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Fullerenes as new colloidal model systems

Abstract Water-soluble $C_{60}(OH)_{22-27}$ (fullerol) particles with different concentrations in D_2O as solvents were used as colloidal spheres. By means of quasielastic neutron scattering (QENS) we determined the dynamic structure factor, $S(Q, \omega)$, for samples with concentrations ranging from 1 to 6 vol%. Recently, it has been shown that C_{60} in CS_2 is a new hard-sphere colloidal model system. In contrast to this lipophilic system with only low solubility in most solvents, hydrophilic $C_{60}(OH)_{22-27}$ can be treated as a new soft-sphere colloidal model system for weakly or even highly charged particles. We show that QENS is well suited for studying the dynamic and static behavior of these fullerol- D_2O systems with different concentrations. At 1 bar and 298 K, for scattering vectors $Q = 0.4 \text{ \AA}^{-1}$ up to $Q = 2.6 \text{ \AA}^{-1}$ $S(Q, \omega)$ can be well described by a sum of a narrow and a broad Lorentzian line. The first is

attributed to the diffusion of $C_{60}(OH)_{22-27}$ colloidal particles in the solvents, whereas the broad Lorentzian is due to the motion of the solvents molecules themselves. From the width of the narrow line we find the translational diffusion coefficient of the fullerol particles to be about $2.74 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$. Taking into consideration the hydrodynamic shell and the resulting larger effective hydrodynamic diameter of the particles this value is comparable to those obtained from the Stokes-Einstein relation. Additionally, we show that the self-diffusion coefficient is significantly influenced by the volume fractions of the fullerol particles in D_2O . This is a direct hint for the beginning of particle-particle self-organization in the sense of a liquid-like-ordered system.

Key words Fullerenes · Scattering · Colloids · Diffusion · Self-organization

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Introduction

The dynamics of dilute monodisperse suspensions of spherical colloidal particles has been extensively studied by means of dynamic light scattering [1] to prove their model system character for the atomic state, which is due to the similar interparticle interaction potential. A tremendous amount of work has been done in the field of soft-condensed-matter research to study and reveal the hydrodynamic behavior [2] or even the liquid-glass

transition in systems of highly charged and hard-sphere particles [3].

In this article we report a study of the dynamic behavior of hydroxylated fullerene molecules, i.e. so-called fullerol $C_{60}(OH)_{22-27}$, which are intermediate between classical colloidal suspensions and binary mixtures of atomic liquids. We consider at a temperature of 298 K dispersions of fullerol, which are highly soluble in polar liquids, in D_2O with different volume fractions, ϕ , ranging from dilute up to 6%. Each of these systems is

Fig. 1 Brief sketch of the spectrometer FOCUS

essentially a monodisperse solution of perfect $C_{60}(OH)_{22-27}$ with a calculated crystallographic (powder) diameter of about 0.9 nm.

We show that neutron time-of-flight (TOF) spectroscopy is a powerful tool to study these dynamic processes of fullerol particles in D_2O as a solvent by analyzing the quasielastic broadening of the elastic scattered intensity at Q values between Bragg reflections. The momentum transfer, Q , and the energy transfer, ω , of the neutron to the sample during the scattering process mainly characterize the method. In contrast to a triple-axis spectrometer, a TOF experiment simultaneously detects several points in the (Q, ω) phase space by time-resolved neutron detection within a large solid angle by the use of typically several hundreds of detectors. TOF spectroscopy uses the de Broglie relation between the wavelength of the neutron and its velocity:

$$\lambda = h/mv \Rightarrow \lambda = 3956/v$$

Typical neutron velocities used in a scattering experiment range from 200 to 3000 ms^{-1} ; therefore, the flight times for experimentally relevant distances of several meters are of the order of milliseconds. By measuring the time the neutrons need to pass a known distance one can calculate the wavelength that directly yields the energy, E .

