PULSED DIFFUSING-WAVE SPECTROSCOPY IN DENSE COLLOIDS

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There is a rich variety of systems in nature which are essentially dense aggregations of particle-like structures whose positions vary randomly in space and time. Some common examples include fog, smog, microemulsions, suspensions of glass or polymer microspheres, red blood cells, and ocean particles. In order to understand better and ultimately to gain control over these suspensions it is highly desirable to characterize the structure and dynamics of these systems.

Light scattering has been widely used and is particularly well-suited for structural and dynamical studies of colloids because the important length scales, such as particle size and interparticle spacing, are comparable to the wavelength of light. Unfortunately, this advantage is often offset by the fact that colloidal particles scatter light so strongly that multiple scattering becomes a significant problem at all but the lowest particle concentrations. As a consequence, progress in the study of dense colloids has lagged that of colloids at very low particle concentrations.

Recently a new spectroscopy has been developed and applied to study the properties of colloidal suspensions which multiply scatter light [1,2,3]. The technique, called diffusing-wave spectroscopy (DWS), exploits the diffusive nature of light transport in strongly scattering media to relate temporal intensity fluctuations of the scattered light to average particle motion. In contrast to more traditional dynamic light scattering methods [4,5], DWS probes particle motion over length scales much shorter than the light wavelength, and offers the possibility of studying the strongly correlated particle motions often present in dense media.

In this contribution we introduce a new diffusing-wave spectroscopic probe which utilizes light pulses and exploits the phase fluctuations of optically gated photons to eliminate the usual average over photon pathways. The principles are discussed and experimentally demonstrated. We have used the method to test several critical assumptions of the original multiple light scattering theories, and we have studied particle diffusion in the high volume fraction limit where hydrodynamic interactions are important. Since the general field is quite new we will review the important aspects of conventional DWS before discussing the pulsed ideas and our experiments.

Review of Diffusing-Wave Spectroscopy

The advances of DWS are best appreciated against the backdrop of the widely successful spectroscopy of quasielastic (or dynamic) light scattering (QELS) [4,5]. In QELS the low frequency noise spectrum of the scattered light is analyzed to obtain dynamical information about the various mechanical degrees of freedom of the scatterers.

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An experimental set-up for a typical QELS experiment is shown in Figure 1. Here a volume of solvent containing N identical macromolecular scatterers is illuminated by a plane wave with a frequency ω and a wavevector $k_0=2\pi/\lambda$. Scattered light is detected far from the sample at an angle θ with respect to the incident propagation direction. For dilute samples we can ignore multiple scattering effects, and the electric field at the detector is *superposition* of the fields radiated by each of the individual particles. Since the position of each particle is random and varies randomly in time, the field at the detector, $\mathbf{E}(t)$ will fluctuate in time. The phase of the electric field at the detector due to the jth particle depends on its position $\mathbf{r}_j$, its field strength $\mathbf{A}_j$, and the scattering wavevector $\mathbf{q}$, where $q = |\mathbf{q}| = 2k_0\sin\theta/2$. The physical content in these fluctuation measurements is contained in the autocorrelation function, $g_1(\tau) = \langle E^*(t)E(t+\tau)\rangle/\langle|E(t)|^2\rangle$, of the scattered electric field. For Brownian motion in dilute systems we typically have $\mathbf{A}_j = \mathbf{A}$ and uncorrelated particle motion. In this case $g_1(\tau)$ reduces to an exponential function with a decay rate that is inversely proportional to the time it takes a particle to move a length ~1/q. Thus by varying the scattering angle θ it is possible to measure the relaxation of particle density fluctuations over length scales of $\lambda/2$ and larger. In practice the intensity autocorrelation function, $g_2(\tau) = \langle I(t)I(t+\tau)\rangle/\langle I(t)\rangle^2$, is often the quantity measured and the Bloch-Siegert [6] relation, $g_2(\tau) = 1+|g_1(\tau)|^2$, is used to derive $g_1(\tau)$ from the data.

QELS is a "single scattering spectroscopy" in the sense that the scattering problem is well posed only within the Born approximation. In more dense systems incident photons experience many scattering events before emerging from the medium and it becomes essential to incorporate the multiple scattering process directly into our interpretation of the fluctuation spectra. Indeed it is precisely because of this limitation that a great variety of systems remain unstudied.

