Light_detectors_for_chemistry+optics-adventures_in_radiative_transport.docx
bilbo: C:/Users/vince/fortran/radtpt 17-19 Nov. 17 and 15-16 Dec. 17

This whole episode arose from trying to verify that a silicon photodiode responds linearly to the flux density of light on it.

If you'd like to skip to a treatment of how a direct beam (e.g., direct sunlight) and diffuse irradiance propagate through nicely layered media (a layer or layers of clouds; cell layers in a photosynthetic leaf), skip down here. Note that that section refers to another fairly large document, which derives the radiative transport model but also has a lead-in about a good enzymatic model of photosynthesis (as I used in several publications) and a follow-on about leaf absorptivity decreasing with depth, leaf clumping, variation of leaf temperature (hence, photosynthetic rate) with depth in a canopy, and exchange of thermal infrared radiation among leaves.

Utility of a light sensor (measuring irradiance)

I'm planning to demonstrate to the middle-schoolers at our Las Cruces Academy a variant of spectrophotometry for chemical analysis, using a simple high-powered yellow LED as a light source shining through a sample of methylene blue to a photodiode as a detector. I've done this similarly with crystal violet in the past, showing reaction kinetics of its decolorization in basic conditions. Making the little (spectro)photometer also teaches the students a bit about electronics, hands-on. We can also examine some basic optics, such as the falloff of irradiance from a point source as $1/r^2$.

The sensor: a photodiode in a current-to-voltage op amp circuit

I made a photodiode-based irradiance detector (call it a PID), using a current-to-voltage converter circuit with an op amp (see separate notes).

Is the response linear? My suspicions, and a failed test

However, the responses seemed extreme, going from 190 mV output in direct sun to 0.1 mV in low room light – low, but that low? (I set the max output to <200 mV so that it could be displayed on the small LCD voltmeter I bought, making a compact, portable light detector.) I suspected nonlinearity. I decided to test it, but this turned out to be rather difficult:
* I didn't have a series of neutral density filters or objects to stack up, testing adherence of the transmitted light to Beers' law.
* I tried stacking various numbers of pieces of white paper on top of the photodiode and then illuminating it with various sources (the stacking is a problem, as I realized later; a silly mistake). I didn't have a strong light source other than a laserpointer (several colors). This is too hard to aim reliably onto the tiny active area of the photodiode, so I turned to the high-powered yellow LED, holding it a fixed distance above the PD (about 1 cm). I got what looked like unusual readings:

Number of layers of paper	V(out)
0	1.720
1	0.330
2	0.116
3	0.036
4	0.009
Darkness	-0.005 (I made a dual voltage supply to check for zero offset)

Ambient light (not recorded, but I recall it was about 0.004)

How should diffuse light propagate through layers of scattering media? Radiative transport theory

The falloff with added layers is clearly not exponential. I decided to simulate how the diffuse light should fall off with depth in layered media that can scatter and absorb light. After a quick stab at deriving the radiative transport equations, I found a 2009 derivation of mine (used as prep for accounting for scattered light in a pecan canopy), in ~/fortran/radtpt on both bilbo and bilbo2: see separate write-up, from Fixing approximations.docx (the first part is about photosynthetic enzymatic reactions, which might also be of interest). It was a very clever solution, if I may say so, enough so that I couldn't immediately recall how I came upon it. There was the challenge that the calculations fail if there is no absorption of light, only scattering – there is obviously a limit, but it's hard to derive by algebra, so I decided to run the Fortran program for it, canopy_abs+scat.f90. There are denominators that go to zero if a → 0, so I ran it with very small values of *a*, 0.001 or 0.0001. This worked nicely.

I set the parameters as follows:
* a_{leaf} = 0.001 or 0.0001 – making absorption negligible while allowing numerical solutions
* s_{leaf} = 0.5 – about 50% scattering in a unit depth (equally up an down)
* x_f = various, as depths of the scattering medium, from 6.4 to 89.6, after a quick estimate that the attenuation might be $\exp(-s_{leaf}x_f)$ at first, and x_f = 6.4 should then give attenuation to about ¼
* D_0 = 1 – unit irradiance, as basis for seeing relative partitioning into various fluxes
* I_0 = 0 – no direct beam
* f_{leaf} = 0.5 –forward scattering of the direct beam (irrelevant here)
* K_{diff} = 0.5 – scattering (attenuation) coefficient for diffuse light; probably more like 0.7, really, but not a problem for the estimation I'm making
* K_{dir} = 0.5 – attenuation coefficient for direct light – appropriate for uniform leaf angle and other isotropic scatterers
* r = 0.001 – absorbance of lower limit ("soil"; here the PD) – complete absorbance, a rough approximation

Results with only diffuse input: see simulation_attenuation_light_at_photodiode_detector.xlsx:

xf	refl., top	abs., bottom	Ratio	W/0.001 --> 0.0001	
6.4		0.383			
12.8	0.758	0.235	0.613577		
25.6	0.857	0.13	0.553191	0.864	0.135
38.4	0.894	0.088	0.676923		
51.2	0.912	0.064	0.727273	0.926	0.072
64	0.922	0.049	0.765625		
76.8	0.928	0.038	0.77551	0.948	0.048
89.6	0.932	0.03	0.789474		
				Not exponential!	

