Fluorescent Monodisperse Silica Ellipsoids for Optical Rotational Diffusion Studies

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We report on the preparation of monodisperse, fluorescent hematite—silica core—shell ellipsoids, with adjustable shapes ranging from spindles to nearly spheres, that are suitable for optical rotational diffusion studies. Hematite cores are grafted with poly(vinylpyrrolidone) which ensures colloidal stability during the silica coating provided by the base-catalyzed hydrolysis and polymerization of tetraethoxysilane. Using tetramethyammmonium hydroxide as base instead of the volatile ammonia facilitates continuous seeded growth of silica to colloids with a desired aspect ratio. A convenient feature of the hematite—silica particles is the rapid dissolution of the iron oxide core by acid, producing hollow silica ellipsoids that can be optically matched to near transparency. The control of shape and size of the silica ellipsoids, their optical properties, and the fairly high yield in comparison to other preparation methods for nonspherical model colloids make the ellipsoids very suitable for quantitative studies. As a case in point, we have measured the rotational diffusion coefficient of fluorescent ellipsoids with rotational fluorescence recovery after photobleaching. Dye-labeled ellipsoids can be imaged with confocal microscopy.

I. Introduction

Monodisperse silica spheres prepared by the Stöber method† were introduced by Vrij and co-workers2—4 into the field of colloidal model fluids and have been since then very instrumental to study static5,6 and dynamic7—9 properties of colloidal spheres. Advantages of silica-based colloids are, among other things, the large variety in chemical surface modifications,10—12 the relative weak van der Waals attractions in organic solvents,4 and the possibility of optically matching silica particles for light scattering studies on concentrated dispersions.13,14 In view of the increasing focus in colloid science on anisometric particles, an equivalent model system of nonspherical silica particles with a well-defined size and shape is clearly of interest. Silica colloids containing a suitable dye, for example, would allow to extend optical studies on sphere rotations15—18 to hindered rotational diffusion in spheroid dispersions, a topic which to our knowledge has not been explored yet.

In view of this desired exploration, we have studied the preparation of fluorescent nonspherical silica particles with adjustable aspect ratio. Since silica formed by the Stöber process is an amorphous substance, it is almost inevitable that such a preparation starts from crystalline cores on which silica polymerizes to form nonspherical core—shell colloids. Examples are boehmite needles19 as “seeds” for silica rods20,21 and gibbsite hexagons22,23 for the synthesis of platelike particles. Though these core—shell colloids are valuable for studying the effect of particle shape,24,25 they have several disadvantages: the range and reproducibility of particle size and aspect ratio is limited, the polydispersity is still significant (typically 20—30%), and the control of colloidal stability is a difficult issue (witness, for example, the precautions needed to avoid aggregation of boehmite needles during silica preparation20,21,26). In this work, we focus on hematite (α—Fe₂O₃) spindles as the starting cores for the reproducible preparation of well-defined, stable silica ellipsoids.

Polymerization of amorphous silica on hematite particles was first studied by Matijevic and co-workers.27 A drawback of their method is the marginal stability of the starting hematite spindles: they easily flocculate before or during the silica deposition process.28 A modified procedure28 improved the colloidal stability of the silica—hematite particles during their preparation. Nevertheless, the formation of aggregates due to coagulation of

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hematite spindles could not be totally avoided. Moreover, due to the hematite core (high Hamaker constant), initially stable silica—hematite particles sometimes slowly aggregated on a time scale of months. We have reexamined the silica—hematite route and found that Ocaná’s synthesis method for hematite spindles first by Matijevic who obtained silica-coated iron spindles by chemically modifying the internal particle structure as demonstrated to the hematite core (high Hamaker constant), initially stable hematite spindles could not be totally avoided. Moreover, due to the hematite core (high Hamaker constant), initially stable silica—hematite ellipsoids. Crucial to avoid hematite aggregation during silica deposition is the adsorption of poly(vinylpyrrolidone) (PVP) on hematite spindles. PVP not only stabilizes the spindles but also facilitates silica growth on the hematite surface, an observation also made for other inorganic cores.