At high concentration (i.e., volume fractions, $\phi>0.2$), the simple system of strong macromolecular scatterers undergoing Brownian motion provides a good example of a class of dense, fluctuating random media that we wish to observe. Consider the experimental geometry depicted in Figure 2. Here a dense sample of Brownian particles is illuminated by a plane wave on the front face, and a portion of the light that has propagated through to the other face is collected through a small aperture at the output plane.

Microscopically one can envision each photon traveling ballistically between particles, and experiencing changes in propagation direction after each scattering event.

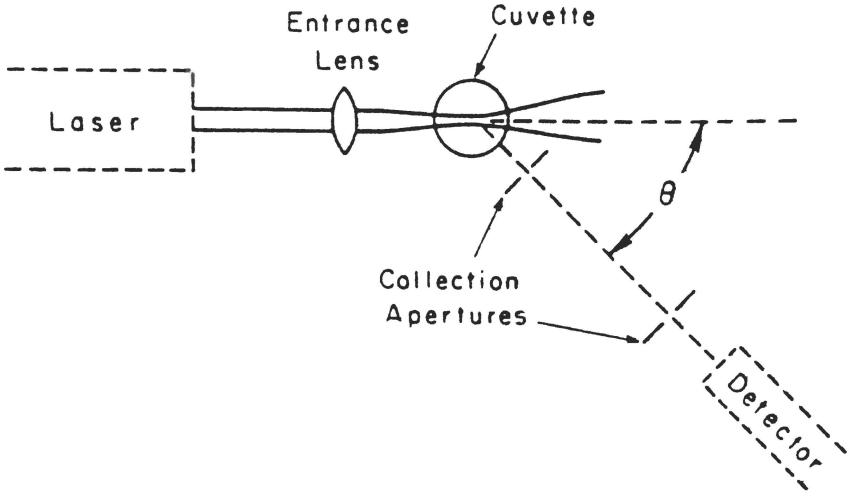

Figure 1. Experimental set-up for a typical QELS experiment. Scattered light is detected at an angle θ with respect to the incident propagation direction.

Three length scales characterize photon transport in the media: (1) s, the total distance traveled by a photon, (2) l, the mean distance traveled by the photon between particle encounters, and (3) l*, the transport mean free path of the photon. Physically, l* corresponds to the mean distance traveled by a photon before its propagation direction is completely randomized. Thus l* is the random walk step size for the "diffusing photons". Typically if s >> l* then the diffusion approximation is quite good. We assume this to be true, and we also assume that the disorder in the sample is uncorrelated.

Consider a single photon path of length s through the media. A typical photon will experience n=s/l scattering events. We can write the phase of the electric field for the light emerging along this pathway in terms of the position of the jth particle $\mathbf{r}_j$, and the momentum transfer $\mathbf{q}_j$ for the jth scattering event [7,8]

$$\mathbf{E}_S(t) \sim e^{-i\omega t} \prod_{j=1}^{N} e^{i\mathbf{q}_j \cdot \mathbf{r}_j(t)} \qquad (1)$$

In contrast to QELS, we note that the phase shifts due to each scattering event enter *multiplicatively* rather than in an additive way , and that the momentum transfer $\mathbf{q}_j$ are different for each scattering event.

The time-averaged autocorrelation function $g_1^s(\tau)$ of the scattered field takes on a particularly simple form when the particles move independently and the particle displacement is a random Gaussian variable. Then, if we assume that the photon momentum transfer is independent of the particle displacement, we can show that [1,7,8],

$$g_1^s(\tau) = \exp[-k_0^2 \langle \Delta r^2(\tau) \rangle (s/l^*)/3] \qquad (2)$$

where $\langle \Delta r^2(\tau) \rangle$ is the mean square displacement of a particle in time τ. Equation 2 is the primary result of the simplest DWS treatment.