Here, abs.,bottom is the assumed interception by the photodiode

Comparison with physical media, the stacks of white paper over the photodiode

For comparison:

My data with high-power LED, stacks of paper

No. strips	Voltage at detector	Corr. for amb. light: -0.007	Ratio	Ratio, orig.	Scaled simul., each step as 25.6	
0	1.72	1.723				
1	0.33	0.333	0.193268	0.195193	0.13	
2	0.116	0.119	0.357357	0.069754	0.072	<-- scaling reference point
3	0.036	0.039	0.327731	0.02286	0.048	
4	0.009					
					Drops faster initially, then more slowly	

Two pieces of paper acted like the simulation with $x_f \approx 51.2$, so I expected that $x_f = 25.6$ would give something like the measured attenuation for 1 sheet of paper. The result is only crudely similar. There's also a crude agreement for $x_f = 76.8$ with measurements with 3 sheets of paper.

Go for a direct beam only

What I learned: of course, scattering of diffuse light is NOT like exponential attenuation of a direct beam; there are new sources in each layer:
* I should detect only the direct beam, which means NOT layering the attenuating media on top of the photodiode – rather, inserting the media at a goodly distance away, so that the direct beam can be fixed readily on the PD, while diffuse light from its scattering is spread out thinly over a wide solid angle. I feel sheepish for not recognizing this!
*I can use a laserpointer as a strongly directional light source, while making it easier to aim by spreading it out with a camera lens.
* It's not appropriate to use layers of paper: they attenuate the direct beam far too much. I did a simulation using only a direct beam as input, calculating the fraction of the direct beam left as (total irradiance at the bottom) – (irradiance from diffuse light at the bottom). The latter quantity is $D(x_f)$, which, fortunately, I had the program print out.

xf	Tmn. = abs., bottom	D(xf)	Apparent I(xf)	U(0)
0	1	0		
6.4	0.384	0.183	0.201	0.615
12.8	0.238	0.197	0.041	0.762
25.6	0.135	0.133	0.002	0.864

Yes, only direct beam follows Beers' law

Note that a thickness of one sheet of paper (roughly equivalent to $x_f = 25.6$) should reduce the direct beam to 0.2% of its original value! → I should use optically thin scattering media. I found that a stack of photo pages attenuates light to 20% (camera exposure reading was 1/500 s at f/7.1 on directly lit concrete, changing to 1/200 s at f/5 for shaded concrete). I used 13 pages and the sleeve, for an effective 16 pages. Of course, this is diffuse light coming back, but it was attenuating direct light on the way in.

This test will be done later

Utility of the radiative transport model: making it more general

My radiative transport model works when the medium through which the light is passing is uniform over its depth (physical depth, or optical equivalent depth, as is leaf area index in plant canopies). I used it in simulations of light interception (plus gas and heat exchange in plant canopies), and a similar version in simulating the distribution of light inside plant leaves. In the latter case, the layers differ in optical properties. The top layer, or adaxial lamina, which gets the most sunlight, has the most chlorophyll and the highest light absorption. It must be modeled differently (that is, with different optical parameters) than the inner mesophyll and also the abaxial lamina.

Setting up a general solution

How difficult is it to "patch" layers together for a total solution? The answer is that it's straightforward, though sometimes a bit tedious algebraically. Take the case of two different layers abutting each other, with the top layer (as of a leaf) getting both direct-beam illumination and diffuse radiation (skylight), and the bottom layer getting only diffuse light. To review what are the givens:

