Summary of radiation in participating media

Governing equations (Chapter 9)

Emission, absorption, scattering

Over a distance ds, the spectral intensity I_η (watts per m^2 of cross-sectional area per steradian per unit wavenumber $\{m^{-1}\}$) a beam of radiation is *attenuated* by absorption by

$$(dI_\eta)_{\text{abs}} = -\kappa_\eta I_\eta \, ds, \qquad (9.3)$$

where κ_η is the *spectral absorption coefficient* at wavenumber $\eta = 1/\lambda$, where λ is the wavelength of the radiation. From Eq. 9.3 it is clear that the units of κ_η are m^{-1} or cm^{-1}. Equation 9.3 is reasonable in that the rate of attenuation is proportional to the amount of radiation there is to attenuate, and is proportional (for infinitesimal path lengths ds, where $dI_\eta << I_\eta$) to the path length ds and thus is proportional the number of molecules or particles the beam encounters. In the unrealistic case κ_η = constant for all η, the medium is called a *gray medium.* Since κ_η will be affected by the number of molecules per unit volume along the path ds, sometimes κ_η is given per unit of partial pressure or density, in which case the units would be $m^{-1}atm^{-1}$ or $m^{-1}(kg/m^3)^{-1}$ respectively. Attenuation of I_η by scattering is defined analogously, i.e.

$$(dI_\eta)_{\text{sca}} = -\sigma_{s\eta} I_\eta \, ds, \qquad (9.8)$$

where $\sigma_{s\eta}$ is the *scattering coefficient* (m^{-1}) at wavenumber η. The *extinction coefficient* of β_η is the sum of the absorption and scattering coefficients

$$\beta_\eta = \kappa_\eta + \sigma_{s\eta}. \qquad (9.9)$$

The *optical thickness* τ_η (dimensionless) for wavenumber η is defined as

$$\tau_\eta = \int_0^s \beta_\eta \, ds. \qquad (9.10)$$

So that

$$I_\eta(s) = I_\eta(0) \exp\left(- \int_0^s \beta_\eta \; ds\right) = I_\eta(0) e^{-\tau_\eta}, \qquad (9.5)$$

$\tau_\eta >> 1$ implies that any given photon is very likely absorbed or scattered over the path length s; $\tau_\eta << 1$ implies that any given photon is very likely not absorbed or scattered over this path length.

The difference between decrease in I due to absorption or due to scattering is that scattering merely redirects incident radiant intensity that was in the direction of s to a different direction, whereas absorption decreases the total radiant power.

I_η increases along the same path due to *emission*

$$(dI_\eta)_{\text{em}} = \kappa_\eta I_{b\eta} \, ds, \qquad (9.11)$$

which is a surprising result on two counts: (1) the emission depends on the **absorption coefficient** (!) and (2) the emission is proportional to the *blackbody spectral intensity* $I_{b\eta}$, not the local intensity I_η. $I_{b\eta} = E_{b\eta}/\pi$, where $E_{b\eta}$ is the blackbody emissive power given by the Planck radiation theory:

$$E_{b\eta}(T, \eta) = \frac{2\pi h c_0^2 \eta^3}{n^2 \left[e^{hc_0\eta/nkT} - 1\right]}, \qquad (n = \text{const}). \qquad (1.14)$$

Note that $I_{b\eta}$ does not depend on the medium in any way except for the index of refraction n, which is very close to 1 for gases; $I_{b\eta}$ just depends on the temperature T and wavenumber η. Recall that

$$\int_0^\infty E_{b\eta} d\eta = \sigma T^4 \qquad \text{(PDR-1)}$$

Combining (9.3) and (9.11) yields, *for non-scatting media*,

$$\frac{dI_\eta}{ds} = \kappa_\eta (I_{b\eta} - I_\eta), \qquad (9.12)$$

which can be integrated from 0 to s to obtain

$$I_\eta(s) = I_\eta(0) e^{-\tau_\eta} + I_{b\eta}\left(1 - e^{-\tau_\eta}\right), \qquad (9.13)$$

