To Christian Hansen :

Thank you for being so cooperative in preparing the different views of the data. Each of us who have been around long enough to be called "experts" have our own favorite way of looking at the data. I hope that you did not feel that any of us belittled your attempts to explain what was going on. You admitted to not knowing much about scattering; I admitted that I don't know much about chemical spectroscopy, and Karl admitted that he confuses what is going on in his neighbor's yard with what's going on in the discussion group. (We should all have his mental problems. He is amazing.) The discussion group is a place where ideas may be discounted, but I hope people never are.

As far as your data goes, it is an interesting set. I am living in a delusional world, where I believe I can explain anything with the representative layer theory. Occasionally I get snapped back to reality. It may happen this time. But here goes!

On your slide { ReflectanceVsTransmission-6677 }, you have displayed both the remission and transmission of "Milk" (before coagulation) and "Milk gel" (after coagulation). In a perfect world, all the light would either be remitted (***R***), transmitted (***T***) , or absorbed (***A***). If you converted the log values back to fractions, the three would add up to 1, so you can estimate the absorption fraction by { 1-***R***-***T*** }. [In reality, some of the light will just be lost in that it will miss both detectors, and it will be counted as absorbed, even though it is not.] The metric { –log(1-***A***) } comes a bit closer [than log(1/***R***) (or log(1/***T***)] to what we are often looking for: absorption n the absence of scatter, though the two are certainly not independent. [You might like to give this a try.]

In transmission, scatter causes a loss of intensity, and an increase in the Absorbance function. (What goes back to the remission detector is not seen by the transmission detector.) In remission, it is scattered light that is detected; so with more scatter, the Absorbance function goes down with increasing scatter.

Looking at your two plots, the scatter from the "Milk gel" is much higher than the scatter from the "milk". Furthermore, we are invited to conclude that **scatter is** in general **decreasing as we go up in wavelength**. This is the expected direction. For infinitesimal particles, the fall off in scatter with wavelength is severe (inverse 4^{th} power). For large particles, there is little wavelength dependence.

Additionally, by looking at the transmission spectrum, we can see a superimposed curve up in the "baseline" of the Absorbance function, which we will attribute to miscellaneous and unresolved absorption peaks. On top of the "baseline", we see the specific peaks we've been discussing.

Now let's turn to the peak at 1445 in the remission spectra: the one that sparked the original question. In the slides { 6663 and 6696 }, we can clearly see the trend that as coagulation occurs (particle size goes up), the top of the peak goes down. This is not surprising given that we have explained above that scatter increases with coagulation, and we know that scatter diminishes the

absorbance function in remission. What was bothersome was that "the differences between the curves at the peaks of approx 1445 nm are considerably less than the differences at 1200 nm" and the" band at 1445 nm clearly becomes more narrow as the Log(1/R) baseline goes down (i.e. as coagulation proceeds)". This is the effect that we have been referring to "non-linearity".

We can readily see this non-linearity is the MSC curves { 6674 } that Dave asked for. Karl wanted to check for it by "comparing the magnitude of the second derivative ratio of the two water bands as coagulation progresses". But what causes the non-linearity?

As Karl pointed out, one cause could be "surface reflection". When the front surface of a particle reflects light, it has not yet been subjected to the absorption that occurs within the particle. Say that this is 5% of the incident light. That puts an upper limit of { log (1/0.05) = 1.3 } in the absorbance function. Of course, the sample is not a solid wall of particles, so much of the light slips through to the next layer of particles. We can estimate that the upper limit depends on that 5% times the fraction of the sample surface that is particle. Now as the material coagulates, there is more scatter, and hence more surface area being made up of particles, so the upper limit should be higher for "Milk" then for "Milk gel". However, without knowing the solids level, I don't like to use the surface reflection explanation in this case. (I never like the "stray light" argument in remission.)

