, \] (8)

which suggests that the increase of the filling factor is the main factor which determines the drop of \( S_0 \). Therefore, the very short range correlation of our model system, which only avoids particle superposition, is able to reduce the scattering intensity by about an order of magnitude for \( \phi \) in the range of 0.2 – 0.3, values that are typical of glass-ceramics.

Furthermore, no medium or long range correlation seems to be needed for quenching Rayleigh scattering. But, in fact, some degree of long range order is produced. A deeper insight is obtained by the following study. The box containing \( N \) particles (\( N=10000 \) in our case) can be decomposed in \( n \) cubic smaller boxes, each containing \( M = N/n \) particles, on average. In the absence of any particle correlation, a Poisson distribution in the number \( M_j \) of particles will be present. For large values of \( M \), it is well approximated by a Gaussian distribution with variance \( \sigma_M^2 = M \). In the inset of Fig. 2 we show the results for \( n = 125 \), \( M = 80 \) and for two values of the volume filling factors, \( \phi = 0.05 \) and \( \phi = 0.3 \). The variance of the
particle number is smaller than $M$ and decreases as the filling volume increases. This can be easily understood, since in the RSA method of box filling the $n$-th particle will have larger probability of being accommodated in a box with smaller particle density. This will produce an equalization of density, reducing its fluctuations over large scales to lower values than those that would be present for a random distribution. Figure 2 summarizes the results of the calculations for different $n$-values of the box partition, $n = 125, 64, 27$ and $8$, showing the normalized variance $\sigma'_M^2 = \sigma_M^2/M$.

*Figure 2 around here*

The above feature is not limited to RSA systems. As a matter of fact, in a system of classical particles, $S_0$ is always related to the fluctuations of the number of particles $M$ within spheres of (large) radius $l$ by the relation [11]:

$$\frac{\langle M^2 \rangle - \langle M \rangle^2}{\langle M \rangle} = 1 + 4\pi \rho N \int_0^l dr r^2 (g(r) - 1)$$

$$\rightarrow S_0,$$  \hspace{1cm} (9)

where the limiting value is approached when $l \rightarrow \infty$ (this explains the observed size dependence of $\sigma'_M$ on the sampling size $M$ in Fig. 2).

In real systems, as also suggested by the model of Eq. 7, $S_0$ can be much lower than what is found in RSA [2,8]. A naive argument, which basically exploits Eq. 9, allows accounting for such a decrease. In fact, even though the processes of nucleation and coarsening are very system dependent, the growth of nanosized particles usually occurs by diffusion within limited spatial region, each particle having its own basin for gathering material. In a volume with a characteristic distance of the order of $1 \mu m$ relevant for Rayleigh scattering, we will find a certain number $N_{BB}$ of the building blocks (BB) that will compose the nanoparticles. If we assume that $M = N_{BB}/n_{BB}$ identical nanoparticles, each one containing $n_{BB}$ BB, are formed by limited diffusion within the given volume, $M$ will have the same relative fluctuation as $N_{BB}$: $\sigma_M/M = \sigma_{N_{BB}}/N_{BB}$. The fluctuations on the particle number will therefore be proportional to $1/n_{BB}$ and, by Eq. 9, so will be $S_0$ and the intensity of the scattered light. Note that since the cross section $\sigma_{Ray}$ is proportional to the square of the particle volume (see the $R^6$ dependence in Eq. 2), $\sigma_{Ray} \rho N$ is proportional to the particle volume (assuming that all the BB have been precipitated in particles and $n_{BB} M = N_{BB}$), and finally $\alpha_c = \sigma_{Ray} \rho N S_0$ becomes size independent. Therefore, no increase of attenuation is expected with the increase of the particle size, since the increase of the cross section for
Rayleigh scattering is exactly compensated by the decrease of the structure factor.

This simple model does not account for other important effects, as the size distribution of particles or the formation of more ordered structures. In any case, the physical mechanism producing high transparency in glass-ceramics even for relatively high particle size is demonstrated to be the low fluctuation in the number of scatterers, due to spatially limited diffusion during coarsening.

The above results indicate two connected methods for estimating the quenching of the Rayleigh scattering in a glass-ceramics. The structure factor can be measured by Small Angle X-ray scattering. If the measurements are extended, as far as possible, down to low-q side of the peak, the very low-q \( S(q) \), \( S_0 \), should be possibly obtained by extrapolation to the parabolic behavior of Eq. 6. The fluctuations in the spatial particle distribution can be measured by counting the particles using TEM tomography. The decrease of Mie scattering is expected to be reduced by the factor \( S_0 = \sigma'_M^2 \) with respect to that calculated for a random distribution of particles. The measure of light attenuation and of the structure factor, combined with the calculation of the Mie cross section for the single particle scattering, should quantitatively confirm this explanation of the observed ultra-transparency of glass-ceramics with nanocrystals.

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FIG. 1: Calculated structure factor for 3-D random sequential addition of equal spherical particles and for different volume filling ratios, $\phi$. The arrows indicate the values of $q = 2\pi/2R$, where $R$ is the radius of the spheres. The inset shows the low-$q$ part as a function of $q^2$. 
FIG. 2: Calculated low-q limit of $S(q)$ (dots). The star shows the value ($S_0 = 0.05$) at the saturation density from ref. [10]. The dashed line shows the $\phi$-dependence given by Eq. 8. Normalized variance of the particle density in cubic boxes containing $10000/8$ (open squares), $10000/27$ (circles), $10000/64$ (triangles) and $10000/125$ (inverted triangles), on average. Inset: distribution of number of particles in the 125 small cubes of size $L/5$ for volume filling ratios $\phi = 0.05$ and 0.3, calculated over 48 and 27 samples, respectively. The curves are fits by Gaussian curves.