Taking advantage of the silica porosity, it is possible to chemically modify the internal particle structure as demonstrated first by Matijevic who obtained silica-coated iron spindles by reducing the precursor hematite cores in hydrogen atmosphere. More recently Hao et al.31 dissolved the inner particle cores in aqueous HCl to create silica capsules. Here, to produce ellipsoidal particles suitable for optical studies, we also exploit this dissolution to obtain hollow ellipsoids, with a reduced Hamaker constant, which can be optically matched in an organic solvent mixture. In addition, we developed a procedure to incorporate fluorescent dye into the silica ellipsoids, analogous to the dyeing of silica spheres, such that particles can be imaged with confocal microscopy. Moreover, labeling with rhodamine B isothiocyanate (RITC) allows the ellipsoids to be monitored with rotational fluorescence recovery after photobleaching (“rotation FRAP”). This recently developed technique has only been applied so far to rotational sphere diffusion. Here we show that rotational FRAP accurately measures the rotational diffusivity of the hollow silica ellipsoids. For future systematic FRAP studies, it is important to have dyed tracer ellipsoids in a host suspension of identical nondyed ellipsoids. For this reason, we have also investigated the oxidation of fluorescent dyes by hydrogen peroxide to nonfluorescent host particles.

II. Experimental Section

A. Synthesis. Materials. Iron (III) perchlorate hexahydrate (Fe(ClO4)3·6H2O, Alfa Aesar), sodium dihydrogen phosphate anhydrous (NaH2PO4, Fluka, ≥99.0%), poly(vinylpyrrolidone) with average molar mass of 10 kg/mol (PVP-10, Sigma-Aldrich), and urea (CH3CONH2, Acros Organics, p.a.) were used as received. Ammonia (29.0 wt % NH3 in water) and hydrochloric acid (fuming, 37%, p.a.) were purchased from Merck. Tetraethoxysilane (TEOS, ≥99.0%), rhodamine B isothiocyanate (RITC, mixture of isomers), and 3-aminopropyl triethoxysilane (APS, 99%) were obtained from Fluka. Tetramethylammonium hydroxide (TMAH, 25% solution in water) and fluoroescin-isothiocyanate (FITC, isomer I, 90%) were purchased from Aldrich. Ethanol (Merck, p.a.), N,N-dimethylformamide (DMF, Merck), and dimethyl sulfoxide (DMSO, Acros) were of analytical reagent quality. Ethanol and TEOS were freshly distilled before each synthesis. Water used in all reactions was doubly distilled.

Hematite Cores. Dispersions of monodisperse α-Fe2O3 (hematite) particles were prepared by precipitation of iron (III) perchlorate in the presence of urea and sodium dihydrogen phosphate following ref 29. Typically, 231.1 g of Fe(ClO4)3·6H2O, 30 g of urea, and 3.25 g of NaH2PO4 were dissolved in a round-bottom flask containing 5 L of water at room temperature. The mixture was kept undisturbed for 24 h at 100 °C in a preheated oven. After this aging, the dispersion was cooled to room temperature and centrifuged at about 6000 rpm (Beckman Coulter AvantiTM J-20 XP, JLA 8100) for 35 min, followed by rediserial of the hematite spindles in demi-water. The purification process was repeated for at least three times, until a clear supernatant was observed. To coat hematite particles with silica, we followed the procedure described by Graf et al.,30 comprising adsorption of a polymer (PVP) onto the particles surface and transfer of the thus-stabilized colloids in a solution of ammonia in ethanol, where the silica-shell growth can be carried out by addition of TEOs. To functionalize the hematite surface, the added amount of PVP was calculated to be about 60 PVP molecules per nm2. In a typical reaction, 7.9 g of PVP was dissolved by mechanical stirring and ultrasonication in 120 mL of demi-water. To this viscous solution was added 0.62 g of hematite dispersion (concentrated 73.5 mg/mL), and the mixture was kept under stirring for 24 h. Ultrasonication (Beckman 82010) was applied for the first 5–6 h to remove unabsorbed PVP molecules, the dispersion was centrifuged for 3 h at 2000 rpm (Beckman Coulter SpinachTM DLX), and sediments were redispersed in 50 mL of ethanol.

