Quantifying the "milky sky" experiment

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Spectra of direct and scattered light that passed through a tank of water mixed with up to 25 ml of homogenized skim milk were measured with a spectroradiometer in a classic experiment used to illustrate why the sky is blue and why the Sun turns red near the horizon. The direct light penetrating the tank was reddened by preferential scattering of short waves by the milk particles (protein casein micelles and fat globules). Scattered light was blue near the light source when the optical thickness was small and red far from the source when the optical thickness was large. The measured radiance spectra and Mie theory were used to estimate that the optically effective mean diameters of protein casein micelles and fat globules were 170 and 610 nm. © 2008 Optical Society of America

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1. Introduction

A well-known, dramatic demonstration in chemistry courses is to mix two colorless liquids, a solution containing starch and a solution containing dissolved iodine and potassium iodide. The mixture turns dark violet because of the chemical reaction in which the product, a starch-iodide complex, has high absorptivity at all but the shortest waves in the visible spectrum.

In atmospheric optics a similarly classic, dramatic experiment is to shine a narrow circular beam of light through a tank of water onto a screen and gradually add skim milk [1,2]. Before the milk is added, the beam is not visible in the tank, and only a circle of white light appears on the screen. As skim milk is added a bluish beam of scattered light beam appears in the tank, and the circle of light on the screen becomes duller and turns redder. The color is not produced by a chemical change but by the scattering of light. Particles in homogenized skim milk are so small that they scatter short waves or blue light more efficiently than long waves or red light. The circle of light on the screen consists almost entirely of direct light that has not been scattered and is therefore red. The fact that scattering rather than a chemical change is the cause of the color is easy to confirm by noting that the beam of scattered light on the side of the tank facing the source has a pale blue cast, while on the far side of the tank the scattered light is redder and becomes redder as milk is added.

The milk experiment is used to illustrate and help explain the colors of the sky and of the Sun (or Moon) at the horizon. On clear days when the Sun is high in the sky, the sky is blue and the Sun is only slightly yellow. When the Sun is near the horizon, much of its light, and especially the blue and violet, has been scattered during the long oblique path through the atmosphere, and so the transmitted light becomes reddish. During twilight, the horizon sky also becomes reddish. Sunlight that has lost most of the short waves only illuminates the distant part of the horizon sky, where some is scattered toward the twilight

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observer. As this skylight approaches the observer, its shortwave components are reduced further by scattering. The scattered light that reaches the observer, like the scattered light at the far end of the water tank from the light source, is reddish.

Clearly, there are differences between the sky and a tank of milky water, but the analogy between the two is quite strong, and similar experiments with small particles immersed in fluids, including milk, have a venerable history [2,3]. Clear air contains two main types of particle, namely, air molecules and aerosol particles. Milk consists of two main types of particle, namely, protein casein micelles and fat globules [4,5]. The light scattering efficiency of particles, defined as the ratio of the area of scattered light to the cross-sectional area of the particle, depends largely on the size parameter, $x \equiv 2\pi r/\lambda$ (i.e., the ratio of the particle's circumference to the wavelength, λ) and is proportional to $\lambda^{-\alpha}$, where α is the Ångstrom coefficient. Air molecules, which are much smaller than the wavelength of visible light, scatter light according to Rayleigh's law with an efficiency that is proportional to λ^{-4}. Most atmospheric aerosol particles have radii, r_a, in the range $20 \leq r_a \leq 500$ nm and scatter light with Ångstrom coefficients in the range $0 \leq \alpha \leq 2$. As a result, the aerosol particles have a much larger light scattering efficiency than the tiny molecules, and the hazy sky is less blue than when the air is clean and dry. As the size and the number density of aerosol particles in the atmosphere increase, the sky takes on an appearance that is often described for good reason as milky.

The dairy industry has devoted a major effort to designing and improving their products. Studies using a variety of techniques, including diffraction of green laser light and filtration, have been used to determine the size spectra of the milk particles [6–11]. The proteins, most of which are encased in casein micelles, have a mean specific gravity of 1.11 and reported diameters of about 100–160 nm. The fat globules have specific gravity of 0.915, typical diameters prior to homogenization of up to about $10,000$ nm, and an index of refraction $n_{\text{lipid}} = 1.462$. Homogenization, designed to reduce the size of the fat globules so they do not rise, breaks them into much smaller and more uniform size particles (but still much larger than the casein micelles), with mean diameters from about 500 to 700 nm, and pasteurization coats them so that they do not clump. Whole cow's milk contains about 3.5% fat and 3.5% proteins, roughly 80% of which are in the casein micelles. Skim milk must contain less than 0.5% fat and often contains about 0.2% to 0.3% fat. As a result, the total volume of casein micelles in skim milk is usually more than 10 times that of the fat particles, but the larger fat globules scatter light more efficiently [7–11].