which is physically reasonable, since as $\tau_\eta \to \infty$, $I_\eta \to I_{b\eta}$, and thus the intensity cannot grow larger than the blackbody intensity $I_{b\eta}$ for that wavenumber. This is the physical reason that emission and absorption have to be tied together though κ_η. Also, the effect of the incident intensity $I_\eta(0)$ (which might be, for example, from an opaque wall located at s = 0 that might be hotter or colder than the medium itself) decays exponentially as s increases. Equation (9.13) motivates a definition of spectral emittance; for no incident radiation ($I_\eta(0) = 0$) the emittance is just the intensity divided by the blackbody intensity for that wavenumber:

$$\epsilon_\eta = I_\eta(s)/I_{b\eta} = 1 - e^{-\tau_\eta}, \qquad (9.14)$$

Note also that the transmittance (fraction of radiation transmitted through a layer of gas) is given by $e^{-\tau\eta}$, and since transmittance + reflectance + absorptance = 1, and the reflectance ≈ 0 for gases, the absorptance = $1 - e^{-\tau\eta} = \varepsilon_\eta$. In other words, as with opaque surfaces, emittance and absorptance are equal.

I_η also increases due to scattering in the direction $\hat{s}$ according to

$$\left(dI_\eta\right)_{\text{sca}}(\hat{\mathbf{s}}) = ds \frac{\sigma_{s\eta}}{4\pi} \int_{4\pi} I_\eta(\hat{\mathbf{s}}_i)\, \Phi_\eta(\hat{\mathbf{s}}_i, \hat{\mathbf{s}})\, d\Omega_i. \qquad (9.17)$$

where Φ_η is the *phase function* for scattering at wavenumber η. $\Phi_\eta(\hat{s}_i, \hat{s})$ gives the portion of incident radiation that is scattered into the direction corresponding to the angle between the incoming direction $\hat{s}_i$ and the outgoing direction of interest $\hat{s}$. To determine the total increase in I_η in the direction $\hat{s}$ due to scattering, the portion of the radiant intensity from all $I_\eta(\hat{s}_i)$ that would be redirected into the direction $\hat{s}$ must be summed via the integral. Φ_η is normalized so that

$$\frac{1}{4\pi} \int_{4\pi} \Phi_\eta(\hat{\mathbf{s}}_i, \hat{\mathbf{s}})\, d\Omega \equiv 1. \qquad (9.18)$$

meaning that all incoming radiation that is scattered goes out somewhere. *The difference between scattering and emission is that increase in I due to scattering is a result of the redirection of incoming radiation, whereas emission creates new radiation.* Note also that *emission is isotropic, that is, the same in all directions, whereas scattering is direction-dependent.* In the special (and unrealistic) case of isotropic scattering, $\Phi_\eta(\hat{s}_i, \hat{s})$ = constant, and inspection of (9.18) shows that this constant must be 1.

Radiation transfer equation

Along a beam of radiation in the direction $\hat{s}$, the effects of emission, absorption and scattering can be combined to determine the total effect of all three on I_η:

$$\frac{dI_\eta}{d\tau_\eta} = -I_\eta + (1 - \omega_\eta) I_{b\eta} + \frac{\omega_\eta}{4\pi} \int_{4\pi} I_\eta(\hat{\mathbf{s}}_i)\, \Phi_\eta(\hat{\mathbf{s}}_i, \hat{\mathbf{s}})\, d\Omega_i. \qquad (9.25)$$

which is called the *radiative transfer equation*, which is basically a statement conservation of radiant energy along a ray. Here ω_η is the *albedo* (ratio of scattering to extinction):

$$\omega_\eta \equiv \frac{\sigma_{s\eta}}{\kappa_\eta + \sigma_{s\eta}} = \frac{\sigma_{s\eta}}{\beta_\eta}, \qquad (9.24)$$