Silica Coating. For the synthesis of the first silica shell, 66 mL of demi-water, 10 mL of TMAH (1%v/v aqueous solution), and 13 g of PVP-stabilized hematite dispersion (3.5 wt %) were added to 911 mL of ethanol in a 2 L round-bottom flask under mechanical stirring and ultrasonication. Then a mixture of 4 mL of TEOs and 2 mL of ethanol was added under the surface of the reaction mixture in three portions every 20 min. The addition of TEOs was continued 1 day up to a maximum of four additions for a total TEOs volume of 16 mL. After the last addition, the dispersion was kept under ultrasonication and stirring for at least 3 h. During the whole process, tap water was pumped inside the cooling system of the ultrasonic bath to keep it at a constant temperature of about 20 °C. The dispersion obtained from this first growing step was centrifuged overnight at 1400 rpm, and the sediments were redispersed in ethanol. To further increase the thickness of the silica shell on the hematite cores, the whole procedure of adding a total volume of 16 mL of TEOs was repeated.

Fluorescent Labeling. The silica coating method described above was also used for growing fluorescent silica shells. The main difference consisted in using a mixture of TEOs and the appropriate dye during the synthesis. The dye (RITC or FITC) was covalently attached to a silane coupling agent (APS) by an addition reaction,11 mixing 0.01428 mmol of dye and a large excess of the coupling agent (3.61 mmol) in 10 mL of anhydrous ethanol. This solution was stirred overnight and then stored at 4 °C in the dark. A mixture of 2 mL of APS-dye and 4 mL of TEOs was used for each growing step. As for the “pure” silica growth, 2 mL of this mixture was added every 20 min. Another important difference with respect to the preparation of nonfluorescent ellipsoids was the addition of PVP to the reaction mixture at the end of each growing step to enhance the particle stability. Typically, for a 1 L batch, 30 g of PVP dissolved in about 200 mL of ethanol was added, followed by stirring the dispersion overnight. Unadsorbed PVP, unreacted dyes, and free APS were removed by sedimenting the particles and redispersing them in absolute ethanol.

Dye Oxidation. Part of the fluorescent ellipsoids were redispersed in an aqueous solution of hydrogen peroxide (15 wt %) and allowed to oxidize for about 1 h at 80 °C. At basic pH (9–10) the oxidation of the dye occurs rapidly, and already after 30 min, the originally pink dispersion turns white. The resulting “bleached” particles were finally transferred in ethanol where they form stable dispersions.

Hollow Ellipsoids. After growing a shell thickness of approximately 30 nm, the hematite cores were dissolved by redispersing the particles in hydrochloric acid (~20% in water). The core dissolution was generally quite fast (about 20 min) and could be followed by observing at the color of the dispersion which changes from orange (Figure 1) to yellow when the cores are completely dissolved. The hollow ellipsoids were redispersed several times in demi-water to remove iron chloride and acid until a neutral pH of the supernatant was reached and finally transferred in ethanol (Figure 2) for (eventually) a new growing step.

B. Characterization. Electron Microscopy. Particle size distributions (Figure 3) were determined by transmission electron microscopy (TEM) using a Philips TECNAI 12 electron microscope operating

typically at 120 kV. Samples were prepared by drying a drop of diluted dispersion on Cu-grids coated with Formvar film. A number-averaged particle length $l$ (or width $w$) and its standard deviation ($\sigma$) were calculated by measuring typically 200 particles. The polydispersity ($\sigma$) of the colloidal systems was defined as $\sigma = \delta l$. Scanning electron microscopy (SEM) was performed with a Philips XLFE30 to obtain information about particles morphology. SEM samples were coated with a 7 nm thick layer of Pt/Pd to minimize particle damaging due to the electron beam.

III. Results and Discussion

A. Preparation. Hematite Cores. The synthesis of monodisperse spindle-type hematite particles was first explored by Matijevic and co-workers. They described the hydrolysis of aqueous ferric chloride solutions with added phosphate or hypophosphite at 100 °C for 48 h. More recently Ocaña studied homogeneous precipitation of uniform $\alpha$-$Fe_2O_3$ from iron salts in the presence of urea. This method was developed to obtain larger amounts of ellipsoids with an axial ratio variable over a wide range and a much shorter reaction time. After some preliminary experiments, we found it straightforward to adapt Ocaña’s method to produce well defined “template” seeds for the preparation of silica ellipsoids. The synthesis method given in section 2.1 results from our optimization of Ocaña’s method to maximize both the yield and the aspect ratio of the hematite colloids. The scaling up to 10 L batch yields an amount of spindles (about 8.3 g of purified particles) large enough to perform all of the following silica growing experiments starting with hematite cores from one and the same batch. Figure 4 shows a TEM picture of the resulting cores with measured dimensions of $l = 285 \text{ nm} (\sigma = 16\%)$ for the longer axis and $w = 45 \text{ nm} (\sigma = 13\%)$ for the shorter axis.