Information on the dynamics of particle motion is contained in the decay of $g_1^s(\tau)$. In contrast to QELS, we see that the field correlation function is sensitive to particle motion

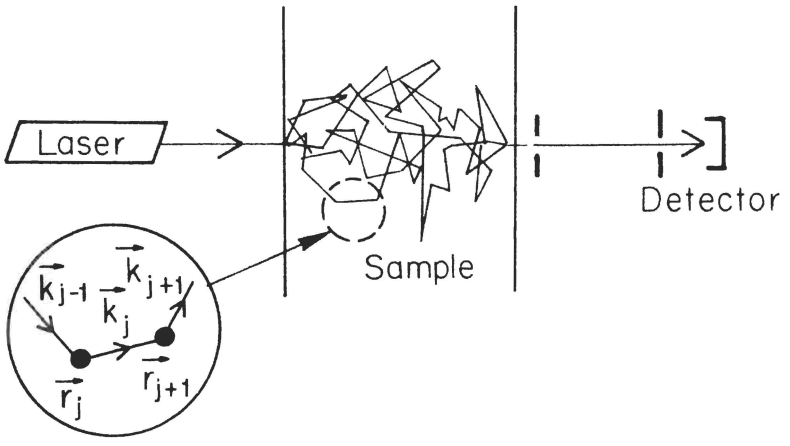

Figure 2.*Top:* Schematic of a typical DWS measurement. Light from laser is directed onto a dense colloidal suspension. Each photon travels through the sample along a complicated path. At the ouput face we collect a portion of the emerging light and direct it onto a photomultiplier tube. *Inset:* Magnification of a portion of a photon path. Here the photon encounters two particles at locations $\mathbf{r}_j$ and $\mathbf{r}_{j+1}$. Thephoton travels ballistically between particles and experiences a momentum transfer in the jth collision given by $\mathbf{q}_j=\mathbf{k}_j - \mathbf{k}_{j+1}$.

over length scales $\lambda/\sqrt{s/l^*}$, which, since $s>>l^*$, is generally much less than λ. Thus, in addition to being able to probe the dynamics of optically turbid samples, DWS is sensitive to motion on a substantially different range of length and time scales than QELS.

Qualitatively we expect all of these dynamic light scattering correlation functions to decay in the time it takes the phase of the scattered field to change by π. In single scattering experiments this occurs when a typical particle position changes by $\sim 1/q$ ($>\lambda/2$) along the direction parallel to $\mathbf{q}$. In the multiple light scattering experiments this occurs when the *total* particle displacement projected along the direction of the output speckle wavevector changes by $\sim\lambda$. Since the scattered photons encounter many particles en route to emerging from the sample, the distance that *each* particle must move is much less than λ. Loosely speaking we can associate a phase shift of $\sim k_0(\Delta r(\tau))$ with each step in the photon random walk. Since the direction of $\Delta r(\tau)$ is random, the total phase shift along any particular direction will scale as the square root of the number of photon random walk steps. Equation 2 is a quantitative statement reflecting this simple idea.

The first experiments demonstrating these ideas were carried out with cw lasers [1,3,7] In this case the total electric field autocorrelation, $G_1(\tau)$, function is computed by incoherently summing the contributions of each path-dependent $g_1^s(\tau)$ weighted by P(s), the probability that a photon will travel a distance s through the medium, i.e.

$$G_1(\tau) = \int_0^\infty g_1^s(\tau)\, P(s)\, ds. \qquad (3)$$

For purely Brownian motion, $\langle \Delta r^2(\tau)\rangle = 6D_0\tau$, and $G_1(\tau)$ is the Laplace transform of P(s) with scale factors that are simply related to D_0. The pulsed-DWS technique (PDWS) which we describe shortly, enables us to isolate the contributions of specific photon pathlengths and thereby directly measure the path-dependent autocorrelation function $g_1^s(\tau)$. This is particularly useful when the mean square particle displacement *does not* depend linearly on time, and in regimes where it is not apparent that the diffusion approximation is valid. In addition, with the same apparatus, we can directly measure l^*.