The purpose in this paper is to quantify the milky sky demonstration by measuring the spectral power distribution of the direct and scattered light with a spectroradiometer and to determine the degree of polarization of the scattered light. Doing so will demonstrate the degree to which milk in water can be considered an analog to the atmosphere in producing light scattering and color. It will also provide a quick means for estimating the size of the particles in each brand of skim milk, given differences in processing, fat content, and additives.

2. Description of the Experiment

The experimental setup is shown in Fig. 1. A 35 mm slide projector served as the light source. Its spectral composition is continuous and warmer than a CIE Illuminant A. A narrow beam of light was created by punching a small almost circular hole in an opaque 35 mm slide. The beam was 2 cm wide at a distance of 1 m from the projector. It was aimed directly at the center of a small plastic tank of water 13 cm on a side, with rounded edges and filled to a depth of 17 cm. The water volume was $2950\,\text{cm}^3$. The tank was placed 40 cm from the projector.

The radiance was measured by a SpectraScan PR-650 spectroradiometer at 4 nm intervals from 380 to 780 nm within a cone of angular diameter 2°. The instrument has a stated error less than 4% for radiance, a spectral accuracy of 2 nm, and CIE 1931 colorimetric errors $x < 0.001$, $y < 0.001$ for a 2856 K blackbody (CIE standard illuminant A) [12]. Radiance of the direct beam was measured 1.2 m from the tank through one 8× and one 64× neutral-density filter, thereby reducing radiance by a factor of 512 to avoid saturating the instrument when little or no milk was included. Unfortunately, for milk volume, $V_{\text{milk}} > 20\,\text{cm}^3$ radiance fell below the level at which the spectroradiometer measured accurately for $\lambda < 540$ nm.

Radiance of the scattered light was measured without neutral-density filters at a distance of 0.75 m from the tank and 90° from the direct beam at 3 cm from the side of the tank nearest the projector and at 3 cm from the far side. Because the beam was directed down the center of the tank, after being scattered it passed through roughly 6.5 cm before emerging from the tank in the direction of the spectroradiometer. Its radiance was measured first without a filter and then with a Hoya 77 mm linear polarizing filter (with stated reflection 5% of incident light) oriented at both maximum and minimum apparent brightness. For 10 ml of milk the radiance of the polarized scattered light at minimum brightness fell below the sensitivity threshold of the spectroradiometer and was not recorded.

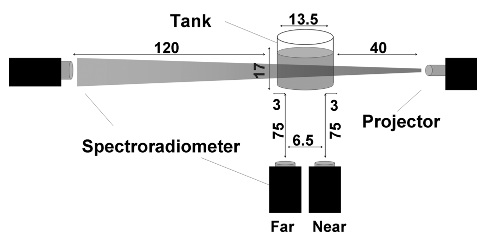

Fig. 1. Design of the experiment, showing positions of the spectroradiometer relative to the light source for scattered and direct penetrating light. All dimensions are given in centimeters.

Three light scattering experiments were conducted. Each used homogenized and pasteurized skim milk that had not been opened before and was not out of date (which often leads to aggregation). In experiment 1, Puleva_AD milk was added in increments of 5 ml up to a total of 25 ml, and only the direct beam was measured. In experiment 2, both direct and scattered beams were measured with 10 and 20 ml of Puleva_Calcio milk. In experiment 3, only the direct beam was measured with both 10 and 20 ml of five types of milk—Puleva_AD, Hacendado, Puleva_Calcio, Covap_ADE, and MAS. Their stated properties are given in Table 1. For example, the stated protein and fat contents in MAS were 3.1% and 0.2%, respectively, by weight. Fat contents were given with an accuracy of only one significant figure, which clearly limited the possible accuracy of any derived properties.

For each experiment spectral radiance of the direct beam was measured first with water only and then with the different volumes of milk. Measurements for each sample were repeated twice, and the accepted spectral range was that where the two values of radiance differed by less than 2%. With $V_{\mathrm{milk}} = 10$ and 20 ml, measurements of the direct beam were reliable for $\lambda > 480$ and $\lambda > 540$ nm, respectively. The two greatest sources of inaccuracy in the experiment were determination by eye of the (1) milk volume in a graduated cylinder 2 cm in diameter and (2) positions of the polarizer at minimum and maximum light intensity. For experiment 3, we conclude that the volumes differed by 7.5% in the worst case, 6% in another case, and by only 0.5% in the other three cases. Finally, the milk was shaken in only some of the cases before the experiments, but this was not recorded.