Defining the *source terms* (for radiant intensity I_η):

$$S_\eta(\tau_\eta, \hat{\mathbf{s}}) = (1 - \omega_\eta) I_{b\eta} + \frac{\omega_\eta}{4\pi} \int_{4\pi} I_\eta(\hat{\mathbf{s}}_i)\, \Phi_\eta(\hat{\mathbf{s}}_i, \hat{\mathbf{s}})\, d\Omega_i. \qquad (9.26)$$

then (9.25) can be written in the simple form

$$\frac{dI_\eta}{d\tau_\eta} + I_\eta = S_\eta(\tau_\eta, \hat{\mathbf{s}}), \qquad (9.27)$$

which has the solution

$$I_\eta(\tau_\eta) = I_\eta(0) e^{-\tau_\eta} + \int_0^{\tau_\eta} S_\eta(\tau'_\eta, \hat{\mathbf{s}})\, e^{-(\tau_\eta - \tau'_\eta)}\, d\tau'_\eta, \qquad (9.29)$$

Note that for a non-scattering medium, $\omega_\eta = 0$ and thus $S_\eta = I_{b\eta}$, which results in Eq. (9.13), which is a much simpler case than with scattering.

Thus, solution of the radiative transfer equation boils down to evaluating the integrals in (9.29), which are integrals of the radiative source terms S_η between the location s = 0 (thus $\tau_\eta = 0$, where the spectral intensity $I_\eta(0)$ is known) and some other location of interest τ_η, with the weighting function $e^{-(\tau_\eta-\tau_\eta')}$, i.e., the importance of the source terms decays exponentially as the distance from the location of interest (τ_η-τ_η') increases. This integration is not as simple as it sounds since S_η depends on the temperature though $I_{b\eta}$ (which may or may not be constant along the path) as well as the incident intensity from all directions $I_\eta(\hat{s}_i)$ at all points between 0 and τ_η (which is generally unknown *a priori* and must be determined as part of the solution). *Thus, in general the intensity at every point depends on the intensity at every other point in the domain. This is unlike most transport relations (e.g. the Navier-Stokes equations of fluid mechanics) that can be expressed in terms of local properties and their derivatives. This makes radiative transfer in participating media very laborious in terms of the computational resources needed even when all of the physical property values are known.* About the only kind thing one can say about the radiative transfer equation is that it is linear and mathematically well behaved without nasty nonlinearities like the $u_j(\partial u_i/\partial x_j)$ terms in the Navier-Stokes equations that lead to shocks, turbulence, etc.

Radiative internal energy and incident radiation function

By analogy with gas molecules, the internal energy of radiation per unit wavenumber u_η can be defined as the total intensity per unit wavenumber (energy per unit wavenumber per unit area per unit time) of radiation passing through a point divided by the speed (c) at which said energy passes through this point, leading to

$$u_\eta \equiv \frac{1}{c} \int_{4\pi} I_\eta(\hat{\mathbf{s}})\, d\Omega. \qquad (9.42)$$

and thus the total radiant internal energy is

$$u = \int_0^\infty u_\eta\, d\eta = \frac{1}{c} \int_{4\pi} \int_0^\infty I_\eta(\hat{\mathbf{s}})\, d\eta\, d\Omega = \frac{1}{c} \int_{4\pi} I(\hat{\mathbf{s}})\, d\Omega. \qquad (9.43)$$

While Modest doesn't mention it, inside of an isothermal volume surrounding by black surfaces, where $I_\eta = I_{b\eta}$ for all solid angles Ω and integrating over all wavenumbers via equation PDR-1 and integrating over all 4π solid angles:

$$u_b = 4\sigma T^4/c \qquad \text{(PDR-2)}$$

Note that the units of u are Joules per m^3. At 300K, PDR-2 yields $u_b = 6.1 \times 10^{-6}$ J/m^3. Just for fun, for a monatomic ideal gas, $u = 3P/2$ where P is the pressure (this independent of temperature since kinetic energy is proportional to temperature but density is inversely proportional to temperature, thus the two effects cancel out), thus $u = 1.5 \times 10^5$ J/m^3 at 1 atm, which is 2.45×10^{10} times larger than the radiant internal energy! For a monatomic ideal gas at 1 atm surrounded by black walls, radiant and gas internal energy would be equal at 119,000K, thus radiant internal energy can obviously be neglected except for solar, astrophysical and nuclear applications!