- The optical properties of the two layers. Examine the list earlier:
  - the fractional scattering of intercepted light into diffuse light (s_{leaf}), which I took as equally up and down;
  - the absorptivity (fractional extinction by a unit depth), a_{leaf};
  - the scattering coefficient per unit depth for direct light, K_{dir}, such that the fraction of intercepted (scattered) light per depth increment dx is $K_{dir}dx$. Over a finite depth, x, the direct beam is attenuated to $\exp(-K_{dir}x)$;
  - the scattering coefficient per unit depth for diffuse light, K_{diff}; it's usually larger than K_{dir} when the direct beam is not at an extreme angel off perpendicular – the diffuse rays at wider angles (closer to parallel to the layer) travel a longer slant distance per unit vertical depth; there are many discussions of leaf optics, to which I have contributed in publications;
  - the absorption fraction at the bottom of the layer, *r* – my photodiode, or soil in a plant canopy; for a free leaf, it's zero, since the light exits unimpeded;
  - of course, the thickness of the layer, x_f.
- Three streams of radiation:
  - On the top surface, a direct beam of irradiance I^0 (in, say, W m^{-2} or $mol_{photons}m^{-2}$ s^{-1}), at a known angle. The angle, along with the medium's geometry, sets $K_{dir.}$ For example, for a plant canopy with a uniform distribution leaf angles, we simulate it as a continuous medium (turbid medium) with $K_{dir} = 0.5$ for normal (vertical) incidence or $0.5/\cos(\theta)$ for inicidence at an angle off-zenith equal to θ.
  - Also on the top surface, diffuse light at an irradiance D^0, measured as projected on the flat surface. For a uniform leaf angle distribution, K_{diff} starts at about 0.7, but varies a bit with depth as more highly angled rays are absorbed or scattered (but, in partial compensation, more of the angled rays are generated by scattering[1]).
  - On the bottom surface, diffuse light at an irradiance U^f, with "U"denoting "up," naturally.

If there is only this one layer, the program gives the solution by the method described in the aforementioned document, Fixing approxmations.docx.

Two abutting media of different properties

We need a separate solution for each layer, specifying I^0, D^0, and U^f for each one ("f" is for "final" depth). For the top layer, I^0 and D^0 are fixed; the presence of a lower layer can't generate more incident light. For the bottom layer, U^f is also fixed; the presence of a top layer can't generated more upwelling light at the bottom of this layer.

We readily calculate the direct beam irradiance reaching the top of the 2nd layer. It's simply I^0 attenuated by the exponential factor $\exp(-K_{dir}x_f)$.

However, we don't know the downwelling irradiance at the bottom of the first layer, D^f_1. It's affected by how the light propagates through the bottom layer, including the light scattered upward from the lower layer and generating more downwelling light in the upper layer by scattering. Similarly, we don't know the upwelling irradiance at the top of the lower layer, which becomes the upwelling irradiance at the bottom of the upper layer. We have to figure out how to make each of these two fluxes match at the boundary between the layers.

A way out, and some necessary terminology

The key to achieving the matching of fluxes is the linearity of the equations of radiative transport. This means that independent solutions, each achieved with different boundary conditions (I^0, D^0, U^f) can be superposed, that is, simply added together.

To keep track of fluxes:

- The flux of diffuse light leaving the top of the upper layer, generated by scattering, we call U^0_1; the superscript identifies the layer and the subscript identifies the location ("1" is at the top of the layer, "f" is "final" or at the bottom)
- The flux of downwelling diffuse light leaving the bottom of the upper layer is then D^1_f.
- The flux of upwelling diffuse light leaving the top of the lower layer is U^2_0.

First, we get "base" solutions with known, thus, fixed irradiances:

- Denoted as B_{110}: the fluxes in the top layer calculated with the known direct-beam and diffuse irradiances at the top of the first layer (e.g., the adaxial surface of a leaf facing the sun).
  - The subscript indicates that it has finite irradiance as the direct beam at the top surface, I^0_1 (1st number in the subscript), finite diffuse irradiance at the top surface, D^0_1 (2nd number in the subscript), and no diffuse irradiance propagating upward from the bottom, U^f_1 (third subscript).
  - The final solution includes diffuse irradiance propagating upward from the bottom of this first layer, but we have to compute this with a flux-matching condition that we'll derive shortly.
  - This solution, B_{110}, gives us fluxes that we will denote as:
    - $U^0_1(B_{1110})$, the upwelling diffuse flux at the top of this layer, exiting from the top as reflected diffuse light. There will we more upwelling flux added to this, generated by the upwelling flux at the bottom of this layer, for which we will solve shortly.
    - $D^f_1(B_{110})$, the downwelling diffuse flux at the bottom of this layer. Again, there will be more such flux, generated by upwelling flux from the second layer.
- Denoted as B'_{100} the fluxes in the second or bottom layer, calculated with only the fixed irradiance from the direct beam that reached the top of this layer; this is readily calculated, as noted above. Clearly, the prime indicates the second layer.
  - This solution gives us fluxes that we denote as:
    - $U^0_2(B'_{100})$, the upwelling flux generated by the incident direct beam irradiance.
    - $D^f_2(B'_{100})$, the downwelling flux generated at the bottom of this layer.
  - Again, there will be additional fluxes of these types generated by the downwelling flux at the top of this layer coming from the top layer.