Silica Coating. As for the hematite, we have investigated several procedures for the silica coating before to obtain the optimized procedure described in section 2.1. Several studies yield nicely silica-coated hematite particles only when the seeds concentration in the reaction mixture does not exceed $5 \times 10^{-2} \text{ g/L}$ and even then the reaction have to be carried out under continuous ultrasonification to avoid formation of clusters during the silica growth. Hematite spindles, in fact, have a large Hamaker constant ($A_H = 6 \times 10^{-20} \text{ J}^3$) across water which results in a relatively strong van der Waals attraction especially when the particles make contacts at their conical ends (maximal surface contact area). Moreover, transferring the hematite seeds from demi-water (pH = 6.5), where the particles carry a positively charged surface ($\text{IEP} = 7.5$) to the alkaline mixture necessary for the silica polymerization causes a further decrease of the particles stability due to the temporarily crossing of the point of zero charge. To circumvent this problem, it appears to be sufficient


Figure 1. Evolution of the particles morphology after different growing. Insert shows a dispersion of hematite-silica core–shell particles, orange due to the hematite core.

Figure 2. Hollow ellipsoids resulting after the treatment with HCl. The typical light orange color of the silica-hematite dispersions turns into a milky-like for hollow silica ellipsoids (see insert).

Figure 3. Change in the particles aspect ratio $\alpha$ due to the silica coating. The curves are calculations assuming: (dashed line) evenly coated particles ($\Delta$ constant), and (solid line) no silica growth at the particle tips. Black dots are experimental data. Error bars are standard deviations obtained from EM-micrographs.

Figure 4. Typical TEM image of hematite cores, here with axial aspect ratio of 6.3, prepared following ref 29. A zoom-in (insert) displays a typical spindle on the nanometer scale, indicating that spindles are composed of anisotropic subunits.
to adsorb PVP onto the hematite particles before their transfer to the alkaline ethanol solution, following Graf et al.\textsuperscript{30} who designed this approach for a variety of other inorganic colloids. The presence of the polymer clearly improves the silica coating as illustrated in Figure 5 where bare and PVP-stabilized hematite particles have been grown without ultrasonic treatment and with a seed concentration ($3.6 \times 10^{-1}$ g/L), more than 1 order of magnitude higher than reported in refs 28 and 32. Silica shells are formed in a seeded growth process (Figure 1) following the well-known Stöber method.\textsuperscript{1} The use of TMAH as catalyst instead of ammonia facilitates a continuous growth avoiding the problems related to the fast NH$_3$ evaporation. With a constant concentration of base, in fact, we found it easier to avoid secondary nucleation and to obtain reproducible results.

Aspect Ratio Control. The particle aspect ratio $\alpha$ can be controlled in the range from $\alpha_0 \approx 6.5$ for bare hematite spindles (Figure 4) to $\alpha \approx 2$ for the blunt-ended prolate in Figure 1. A characteristic feature of silica growth on hematite cores is that initially the silica shell thickness is not uniform because the silica prefers to precipitate on areas with a large radius of curvature. Figure 1, for example, illustrates that in the early stage of silica growth, the silica avoids the tips of the spindles. This is due to the enhanced solubility (enhanced Laplace pressure) of silica on such a tip relative to a flat surface. As a result, the aspect ratio drops faster due to silica growth than expected from the initial aspect ratio $\alpha_0 = L/D$. If the spindle is evenly coated with a uniform silica shell thickness $\Delta$, the aspect ratio reduces to

$$\alpha(\Delta) = \frac{\alpha_0 + 2\Delta}{D}$$

In the limiting case when no silica deposition on the tip occurs, we have

$$\alpha(\Delta) = \frac{L}{D + 2\Delta} = \frac{\alpha_0}{1 + \frac{2\Delta}{D}}$$

The experimental aspect ratios as function of silica shell thickness $\Delta$ (Figure 3) indeed initially follow closely eq 2, and bend at larger $\Delta$ to the less steep slope from eq 1: when a sufficient amount of silica has precipitated, the coating thickness becomes uniform, as illustrated by Figure 1.