A closely related property that is of more use for radiation calculations is the *incident radiation function*, which is the same as u but without the 1/c factor:

$$G_\eta \equiv \int_{4\pi} I_\eta(\hat{\mathbf{s}})\, d\Omega = c\, u_\eta; \quad G = cu. \qquad (9.44)$$

Radiative heat flux

Generally for engineering applications, rather than the intensity I *along a particular ray* we want to know the *radiative heat flux* **q**, i.e. the total radiation *in a direction* $\hat{s}$ *normal to an imaginary plane*, independent of what angle the incoming intensity passes through that plane. To determine this we integrate the intensity I over all solid angles weighted by the angle between the incident rays and the plane:

$$\mathbf{q} = \int_0^\infty \mathbf{q}_\eta\, d\eta = \int_0^\infty \int_{4\pi} I_\eta(\hat{\mathbf{s}})\, \hat{\mathbf{s}}\, d\Omega\, d\eta. \qquad (9.46)$$

where the notation $I_\eta(\hat{s})\,\hat{s}$ means the portion of the incident radiation I_η (which is coming from all directions $\hat{s}_i$ with respect to the direction $\hat{s}$ normal to the plane) that is in the direction $\hat{s}$. I think better notation would be $I_\eta(\hat{s}_i)\,(\hat{s}_i \bullet \hat{s})\hat{s}$, which clearly means the component of the intensity coming from direction $\hat{s}_i$ headed in the direction $\hat{s}$. For an axisymmetric (or one-dimensional) system we can immediately integrate over all 2π azimuthal angles and write $d\Omega = 2\pi\sin(\theta)d\theta$, where θ is the angle between the incoming ray of direction $\hat{s}_i$ and the direction $\hat{s}$ normal to the plane (thus $\cos(\theta) = \hat{s}_i \bullet \hat{s}$.) In this case it's particularly easy to see the difference between G and **q**:

$$G = 2\pi \int_0^\pi I(\theta)\sin(\theta)d\theta; \mathbf{q} = \hat{s}2\pi \int_0^\pi I(\theta)\sin(\theta)\cos(\theta)d\theta \qquad \text{PDR-3}$$

Note that **q** is a vector like velocity whereas G is a scalar like internal energy. With the substitution $\mu = \cos(\theta)$, the above equation can be written in the compact form for a one-dimensional problem

$$G = 2\pi \int_{-1}^{1} I\, d\mu \qquad q = 2\pi \int_{-1}^{1} I\mu\, d\mu \qquad (14.33)\ (14.34).$$

An important reason for determining the radiative heat flux **q** is to perform a radiative energy balance *at a point, integrated over rays from all incoming directions*, as opposed to *along a ray* (which leads to Equations 9.25, 9.27 and 9.29). Expressing radiative energy conservation at a point allows one to incorporate radiation as a source term in energy conservation equations including other modes of heat transport (Eq. 9.60 below). This energy balance leads to, for a particular wavenumber,

$$\nabla \cdot \mathbf{q}_\eta = \kappa_\eta \left(4\pi I_{b\eta} - \int_{4\pi} I_\eta \, d\Omega \right) = \kappa_\eta \left(4\pi I_{b\eta} - G_\eta \right). \tag{9.53}$$

or, for a gray medium (κ_η = constant), integrating over all wavenumbers from 0 to ∞:

$$\nabla \cdot \mathbf{q} = \kappa \left(4\sigma T^4 - \int_{4\pi} I \, d\Omega \right) = \kappa \left(4\sigma T^4 - G \right). \tag{9.55}$$

Equations 9.53 or 9.55 state that the divergence of the radiative flux ($\nabla \cdot \mathbf{q}$) (which is the difference between the flux going out of an infinitesimal volume and that going into the volume, units Watts/m^3) is increased by emission (the $\kappa 4\sigma I_{b\eta}$ term on the right hand side of Equations 9.53 or 9.55, which is the absorption coefficient multiplied by the blackbody intensity and integrated over all 4π steradians) and is decreased by absorption (the κG term, which is the total radiation incident on that volume multiplied by the absorption coefficient). Scattering does not appear explicitly in Equations 9.53 or 9.55 because scattering does not change the radiant energy, scattering only redirects radiant energy. Of course, the redistribution of radiant energy in the system via scattering will affect G.