Experimental

Spectrometer

The SINQ TOF spectrometer FOCUS, Fig. 1, is based on the hybrid-TOF principle and combines a double-focusing crystal monochromator with a Fermichopper. The disc chopper in front of the monochromator serves as an antioverlap device. At a distance of 2.5 m from the sample position, three banks of detectors equipped with 383 3He single-tube detectors cover a range of scattering angles between 30° and 130°. One main purpose of the concept is the high flexibility of the instrument. The pyrolytic graphite monochromator allows a continuous and large range of initial energies, E_i : 2.3 meV < E_i < 20 meV. A Fermichopper with a straight collimation of 2.0° and 1°, respectively, is located

between the monochromator and the sample at a distance of 0.5 m in front of the sample. The elastic energy resolution ranges from 50 μeV (full width at half maximum, FWHM) at $\lambda_i = 6 \text{ \AA}$ to 131 μeV at 4 $\text{\AA}$ and 1300 μeV at 2 $\text{\AA}$ [4]. An elastic scattering vector Q range from 0.2 to 5.6 $\text{\AA}^{-1}$ can be applied with the following relationship for Q :

$$Q = \frac{4\pi}{\lambda} \sin \Theta, \quad (1)$$

with Θ the scattering angle and λ the wavelength. The optical parameters of FOCUS can be adapted to the requirements of the experiment by the variable curvatures of the monochromator in the horizontal and vertical directions and flexible distances between the main spectrometer components. A novel concept of FOCUS consists of the option to operate the machine either in time-focusing or in monochromatic-focusing conditions [5]. Whereas the time-focusing option allows a sharp energy resolution with enhanced intensity at a certain energy transfer window, the monochromatic-focusing option of the instrument provides an almost constant resolution within a broad range of energy transfers, especially on the neutron-energy-loss side of the spectrum.

We performed all measurements using a conventional closed-cycle refrigerator at 298 K with a standard aluminum hollow cylinder sample can. As a first instrumental setup we chose an incident wavelength of 6 $\text{\AA}$, which corresponds to a primary energy, E , of 2.27 meV, with an instrumental resolution of $\Delta E = 50 \mu eV$ covering a scattering vector window between $Q = 0.3$ and $Q = 2.0 \text{ \AA}^{-1}$. The second setting consisted of $\lambda = 4.2 \text{ \AA}$ and $E = 4.6 \text{ meV}$ with $\Delta E = 120 \mu eV$ and an elastic Q range of 0.8–2.6 $\text{\AA}^{-1}$. Different detector efficiencies were corrected using the completely incoherent and elastic scatterer vanadium in the same sample geometry.

Sample

The hydroxylated fullerene, i.e. so-called fullerol, was purchased from MER, Tucson, USA, as a dry powder. The particles were further dissolved in analytical grade D_2O . All scattering curves from the sample were corrected using pure D_2O in an aluminum cuvette in order to gather the pure contribution of the fullerol. The determinations of the dynamic character of the more highly concentrated samples were carried out in the presence of a mixed-bed ion exchanger (Fluka) in the deuterated modification in order to remove all excess ions within the sample; only the counterions of the surface were present.

Theory

Static properties

The molecule has a total scattering cross-section of 2,485 barn (1 barn equals 10^{-24} cm^2), which is built up by an incoherent scattering cross-section of 2,005 barn mainly caused by the hydrogen atoms and a coherent scattering cross-section of 480 barn resulting from the carbon and the oxygen atoms. In a thought experiment, filling the volume of one particle completely with D_2O means that the particle scatters 1.5 times more strongly than the solvent particles themselves, which is not the case for pure C_{60} . For a spherical, monodisperse hollow particle the normalized integrated scattering intensity