- Denoted at B'_{001}: the fluxes in the bottom layer, calculated with only the fixed diffuse irradiance at the bottom of this layer – e.g., diffuse light on the lower or abaxial surface of a leaf.
  - This solution gives us fluxes with ready interpretations:
    - $U^0_2(B'_{001})$
    - $D^f_2(B'_{001})$

Then we need purely "supplemental" solutions, with arbitrary incident irradiances (say, 100 units) that we can scale after calculating the matching conditions:

- Note: not needed: Denoted as S_{010}: fluxes in the top layer generated by extra diffuse irradiance at the top. We've already accounted for the known and fixed diffuse flux at the top. Although upwelling flux from the second layer generates downwelling flux in the top layer, the magnitude of this goes to zero at the top of the second layer – there's a vanishing amount of scattering power at the top surface. No extra downwelling flux is generated.
- Denoted as S_{001}: the fluxes in the top layer generated by upwellling diffuse fluxes at the bottom of this layer.
  - This gives us fluxes that we denote as:
    - $U^0_1(S_{001})$ –again, readily interpreted
    - $D^f_1(S_{001})$ - ditto
- Denoted as S'_{010}: the fluxes in the bottom layer generated by downwelling diffuse fluxes at the top of this bottom layer.
  - This gives us fluxes that we denote as:
    - $U^0_2(S'_{010})$
    - $D^f_2(S'_{010})$

Basic algebraic solution

We now have enough independent solutions to construct the full solution to the case in which:

- There are two layers, plane parallel, each one optically uniform through its depth, but potentially different from each other. We ignore edge effects and consider the layers are of great extent laterally.
- Incident on the top of the first layer are:
  - a direct beam of light (sunlight, e.g.) of a known irradiance, as projected on a horizontal surface. Its magnitude is defined as I^0_1. We take care of an angled incidence with the proper specification of the extinction coefficient, K_{dir};
  - diffuse light, of uniform angular dependence, of magnitude D^0_1 as irradiance projected onto a horizontal surface..
- Incident on the bottom of the second layer is:
  - diffuse light, of magnitude U^f_2

At the interface between the two layers the upwelling and downwelling fluxes are initially unknown. We have to solve for them using matching conditions:

- The downwelling flux exiting the bottom of layer 1 must equal the downwelling flux entering the top of layer 2: that is,

  $D^f_1 = D^0_2$

  We take the fluxes that are already determined from the external lighting and add fluxes from scattering between the layers, with coefficients α (multiplying the test solution S_{001}, for diffuse upwelling light entering the bottom of layer 1, generating some more downwelling light) and β (multiplying the test solution S'_{010} for diffuse downwelling light at the top of layer 2):

$$D^f{}_1(B_{110}) + \alpha D^f{}_1(S_{001}) = \beta D^0{}_2(S'_{010})$$

- The upwelling flux at the bottom of layer 1 must equal the upwelling flux exiting the top of layer 2: that is,
  $U^f{}_1 = U^0{}_2$
  Similarly to the above for downwelling fluxes:
  $$\alpha U^f{}_1(S_{001}) = U^0{}_2(B'_{100}) + U^0{}_2(B'_{001}) + \beta U^0{}_2(S'_{010})$$

A critical test

Take a single layer of what we'll call full thickness. I chose to call its thickness $2x_f$. Allow direct and diffuse light incident on its top surface. For simplicity any diffuse light incident on the bottom – the solution is trivially generalized.

Get the solutions for the direct flux and diffuse fluxes exiting the bottom and for the diffuse flux exiting the top. That is, solve for I^f (no need for a "1" subscript), D^f, and U^0.

Now split this into two equal layers, each of thickness x_f and solve for the exiting fluxes when the layers are joined and the fluxes are solved using the matching methods above. That is, solve for $I^f{}_2$, $D^f{}_2$ (which must equal D^f from the first simulation), and $U^0{}_1$ (which must equal U^0 form the first simulation).