There can be a difference between the emission and absorption only when this difference is compensated by either (1) an increase or decrease in the temperature of the medium over time, i.e. $\rho C_v(\partial T/\partial t)$, (2) heat transfer by other modes, i.e. conduction or convection, or (3) a heat source or sink within the volume (Q'''). If the first two are absent, it is said that the system is at *radiative equilibrium* whereby

$$\nabla \cdot \mathbf{q}_R = \dot{Q}''', \tag{9.62}$$

(Of course, Eq. 9.62 also applies when Q''' = 0). If other modes of heat transport and/or unsteadiness are present, then the divergence of radiative flux $\nabla \cdot \mathbf{q}$ becomes a source/sink term in the more general relation for energy conservation including conduction and convection:

$$\begin{aligned} \rho c_v \frac{DT}{Dt} &= \rho c_v \left(\frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla T \right) \\ &= \nabla \cdot (k \nabla T) - p \nabla \cdot \mathbf{v} + \mu \Phi + \dot{Q}''' - \nabla \cdot \mathbf{q}_R. \end{aligned} \tag{9.60}$$

which reduces to (9.62) if there is no conduction, convection or unsteadiness.

The complete set of equations needed to describe radiative heat transfer in a participating media is given by

1. The conservation of radiative energy at a point, Eq. 9.53 (spectral) or 9.55 (gray), which is a relationship between the heat flux vector **q**, temperature (through $I_{b\eta}$) and radiative intensity I_η from all incoming directions to that point.
2. The conservation of radiative energy along rays coming into that point, Eq. (9.25)
3. The coupling (if any) of radiative transport to other modes of heat transport and/or energy generation, Eq. (9.60) or (9.62).

This is basically three equations for three unknowns, T, **q** and I, of which **q** and I may be used in integrated for a gray medium but in general must be applied for every wavenumber η. T is of course a scalar (units: Kelvins), **q** is a vector (units: W/m^2) and I is a scalar (units: W/m^2). The intensity I is the most problematic of the three since it is a function not only of the spatial position (like T and **q**) but also the solid angle Ω (unlike T and **q**).

Physics of radiating gases (Chapter 10)

In order for a gas molecule to emit or absorb energy, it must change its state to a lower (for emission) or higher (for absorption) energy state. In order to change its energy state, there must be a change in the translational, rotational, vibrational, or electronic energy levels of the molecule or some combination thereof. Quantum mechanics dictates that these energy levels are discrete, not continuous, and that only certain transitions between energy levels are possible. Quantum mechanics also dictates that not all molecules may emit and absorb radiation; in particular homonuclear diatomic molecules like N_2 and O_2 cannot emit or absorb radiation, thus in combustion and atmospheric problems the primary radiating gases are CO_2, H_2O and to a lesser extent CO. Because of the small size of gas molecules, scattering is negligible in gases except on very long length scales, e.g. in the atmosphere.

The spacings of the translational energy levels are too small (that is, the spacings are much smaller than the thermal energy of the molecule = 3kT/2) to be of any consequence except at very low temperature (a few K). For radiation problems with gases from room temperature (300K) up to combustion temperatures (<3000K) the vast majority of radiant emission and absorption is due to changes in rotational and vibrational energy levels of the molecules. Generally the spacings of vibrational energy levels are much larger than the rotational energy levels. At still higher temperatures, characteristic of astrophysics, atmospheric reentry and electrical (e.g. spark) discharges, changes in electronic energy levels along with ionization and dissociation (or the opposite process of recombination) become important as well. For transitions involving ionization, dissociation or recombination of the molecules, the ions or dissociated species being created or recombined may have any kinetic energy, thus for these transitions there is a continuous, not discrete emission/absorption spectrum.