Fig. 2 The fullerol particle: C₆₀(OH)₂₂₋₂₇

due to intraparticle interactions, $P_{\text{coh}}(Q)$, the single-particle form factor, is:

$$P_{\text{coh}}(Q) = \left(\frac{A(Q)}{C} \right)^2 \quad (2)$$

and

$$A(Q) = 3 \left(\frac{\sin(QR_o) - QR_o \cos(QR_o)}{(QR_o)^3} \right) - 3 \left(\frac{\sin(QR_i) - QR_i \cos(QR_i)}{(QR_i)^3} \right) \quad (3)$$

$$C = 1/3(R_o^3 - R_i^3),$$

with R_i and R_o the inner radius and the outer radius of the hollow sphere, respectively. This relation only holds for the situation of coherently scattering surface elements in the sense that the scattered waves are able to interfere in a coherent manner and is directly related to the scattering properties of the carbon and the oxygen atoms of fullerol. By considering the scattering behavior of the hydrogen atoms a completely different picture is drawn. The incoherent scattered waves originating from the hydrogen atoms on the surface are not able to interfere coherently, with the result that $P_{\text{inc}}(Q)=1$ over the complete Q range; therefore, the complete form factor should consist of 20% $P_{\text{coh}}(Q)$ and 80% $P_{\text{inc}}(Q)$.

For interacting particles a second static contribution, that is to say the static structure factor, $S(Q)$, also plays a prominent role. For a 20% coherent scatterer and the volume fractions we are dealing with this means that the static coherent scattering intensity is additionally superimposed by a 5–10% effect, which is essentially negligible.

Dynamic properties

The neutron spectra of a diffusing particle are given by

$$I(Q, \omega) = IP(Q) \int_{-\infty}^{\infty} S(Q, \omega') R(Q, \omega - \omega') d\omega' , \quad (4)$$

where I is a Q - and ω -independent normalization factor, $P(Q)$ is the normalized single particle form factor, $S(Q, \omega)$ represents the dynamic structure factor of the diffusing species and $R(\omega)$ is the resolution function of the spectrometer. For isotropic processes $S(Q, \omega)$ is described by a Lorentzian line [6]:

$$S(Q, \omega) = \frac{1}{\pi} \frac{\Gamma(Q)}{\Gamma(Q)^2 + (\hbar\omega)^2} , \quad (5)$$

with $\Gamma(Q)$ the Q -dependent half width at half maximum (HWHM) and $\hbar\omega$ the energy transfer with respect to the sample. The HWHM is directly connected to the nature of diffusion. The rotational diffusion is considered to be too fast and so with our instrumental setup not determinable [7]. For translational diffusive processes the well-known Q^2D law, with D the diffusive constant, describes the HWHM. For particles much larger than the solvent molecules, the Stokes–Einstein continuum relation for solvents with viscosity, η , holds for the free diffusion constant, D_{free} :

$$D_{\text{free}} = \frac{k_B T}{6\pi\eta R} . \quad (6)$$

That is why we are on the cutting edge when applying this theory because the fullerol particles are only about 10 times larger than D₂O [8].

As mentioned earlier the incoherent scattering hydrogen atoms on the surface dominate the scattering

Fig. 3 Raw scattering function at highest applied Q (2.6 Å⁻¹)

function of the fullerol particles. The direct consequence is the determination of the free diffusion constant for the dilute systems and a self-diffusion constant for the more highly concentrated samples.

Results and discussion

Dilute systems

The raw scattering curves of all the samples investigated are excellently describable by two Lorentzian curves due to the motion of water molecules and fullerol plus an elastic contribution of the aluminum container (Fig. 3). The data were further corrected with the neutron spectra of pure D₂O in the same cuvette to collect only the scattering curves of the colloidal fullerol particles.

For the dilute sample we determined from the Q dependence of the FWHM, $\Gamma(Q)$, at room temperature a diffusion constant of $2.74 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ which, by applying the Stokes–Einstein relation leads to an effective particle radius of about 8.0 Å; for pure C₆₀ the radius is about 3.5 Å [9] and for dilute C₆₀ in CS₂ a value of 4.5 Å was recently obtained by Smorenburg et al. [8]. Taking into consideration the hydrodynamic solvent shell of one or even more molecular layer on the surface of all the diffusing particles in solution the discrepancy of the values is reasonable.