3. Measurements and Analysis

The incandescent bulb of the 35 mm slide projector provided a continuous light spectrum that was not Planckian and peaked at a much longer wavelength ($\lambda_{\max} = 708$ nm) than sunlight. The spectra of direct light radiances (I_0, I_{10}, I_{20}) with $V_{\mathrm{milk}} = 0$, 10, 20 ml, respectively, in the tank are shown in Fig. 2 for Puleva_AD milk. As milk was added, radiance at all wavelengths decreased, and the peak of the radiance spectra shifted slightly toward longer wavelengths ($\lambda_{\max} = 716$ nm for $V_{\mathrm{milk}} = 20$ ml). The fractional decrease of radiance was much greater at short wavelengths (99.3% at $\lambda = 550$ nm versus 88.7% at 750 nm for an increase of $V_{\mathrm{milk}} = 20$ ml). Figure 3 shows that the ratios of radiances, $I_{20}:I_{10}$ was consistently 7.5% smaller than $I_{10}:I_0$ at all wavelengths, whereas for three of the five types of milk the ratios $I_{10}:I_0$ and $I_{20}:I_{10}$ differed by 0.5% at all wavelengths. These results demonstrate that the reduction of radiance I of the direct beam in the tank is governed to a high degree of accuracy by Bouguer's (also called Lambert's or Beer's) law for a light passing through a medium with optical depth τ,

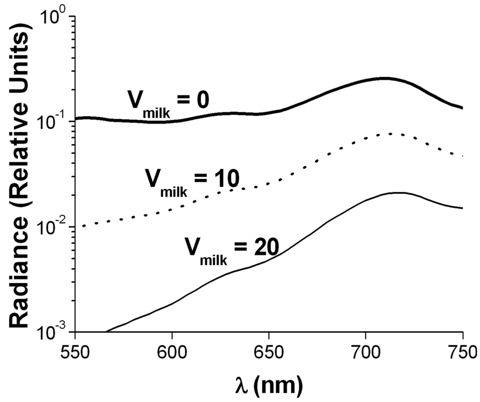

Fig. 2. Spectra of direct light penetrating a tank of 2950 ml of water with 0, 10, and 20 ml of Puleva_AD skim milk.

$$I(\lambda) = I_0(\lambda)e^{-\tau}. \tag{1}$$

Bouguer's law then indicates that for the Puleva_AD milk 7% more milk was added in the second increment of approximately 10 ml than in the first increment, and that in 3 of the 5 cases both increments of milk differed by only about 0.5%. Bouguer's law was next used to determine the optical depths, $\tau(\lambda)$, of the water with $V_{\mathrm{milk}} = 20\ \mathrm{cm}^3$ for each of the five types of milk. It was also applied to the measurements to obtain the Ångstrom power α by using the equation

$$\alpha = -\Delta \ln(I)/\Delta \ln(\lambda). \tag{2}$$

Measured values of the Ångstrom coefficient α varied little with wavelength for each type of milk and ranged from 2.54 to 2.68 for the five different types of milk. Figure 4 shows the measured values of τ (solid curve) and α (dashed curve) as a function of λ for 20 ml of Puleva_AD. The small, irregular variations

Table 1. Mie Scattering Theory Calculations of r_{FAT} r_{PRT}[a]

Milk Brand	Protein (%)	Fat (%)	α	τ	r_{PRT} (nm)	r_{FAT} (nm)
PulevaAD	3.2	0.3	2.68	3.98	79	287
Haciendado	3.1	0.3	2.58	4.51	87	314
Puleva_Calcio	3.94	0.3	2.54	5.98	97	320
CovapADE	3.2	0.3	2.60	4.53	85	315
MAS	3.1	0.2	2.67	3.22	78	289

[a]Calculations of optically effective mean radii of fat globules, r_{FAT}, and protein casein micelles, r_{PRT}, in five types of milk using protein and fat contents stated on the milk cartons and Ångstrom coefficients α and optical depths τ measured with a spectroradiometer.