Pulsed Diffusing-Wave Spectroscopy

The basic ideas of PDWS are illustrated with the use of Figure 3. We employ a laser that emits a train of identical light pulses. Each pulse has a temporal duration Δt, and a carrier frequency ω_0. Adjacent pulses within the train are separated by a time T. A beam splitter divides the pulse train into reference and sample pulse trains. The reference train is optically delayed, and the sample train is directed into the suspension which is contained in a rectangular glass cell. Light pulses emerging from the opposite side of the cell are "stretched" due to the distribution of photon path lengths through the sample. In order for PDWS to be most effective, the pulse broadening due to multiple scattering must be large compared to the input pulse width and small compared to the train repitition rate, i.e., $\Delta t<<\Delta s/c<<T$, where Δs represents the characteristic width of P(s). The scattered pulse train is then recombined with the reference train in a frequency doubling crystal, and a second harmonic (SH) pulse train is produced when the two input fields nonlinearly mix [9,10]. If s' is the *difference* in path length between the reference and sample arms when the sample is *removed*, then each pulse within the SH train will have a field $\mathbf{E}_{S'}(2\omega_0,t)$, proportional to the reference field, $\mathbf{E}_R(t)$, and the *path-dependent scattered field* $\mathbf{E}_S(t,s')$. When fluctuations in the reference field are negligible, $\mathbf{E}_R(t) = E_R$, and we have

$$\mathbf{E}_{S'}(2\omega_0,t) \sim E_R\ \mathbf{E}_S(t,s')\,. \qquad (4)$$

In most cases of interest, the time scale of the fluctuation in the phase of $E_S(t,s')$ is much longer than T, and the autocorrelation function of the SH photons is given by

$$g_1(2\omega_0,\tau) \sim |E_S(t,s')|^2 \langle (E_S(t,s'))^* E_S(t+\tau,s') \rangle \sim P(s') g_1^s(\tau). \quad (5)$$

Thus we see that the SH electric field will experience the *same fluctuations* due to particle motion as the scattered electric field for a single pathlength. By varying the path length difference, s', between the sample and reference arms, the reference pulse "gates" the total sample electric field, so that only a very narrow range of photon paths centered about s=s' contribute to the fluctuations of the upconverted field. The autocorrelation function of the SH field is simply the integrand of Equation (3) evaluated at the appropriate s,

$$g_1(2\omega_0,\tau) \sim \exp[-k_0^2 \langle \Delta r^2(\tau) \rangle (s/l^*)/3] . \quad (6)$$

Note that the temporal behavior of the autocorrelation function no longer depends on the shape of P(s), and for fixed s, a plot of $\ln[g_1(2\omega_0,\tau)]$ *vs* τ directly yields the time dependence of $\langle \Delta r^2(\tau) \rangle$. In DWS any process that affects P(s), such as sample geometry or absorption, modifies the temporal decay of the measured autocorrelation function. Thus even processes that *do not* affect particle diffusion must be properly accounted for when analyzing DWS data. Since PDWS is insensitive to P(s) these types of problems are eliminated.