**Labeling.** In our experiments, we observed that the presence of dye molecules in the reaction mixture sometimes induce particles flocculation. A similar effect, for synthesis of spherical fluorescent silica particles was reported in ref 11 and explained in terms of particle surface coverage with free APS. However, we found that the undesired and (often) irreversible coagulation of the system can be easily avoided with few precautions. First, the addition of PVP at the end of the reaction seems to be essential to prevent aggregation, especially during the purification process. Moreover, addition of TEOS/dye mixture was alternated with pure TEOS in order to lower the free APS-dye concentration, and the last addition was always made with pure TEOS. Finally, in the presence of APS-dye, ultrasonification during the synthesis was always used. Once redispersed in absolute ethanol, the particles so prepared can be used for further growth, or stored as a stable colloid.

**Hollow Ellipsoids.** Hollow ellipsoids (Figure 2) can be easily prepared by treating core−shell particles with concentrated HCl. Interestingly, for core−shell ellipsoids prepared in the absence of PVP, the time needed to completely dissolve the hematite core strongly depends on the silica shell thickness, and for thickness above 20 nm, it is hardly possible to obtain hollow particles. Remarkably, when PVP is used after each growing step, the cores rapidly dissolve even in the case of a silica shell thickness of 60 nm. Apparently the presence of the polymer on the particles surface increases the porosity of the silica shell, whereas without PVP, denser shells obstruct diffusion of ions in and out the core.

**B. Properties.** *Electron Microscopy.* The low polydispersity of the final silica-hematite core−shell particles was confirmed by electron microscopy, and it typically ranges around 12% for the long axis and 5% for the short axis. The absence of fused doublets or clusters (see for instance Figure 6), demonstrates that the ellipsoids are efficiently stabilized by PVP. Weakly stable seeds, in fact, easily yield typical heart-shape doublets or bigger aggregates (Figure 5a) which inevitably grow larger after each growing step.

**Color.** The color of the dispersion (see inserts in Figures 1, 2, 7, and 9) is a useful indicator to keep track of the different stages of the ellipsoids preparation. Due to the contribution of the light scattered from silica shells, for instance, the dark red of the pure hematite seed dispersions slowly turns into light orange when the shell thickness increases. When HCl is added to dispersions of core−shell particles to make them hollow, the hematite core slowly dissolves, generating free Fe$^{3+}$ ions which changes the dispersion color into light yellow. By redispersing

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**Figure 5.** (a) Silica-hematite core−shell particles prepared starting with hematite cores not treated with PVP and seeds concentration of $3.6 \times 10^{-1}$ g/L. (b) Similar core−shell particles prepared with PVP-stabilized hematite.

**Figure 6.** SEM image of multi-shell silica−hematite ellipsoids resulting after four growing steps. In the insert a TEM view clearly shows the core shell morphology.
the hollow particles in water, we finally obtain the typical milky appearance of silica colloidal dispersions (Figure 2). Moreover, when dyes are present, hollow ellipsoids show intense fluorescence emission (green for FITC and pink for rhodamine dye) specially if they are dispersed in a refractive index matching media and exposed to UV-light (see inserts in Figures 7 and 9b).

**rFRAP.** Each of the two different dyes incorporated into the particle shells were intended to optimize the colloidal system for various experimental techniques. Rhodamine labeled ellipsoids, for instance, were successfully tested for rotational diffusion measurements performed by rotational FRAP (Figure 7). In this experimental technique, a short, intense, linear polarized laser pulse bleaches dye molecules inside the ellipsoid, with their absorption dipole moment preferentially parallel to the polarization direction of this exciting (pump) beam. When they are probed with a linear polarized, continuous-wave laser beam, the resulting fluorescent intensity will be high or low, depending on whether the polarization direction of the probe beam is parallel or perpendicular to the initial bleach polarization, resulting in an anisotropy of the signal. Due to the rotational Brownian motion of the ellipsoid, the anisotropy disappears. Figure 7 shows preliminary test measurements performed on 300 nm (TEM) elongated ellipsoids dispersed (at about 1% concentration in weight) in a refractive index matching solvent mixture of DMSO/DMF (3:2 v/v). The longest decay time measured, lead to an apparent diffusion coefficient $D_{app}$ of $44.3 \times 10^{-1}$ s$^{-1}$, which is a reasonable value in comparison to the average ellipsoid length of 300 nm. Thus, the silica ellipsoids are in principle suitable for rotational FRAP studies; in future work, we will focus in more detail on the effect of the nonspherical particle shape on the decay rate of the anisotropy.