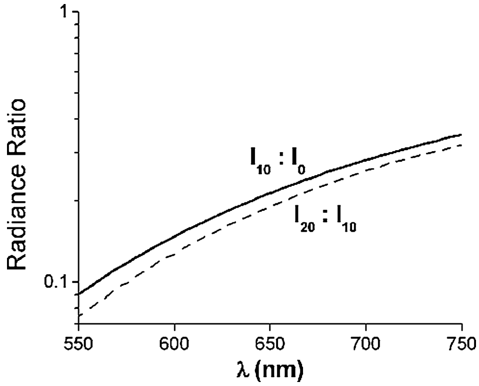

Fig. 3. Spectra of the ratios of direct light radiance $I_{20}:I_{10}$ and $I_{10}:I_0$ for Puleva_AD milk, confirming the validity of Bouguer's law. Spectra indicate that the second increment contained 7.5% less milk than the first.

of α result from the small wavelength increment ($\Delta\lambda = 4\,\mathrm{nm}$) and are much reduced when averaged over a larger range of wavelengths.

A Mie scattering program was run for particles with a range of radii encompassing protein and fat particles to determine effective particle sizes in the five types of milk. The effective index of refraction for fat globules immersed in water was set at $n_{\mathrm{fat}} = 1.462/1.33 = 1.10$. Because the index of protein casein micelles, n_{prot} is not well known, the Mie program was run using several values for n_{prot}. In all calculations shown here we use $n_{\mathrm{prot}} = n_{\mathrm{fat}}$ as in [7], because this value produced the most consistent particle sizes for the five types of milk. Thus another outcome of the experiment was to determine that the likely value of $n_{\mathrm{prot}} = 1.10$.

In Table 1 we matched measured values to calculated values of α and τ for each type of milk. Figure 5 shows contoured values of α and τ as functions of r_{fat} and r_{prot} for milk with fat content 0.3% and protein content 3.2%. The filled circles show the unique $(r_{\mathrm{fat}}, r_{\mathrm{prot}})$ coordinates of the (α, τ) pairs for Puleva_AD and Covap milk brands. Of the five milk types, only Puleva_Calcio mapped its (α, τ) pair onto two $(r_{\mathrm{fat}}, r_{\mathrm{prot}})$ points, namely, (320, 97) and (253, 106). We rejected the second point because it was far outside the range of sizes for the other milk types. This yielded calculated values of optically effective mean radii $r_{\mathrm{prot}} = 85\,\mathrm{nm}$ and $r_{\mathrm{fat}} = 305\,\mathrm{nm}$, which are similar to the above-mentioned published values ($50\,\mathrm{nm} \le r_{\mathrm{prot}} \le 80\,\mathrm{nm}$ and $250\,\mathrm{nm} \le r_{\mathrm{fat}} \le 350\,\mathrm{nm}$). Of the five types of milk, Puleva_Calcio had the largest calculated values of r_{fat} and r_{prot} (as well as the lowest value of α and the highest value of τ). This suggests that fortifying milk with calcium either enlarges the particles or restricts their breakup.

To see the individual particles, electron micrographs of the water–milk mixture were made for a dilute mixture of MAS milk in distilled water, one of which is shown in Fig. 6. In the process of preparation for analysis, the samples are desiccated, and the particles almost surely shrink. The photos appear to contain two distinct sizes of particles. The larger particles, which range from about 150 to over 500 nm in diameter, may be the dried fat globules. The smaller particles, which appear faintly, may be the protein casein micelles. They are much more numerous and range from about 50 to 100 nm in diameter.

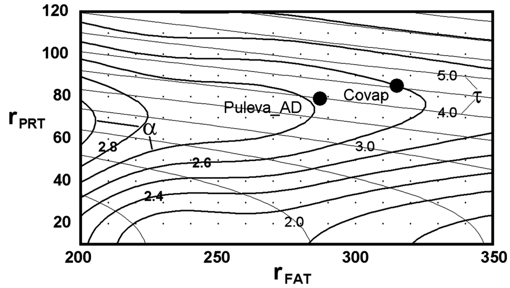

Fig. 5. Mie scattering model values of τ (thin contours) and α (thick contours) as a function of r_{FAT} and r_{PRT} for milk with fat content 0.3% and protein content 3.2%. Filled circles are measured values of τ and α for Puleva_AD and Covap milk.

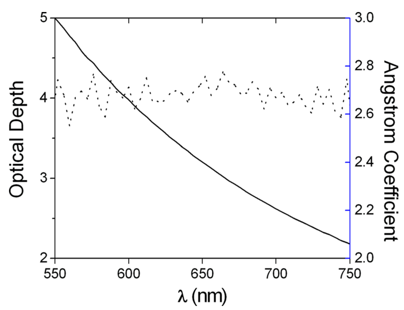

Fig. 4. (Color online) Measured values of optical depth, τ (solid line) and Ångstrom coefficient, α (dotted line) for direct light passing through the tank with 20 ml of Puleva_AD milk. The small, irregular variations for α result from the small wavelength increment ($\Delta\lambda = 4\,\mathrm{nm}$).