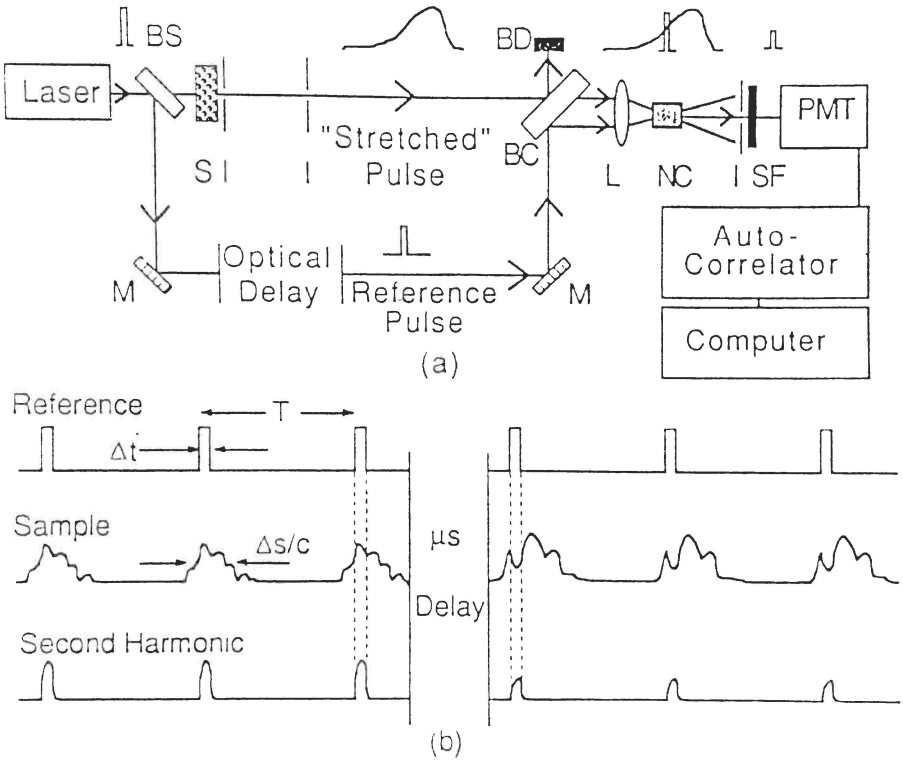

Figure 3. (a) Schematic of the PDWS experimental set-up: BC, beam combiner; BD, beam dump; BS, beam splitter; I, iris; L, lens; M,Mirror; NC, nonlinear crystal; PMT, photomultiplier tube; S, sample; SF, second harmonic spectral filter. (b) Sketch of the reference, sample, and second harmonic pulse intensities during two intervals separated by several microseconds. Temporal fluctuations in the sample pulse intensity arise from particle motion on the microsecond time scale.

An important additional feature of this scheme is that the dependence of the average SH intensity on the reference delay s, is proportional to P(s). Thus we can directly measure P(s) for any geometry. By fitting the results to predictions of photon diffusion theory, we can experimentally determine l^* and the photon absorption length l_a.

Optical gating has been used with considerable success in time-resolved luminescience studies of semiconductors [10], and more recently in coherent backscattering measurements [11,12]. In contrast to these cases, the present application is the first to exploit the *phase fluctuations* of the gated photons. By eliminating the average over photon pathlengths, the new technique is essentially a very high resolution version of DWS. We expect that just as a number of high resolution laser spectroscopic techniques such as saturation spectroscopy for example, have revealed microscopic perturbations in the frequency domain, the spatial precision of PDWS will yield new information on problems concerning particle motion on different length scales.

To illustrate the basic features of PDWS we have carried out a number of measurements on the Brownian dynamics of dense colloidal suspensions. The light source was a mode-locked Nd:YAG laser (λ = 1.06 microns) that produced a 100 MHz train of 90-psec pulses. The average ouptut power of 5 Watts, was split evenly between the reference and sample beams (see Figure 3). A portion of the transmitted output from the sample was collected by two irises and imaged along with the reference beam into a KTP doubling crystal (5x5x5 mm, Type II). The second harmonic photons were spatially and spectrally filtered from the fundamental photons, and collected. Typical photon count rates were between 80 and 600 KHz, allowing normalized intensity autocorrelation functions, $g_2(\tau)$, to be obtained with 100 nsec time resolution in 2 to 20 minutes. The intensity correlation functions are related to the field correlation functions through the Siegert relation.

In the inset of Figure 4a we plot the log of a typical SH intensity autocorrelation function $[g_1(2\omega_0,\tau)]^2$ *vs* τ. The sample used in this case was a suspension of 0.460 μm-diameter polystyrene spheres in water. The volume fraction of spheres was $\phi = 0.30$, the sample thickness was 2 mm, and the reference arm delays were s=7.0 cm and s=13.0 cm. We emphasize that in contrast to DWS measurments the curves decay exponentially. Some of our runs exhibited a slight upward curvature at longer times. This effect was due to our relatively long pulse durations and will be eliminated in the future by using shorter laser pulses.

Using this sample we have performed measurments at different optical delays s. In figure 4a we plot the slope, Γ_1, of the $\ln[g_1(2\omega_0,\tau)]$ *vs* τ curve as a function of s. Below this plot, in figure 4b we show our measurment of P(s) obtained by the time averaged SH photon yield as a function of reference delay. We also calculated P(s) by solving the diffusion equation [13] subject to boundary conditions which insure there is no flux of diffusing photons into the medium [14] (dashed curve). The solid line through the data represents the best fit of theory to experiment after we account for finite pulse duration and the small absorption of light by water. Aside from an overall normalization, the only adjustable parameter is l^*. From our P(s) data we deduce that l^*=31.6 μm. This value of l^*, coupled with the measured slope of the Γ_1 *vs* s curve yields a particle diffusion constant of D=6.20x10-9 cm^2/sec for this sample.