It is convenient to explain (argue) using the properties of a single particle or a single phenomena (like surface reflection), and that frequently is very effective. The explanation here is one that uses all the layers , and is embodied in the Dahm equation. We are saying that to understand what is going on in this case, it may be helpful to look at all the terms in the equation which describes the collective remission from all the layers in the sample. The "full blown" Dahm equation describing this is:

$$A(\boldsymbol{R},\boldsymbol{T}) = (1 - \boldsymbol{R}^2)\text{-}\boldsymbol{T}^2 \,/\, \boldsymbol{R} \;=\; (2\text{-}\boldsymbol{a}\text{-}\boldsymbol{r})\,\boldsymbol{a}/\boldsymbol{r}$$

The symbols ***R*** and ***T*** represent the fractions of light remitted by and transmitted through your sample (which you have measured). The symbols ***a*** and ***r*** represent the fraction of incident light absorbed and remitted by a single particle. A(***R***,***T***) is what I call the Absorption/Remission function. The name emphasizes the fact that absorption causes the metric [or a surrogate for it like log(1/R)] to go up, and remission (backscatter)causes it to go down.

Now if you take the same 5% surface reflection for an opaque particle where { ***T*** = 0 }, you are going to get { (2 - 0.95- 0.05) (0.95/0.05) = 19 } as the maximum value for the metric (which happens to convert to the 1.3 value for log(1/R) above). (Remember the observed value of this depends on the surface area fraction.) Now if the remission (scatter) increases (as it does with coagulation), you can see that, with ***r*** in the denominator, the metric will decrease, just as was argued above.

But all that argument applies to the particles themselves. We must examine what is happening in the water, which is in the continuous phase. As Karl points out, as we increase scatter in the sample, we increase the effective pathlength of light through the water, and thus expect to increase the height of the absorption maxima.

However, in transmission we also are losing light due to scatter. Consequently there is much less light carrying the absorption signal to the transmission detector. The net effect shown in { 6687} is that, compared to the "baseline" level, the height of the 1445 peak does down.

In remission, as scatter increases, we drive the metric down. However, as you can see in { 6674}, after the linear portion of the scatter is removed, we are able to observe the increase in peak height as scatter increases. We would see this effect in the Dahm Equation as an increasing ***a*** (making the metric go up)and an increasing ***r*** (making the metric go down).

Finally, we can ask ourselves if there is anything that is obviously unexplained by our argument here. To this end, I asked for the plots shown in {6699}. Using "Milk", the sample with the least scatter as the reference, we plot the corresponding values of the spectra with more scatter. This separates the effects of absorption level from those of wavelength.

Looking at the 49 minute sample, we can clearly see that as we go up in wavelength, the plots depart further and further from the 45 degree line. If the values with the same absorbance, say on each side of the minimum around 1650 fell on top of each other, this would be evidence that the scatter was NOT wavelength dependent. However, in this case, we have plenty of evidence that there is wavelength dependence of scatter (not only in this plot but the ones discussed earlier).

However, the main reason I wanted the plots was to see if there were any ill behaved regions on the sides of the 1445 peak that could indicate changes in the position of the –OH stretch band as a function of coagulation (that you wondered about). Seeing none, I fall in the camp that says there is no reason to "start theorizing yet about hydrogen bonding".

As long as we have your plots (complete with color), we might as well finish the story. We first see the blue linear potion with an offset from and a different slope than the "Milk". Then in the early part of the red portion, we see the slope changing taking the curve away from the 45 degree line as we go through absorption due to material within the particles. Following that the red curve bend back toward the line as we go through the aqueous peak. The final part of the plot is dominated by the wavelength dependence of scatter.

Don Dahm

PS If you find this helpful, I'm expecting you to buy our book. After all, Ian (Michael, the publisher of the book and host of this website) needs a new Volvo.

Just to warn you, Gerry Downey asked me to summarize this discussion for *NIRnews*. If anyone has anything they want to get on the record, post it.