For the FRAP measurements, it is very convenient that the ellipsoids can be made hollow: it significantly improves the quality of the FRAP data in comparison to measurements on silica–hematite core–shell particles. In fact, the high energy bleaching pulse used to create the fluorescence anisotropy, if absorbed by the particle cores, can generate temperature gradients within the sample and cause local variations of the solvent viscosity which compromise the good quality of the measurement. Figure 8 shows a typical measurement performed on particles with hematite core present, in which the signal is sensibly distorted with respect to the signal resulting from measuring on samples of hollow particles (see Figure 7).

**Confocal Microscopy.** Confocal laser scanning microscopy was done using a Nikon TE 2000U inverted microscope equipped with a Nikon C1 confocal scanning head in combination with an oil-immersion lens (100 × CFI Plan Apochromat, NA 1.4, Nikon) and two laser sources: ArKr (488 nm) and HeNe (543 nm). Tests were performed on both fluorescein- and rhodamine-labeled ellipsoids. However, FITC dyes which excite (and emit) at lower wavelengths with respect to rhodamine dyes ($\lambda_{em} = 525$ nm; $\lambda_{ex} = 495$ nm for FITC, $\lambda_{em} = 570–580$ nm; $\lambda_{ex} = 550–560$ nm for RITC$^{11,13}$) gave slightly better resolved images. Figure 9a shows a 2D snapshot of a sample containing 300 nm elongated...
and 60 nm thick FITC-labeled ellipsoids prepared as described in section 2.1 and dispersed in DMF/DMSO to optically match the silica. Surprisingly, hollow particles, which we aspected to be easier to image (better index matching) compared to silica—hematite core—shell ellipsoids, were poorly fluorescent and gave noisy pictures. This could be due to the severe conditions (low pH) the particles experienced during the core dissolution step. However, this problem could be solved by edging the hematite core off in an early stage of the particle coating and subsequently use the hollow particles as a seed for the “fluorescent” coating. Figure 9a gives information on both the position and orientation of the ellipsoids, although the small particle size and the particle Brownian motion (the sample analyzed was fairly concentrated but it was still fluidlike) contributed to blurring considerably the image. Immobilized particles, or sediments such as in Figure 9b are better resolved, and they could be three-dimensionally imaged to measure, for instance, close packing densities as a function of particles aspect ratio. However, obtaining a good quality 3D space image for quantitative studies, still requires, ellipsoids with a core—shell morphology with an outer nonfluorescent shell to precisely locate center and orientation of contacting particles.

IV. Conclusions and Outlook

We have demonstrated that monodisperse ellipsoidal silica—hematite core—shell particles with a tunable aspect ratio can be reproducibly prepared. Different fluorescent dyes (RITC and FITC), for confocal microscopy and photobleaching techniques, can be incorporated into the silica shells without loss of particle stability. Furthermore, we have shown that hematite cores can be easily dissolved, yielding hollow ellipsoids optically transparent in an organic solvent mixture. We also show that the diffusion coefficient of such hollow particles (when labeled with RITC) can be accurately measured by rotational FRAP, which allows us to investigate, for instance, rotational self-diffusion of ellipsoids in concentrated fluids or glassy phases. For this purpose, a system of fluorescent tracers and identical nonfluorescent host particles can be prepared by chemically “bleaching” part of the ellipsoids. Moreover, by employing hematite core particles, rotational diffusion studies could be potentially performed also in the presence of an external magnetic field. Finally, we have shown that FITC labeled ellipsoids can be used to obtain 3D real space images of particle sediments by confocal microscopy, which would allow, for example, to study the random close packing density of prolate particles as function of their aspect ratio by measuring volume fractions with single particle accuracy.

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