To gather information about the static properties of the dilute colloidal fullerol, i.e. the single particle form factor, we illustrate in Fig. 4 the intensity of the quasielastic peak with respect to Q . Using the function for a hollow sphere with nonnegligible thickness, Eq. (2), the Q dependence of the intensity is well describable with

Fig. 4 Single-particle form factor, $P(Q)$, for a dilute fullerol system

a fixed inner radius of 3.5 Å for pure C₆₀ and an outer radius of 4.7 Å by taking into consideration the contribution ratio of the coherent and incoherent surface scattering of one particle, i.e. $P_{\text{coh}}(Q)$ and $P_{\text{inc}}(Q)$.

Concentrated systems

The high solubility of the fullerol particles in polar solvents makes a determination of the dynamic properties at high volume fractions possible; therefore, we were able to probe samples at a volume fraction of $\phi = 1, 4$ and 6%. The particle dispersions in D₂O showed an acidic pH of about 5, which can be interpreted as a direct hint for the partial deprotonation of the surface hydroxyl groups and leads to a categorization of the particles as at least weakly charged systems. After removing all the excess ions by means of a mixed-bed ion exchanger only the counterions are present and the surface charges are not shielded anymore. The direct consequence is a relatively long range repulsion, which at appropriate number densities can cause collective ordering phenomena, like a liquid-like-order phase, a crystalline phase or even a glassy phase [10].

The FWHM is displayed in Fig. 5 with respect to Q^2 for the three different volume fractions. The influence of the increasing concentration on the velocity of the particles is clearly visible. For the most concentrated system we determined a diffusion constant of $1.36 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, whereas the dilute system revealed a value of $2.74 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ (Table 1). The slowing of the diffusion has to be interpreted in terms of the beginning of self-organization of the system, i.e. a liquid-like-ordered system. Thus the diffusion constant, D ,

Fig. 5 Following the Q^2D law for fullerol samples with a volume fraction, ϕ , of 1, 4 and 6%

Table 1 Diffusion constants of the fullerol systems in comparison to dilute, pure C₆₀ [8]

System	D (m ² s ⁻¹)	$D^* = D/D_{\text{free}}$
Fullerol: $\phi = 1\%$	2.74×10^{-10}	1
Fullerol: $\phi = 4\%$	2.02×10^{-10}	0.7
Fullerol: $\phi = 6\%$	1.36×10^{-10}	0.5
Pure C ₆₀ : $\phi < 1\%$	1.5×10^{-9}	1

mirrors the self-diffusional behavior of the colloidal fullerol particles: D shows no Q dependence in contrast to the collective diffusion constant [2]. The reduced self-diffusion constant, $D^* = D/D_{\text{free}}$, will slow to a value of 0.1 with respect to the concentration, where a phase transition will occur [11]. For our colloidal systems we measured a course of the value of D^* from 1 to 0.7 to 0.5, which indicates the regime of a liquid-like-ordered system.

Conclusion

We showed that water-soluble fullerol particles with different concentrations in D₂O as a solvent are suitable colloidal model systems. The inelastic neutron scattering

facility FOCUS was used to determine the dynamic and static behavior for samples with concentrations ranging from 1 to 6 vol%. In contrast to the lipophilic hard-sphere C₆₀ system in nonpolar solvents, hydrophilic fullerol can be treated as a new soft-sphere colloidal model system for weakly or even highly charged particles. After the correction of the raw scattering data the scattering function can be well described by a single Lorentzian line, which is attributed to the diffusion of colloidal particles in D₂O. For a dilute system we extracted from the FWHM the self-diffusion coefficient of the spheres to be about 2.74×10^{-10} m²s⁻¹. By taking into consideration the hydrodynamic shell and the resulting larger effective hydrodynamic diameter of the particles this value is comparable to those obtained from the Stokes–Einstein relation. A direct hint for the beginning of particle–particle self-organization in the sense of a liquid-like-ordered system is revealed by the reduced self-diffusion constant with respect to the free counterpart.

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