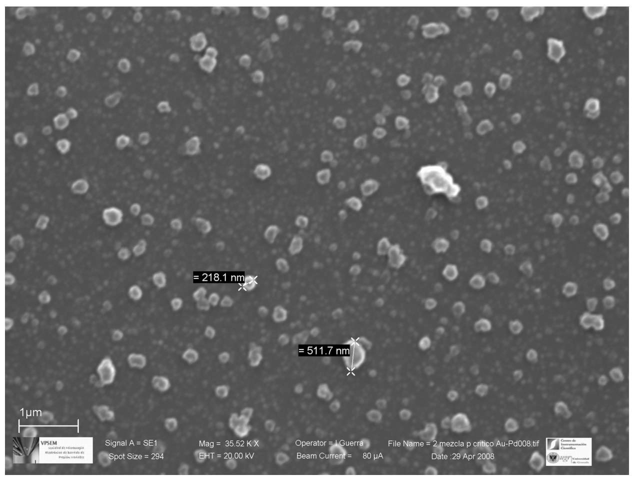

Fig. 6. Electron micrograph of a dilute mixture of MAS skim milk in distilled water. There are two distinct sizes of particles. These may be desiccated remnants of the smaller protein casein micelles and the larger fat globules. The scale is shown at lower left, and measured diameters of two particles are shown.

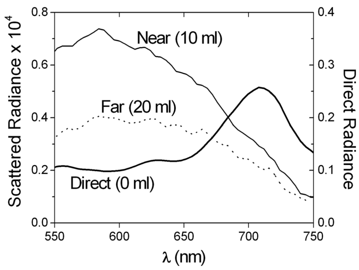

Fig. 7. Spectra of radiance of direct light with no milk (thick curve), and scattered light deflected by 90° both 3 cm from the near end of the tank with 10 ml (thin curve) and 3 cm from the far end of the tank with 20 ml (dashed curve) of Puleva_Calcio milk.

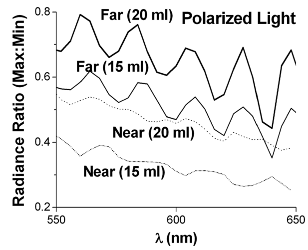

Fig. 8. Ratio of minimum to maximum radiances of polarized light scattered by 90° from the direct beam on near and far sides of the tank and with 15 and 20 ml of Puleva_Calcio milk.

The radiance and degree of polarization of the scattered light from the tank of milky water also mimic to some degree the behavior of skylight. In experiment 2, the scattered light was viewed and measured at two points along and at 90° from the direct beam. Figure 7 compares the spectra of the direct and the scattered light on the near side of the tank with 10 ml of milk and on the far side with 20 ml of milk. Both beams of scattered light are much bluer than the direct light beam. The scattered light is also more intense and bluer on the near side with only 10 ml of milk than on the far side with 20 ml of milk. Thus, as with the atmosphere, even the scattered light turns redder as it penetrates more. For all quantities of milk the radiance of the scattered light is greater on the near side, but changes relatively little as milk is added and is therefore not governed by Bouguer's law, because optical thickness is so large that much of the light has been scattered more than once.

The effect of multiple scattering could be seen in two other ways. First, the entire tank of milk and not just the direct beam brightened when at least 10 ml of milk was added to the water. Second, the ratio of minimum to maximum radiance of polarized light was larger (and the degree of polarization smaller) when there was more milk and when the path length was longer (Fig. 8). This ratio is shown only for 15 and 20 ml of milk, because when the water contained 10 ml or less of milk and the polarizer was turned to minimum brightness, the radiance of the scattered light was below the minimum sensitivity threshold of the spectroradiometer.

4. Summary and Conclusions

We quantified the "milky sky" experiment by using a spectroradiometer to measure the spectral power distribution of the radiance of both direct and scattered light that passed through dilute mixtures of homogenized skim milk in water. Between 5 and 25 ml of five types of milk were added to 2950 ml of water. When 5 or 10 ml of milk was added, the light scattered by 90° was bluer than the direct beam and was highly polarized. As milk was added, the directly penetrating light dimmed and turned red, and the scattered light also turned redder and became less highly polarized. Values of the Ångstrom coefficient α and optical depth τ calculated by using Mie theory for the stated fat and protein contents of the five milk types (given to two significant figures for protein contents and one significant figure for fat contents) were matched to measured values of α and τ. This yielded mean optically effective diameters of 170 nm for protein casein micelles and 610 nm for fat globules, which compares closely with measured values in the literature.

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