For this test I chose parameters and inputs as follows, akin to sunlight penetrating a modest cloudbank. The parameters are still set as if were considering a leaf:

- a_{leaf} = 0.0001 – effectively, no absorption. I can't set this to exactly zero or the formulation breaks down
- s_{leaf} = 0.5 – per unit optical depth, half the diffuse radiation is scattered
- D^0, which is $D^0{}_1$ in the two-layer simulation = 100, like watts per square meter
- I^0 = 1000
- f_{leaf} = forward scattering of the direct beam = 0.5
- K_{diff} = interception coefficient for diffuse light = 0.5; that is, an initial flux density is cut by the factor $\exp(-K_{diff}x)$ in traversing a distance (optical depth) x.
- K_{dir} = same for the direct beam = 0.5 – as if for a beam incident vertically on a canopy with a random distribution of leaf angles (I used this a lot)
- r = reflectivity of the soil for light exiting the bottom = 0.0001 – absorb it all and count it up
- $2x_f$ = 3.0

Results

For the solution as a single layer of depth 3.0:

- $I^f{}_1$ = 223.097
- $D^f{}_1$ = 405.398
- $U^0{}_1$ = 471.404

For the solution as two layers:

- Solution B_{110}: Layer 1, with known incident irradiances 1000 in the direct beam, 100 diffuse:
  - $I^f{}_1(B_{110})$ = 472.331 (a fraction 0.472 transmitted)
  - $D^f{}_1(B_{110})$ = 327.630
  - $U^0{}_1(B_{110})$ = 300.037

- Solution S_{001}: Layer 1, with notional diffuse irradiance, 100, incident from the bottom:
  - $U^0_1(S_{001})$ = 72.724
  - $D^f_1(S_{001})$ = 27.276
- Solution B'_{100}: Layer 2, with known direct beam irradiance on top (=$I^f_1(B_{110})$)
  - $I^f_2(B'_{100})$ = 223.096 (a fraction 0.472^2 transmitted from the top of layer 1...and it equals I^f_1 of the single-layer solution, as it must, within rounding errors
  - $D^f_2(B'_{100})$ = 120.400
  - $U^0_2(B'_{100})$ = 128.833
- Solution S'_{010}: Layer 2, with notional diffuse irradiance, 100, incident on top
  - $D^f_2(S'_{010})$ = 72.724 – same as $U^0_1(S_{001})$, which looks like the mirrored case of S_{001}
  - $U^0_2(S'_{001})$ = 27.276 – same as $D^f_1(S_{001})$, for the same reason

Solving for the matching conditions:
Downwelling fluxes, $D^f_1 = D^0_2$:

$$D^f{}_1(B_{110}) + \alpha D^f{}_1(S_{001}) = \beta D^0{}_2(S'_{010})$$

327.630 + α 27.276 = β 100

or

β = 3.2763+ 0.27276 α

Upwelling fluxes, $U^f_1 = U^0_2$:

$$\alpha U^f{}_1(S_{001}) = U^0{}_2(B'_{100}) + U^0{}_2(B'_{001}) + \beta U^0{}_2(S'_{010})$$

α 100 = 128.822 + 0 + β 27.276

Substituting β from above:

α [100 – 27.276*0.27276] = 128.822 + 27.276*3.2763

→ α = 2.35736

→ D^f_1 = 327.630 + 2.35736*27.276
= 391.929

→ $D^f_2 = D^f_2(S'_{100}) + D^f_2(S'_{010})*D^f_1/100$
= 120.400 + 72.724*(391.929/100)
= 405.427

Aha; this closely equals D^f from the single-layer solution, allowing for rounding errors

Finally,

$U^0_1 = U^0_1(B_{110}) + U^0_1(S_{001})*U^f_1/100$
$= U^0_1(B_{110}) + \alpha*U^f_1(S_{001})/100$
= 272.761 + 2.35736*72.724/100
= 471.474

Aha, again – matches the single-layer solution, allowing for rounding errors

The method works.

Extensions

Extension to more than 2 layers

The method is clear, if tedious algebraically: Solve for the first two layers (with notional input from the bottom); recast this as base and supplemental solutions; solve for layers 1+2 matching layer 3.

For non-layered media

The radiative transport equations become 2- or 3-dimensional. There are some interesting "tricks" in these cases. For example, I simulated light within a regular array of trees, using some basic numerical methods but exploiting symmetries for ellipsoidal canopies. Fully generally, Michaël Chelle at INRA in France has a powerful method called radiosity[2], similar to that used in CGI simulations of lighting in movies. You have to be serious about math and computing to use these.

Footnotes

[1] Gutschick VP, Wiegel FW (1984) Radiation transfer in vegetative canopies and other layered media: Rapidly solvable exact integral equation not requiring Fourier resolution.
Journal of Quantitative Spectroscopy and Radiative Transfer 31: 71-82.

[2] Chelle M, Andrieu B (1998) The nested radiosity model for the distribution of light within plant canopies. Ecological Modelling 111: 75-91.