Within the limitations of the current apparatus, these measurements corraborate the primary result of DWS. That is, the electric field autocorrelation of a photons that have diffused s/l^* steps, decays by $\exp(-\tau\, 2k_0^2\, D)$ per step. This is explicitly demonstrated over path lengths ranging from 2200 to 4100 steps. Experiments are currently underway to test this hypothesis in the more complicated backscattering geometry where it is expected to breakdown.

Table 1. Summary of diffusion and l* data for various volume fractions of polystyrene in water. Also shown are the theoretical extimates for the self diffusion coefficient, $D=D_0(1-1.83\phi)$, [15], where D_0 is the Stokes-Einstein diffusion coefficient ($k_BT/6\pi\eta a$) and ϕ is the volume fraction of spheres.

Concentration (volume fraction)	l*(μm) (exp.)	D(cm^2/s) (exp.)	D(cm^2/s) (theo.)
0.05	148±16	$1.06\pm0.10\times10^{-8}$	1.14×10^{-8}
0.10	61.8±4.0	$7.34\pm0.8\times10^{-9}$	1.03×10^{-8}
0.20	41.7±3.4	$7.85\pm0.78\times10^{-9}$	7.97×10^{-9}
0.30	31.6±2.2	$6.20\pm0.47\times10^{-9}$	5.67×10^{-9}

It addition to the measurements described above we report some preliminary results of a concentration dependent study undertaken with this technique in the high volume fraction limit. In Table 1 we have tabulated our measured values of l*, and D for various particle volume fractions. We also indicate theoretical estimates of D based on hydrodynamic corrections to the motion [15]. There clearly exists a substantial deviation between theory and experiment as we approach the highest densities. At present we are not sure of the origin of these deviations, but quantitative studies are underway to try and understand these differences.

In conclusion we have introduced a pulsed DWS technique which substantially improves on the spatial resolution and the interpretation of conventional DWS experiments. With shorter light pulses it will be possible to observe ballistic particle motions, and more complicated systems in greater detail. The technique has enabled us to explicitly test a fundemental assumption of DWS theory, and it can be applied in the important backscattering geometry where some of the diffusive assumptions are known to break down. We note also that this general idea of performing an autocorrelation measurement on optical gated photons can be extended to conventional QELS measurements. In this

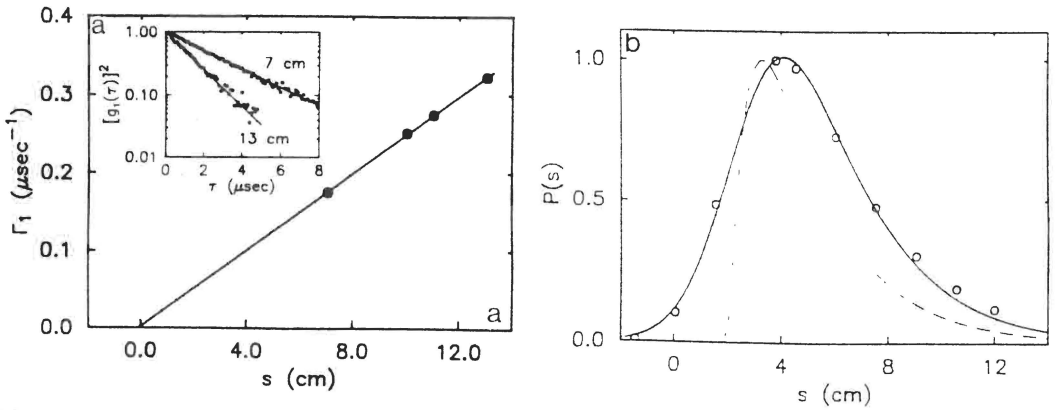

Figure 4. (a) Plot of the decay rate, Γ_1, of the SH temporal field correlation function *vs* reference arm delay s (same scale as (b)). Solid line is a least squares fit to the data. Inset: Plot of the log of the SH intensity autocorrelation function $[g_1(2\omega_0,\tau)]^2$ *vs* τ for s=7.0, 13.0 cm. Both curves exhibit the expected single-exponential decay. (b) P(s): measured (open circles) and calculated (solid line). Dashed curve represents P(s) for delta function input pulses.

case the gating feature can be used to do optical ranging since there is no multiple light scattering. Projects along these lines are underway in our laboratories.

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