For the rotational and vibrational transitions, each allowable transition yields a *line* in the $\kappa_\eta(\eta)$ spectrum (absorption coefficient κ_η as a function of wavenumber η) at $\eta_0 = \Delta E/hc$, where ΔE corresponds to the *difference* in energy levels before and after the transition. Most of the radiation from gases occurs due to a single vibrational transition accompanied by a family of rotational transitions; this yields an emission-absorption *band* such as that shown in Fig. 10-6. For simple models of molecules (e.g. rigid rotor for rotational modes, harmonic oscillator for vibrational modes) it is possible to derive exact predictions for the energy levels, the allowable transitions between energy levels, the probability of transition and the number of molecules in each particular rotational and vibrational state. However, because real molecules do not behave exactly this way and because of the coupling between modes, for real molecules, even simple ones like CO, CO_2 and H_2O, in practice one generally has to resort to experiments to determine the number of lines, their corresponding wavenumbers η_0 and line strengths (S, defined below).

The quantization of energy levels in molecules would suggest infinitely narrow lines (that is, no width in η space), but in fact the lines are *broadened* due to several factors including

1. "Natural" broadening due to the "uncertainty principle" of quantum mechanics that prevents one from knowing precisely the energy of the photons emitted by the gas. This broadening effect is small compared to the other two modes given below. It has the same line shape as the collision broadening discussed below, so it is sometimes lumped together with collision broadening to form "Lorentz broadening."
2. "Collision" broadening, sometimes called "pressure broadening", is due to (as advertised) collisions between molecules. This is the most important mechanism of broadening for most cases of interest except at very high temperatures and low pressures. Collision broadening results in a line whose absorption coefficient κ_η varies with η according to

$$\kappa_\eta = \frac{S}{\pi}\frac{b_C}{(\eta-\eta_0)^2+b_C^2}, \quad S \equiv \int_{\Delta\eta} \kappa_\eta d\eta, \qquad (10.23)$$

where $\eta_0 = \Delta E/hc$ is the wavenumber corresponding to the center of the line and S is the "line strength" (units cm^{-2}, or $cm^{-2}atm^{-1}$ or $cm^{-2}(kg/m^3)^{-1}$) i.e. the absorption coefficient integrated over the small range of wavenumbers $\Delta\eta$ corresponding to the absorption spectrum of this broadened line. Also, b_c is the "line width parameter" for collision broadening (units cm^{-1}, i.e. line width in units of η):

$$b_c = \frac{2}{\sqrt{\pi}}\frac{D^2 p}{c_0\sqrt{mkT}} \tag{10.24}$$

where D is the effective collision diameter for the molecules (typically a few Angstroms, e.g. 4 x 10^{-10} m for CO), p is the pressure, m is the molecular mass, k is Boltzman's constant, T the temperature and c_0 the usual speed of light in a vacuum. Equation (10.24 may be physically interpreted in the following way. All of the terms other than c_0 as a group have units of s^{-1} and physically corresponds to the number of collisions between molecules per unit time (call this ν_c). For CO at standard temperature and pressure, $\nu_c \approx 1.3 \times 10^9/s$. In the absence of broadening, the radiation emitted or absorbed by this line would have a frequency of exactly $\nu_0 = \eta_0 c_0$. In the presence of collision broadening, the frequency would be broadened to $\nu_0 \pm \nu_c$, i.e. the beat frequencies obtained when signals of frequency ν_0 and ν_c are mixed. The corresponding wavenumbers are $(\nu_0 \pm \nu_c)/c_0$, thus the line width should be of the order ν_c/c_0, which is exactly what Eq. (10.24) shows. For CO at standard temperature and pressure, $b_c \approx (1.3 \times 10^9/s)/(3.0 \times 10^8 \text{ m/s}) \approx 4.4 \text{ m}^{-1} = 0.044 \text{ cm}^{-1}$. Another way of interpreting collision broadening is that during the small portion of time when the molecules are close enough to each other to affect each other's energy levels, the molecule momentarily behaves somewhat more like a solid that emits and absorbs continuously across the spectrum due to the large number of degrees of freedom that the solid has as a result of the coupled motions of many molecules as opposed to the few degrees of freedom that an isolated gas molecule has.

Since natural and Doppler broadening have the same functional form, b_c in Eq. 10.23 may be replaced with the Lorenz line width $b_L = b_c + b_N$, where b_N is the (very small, almost always neglected) line width parameter for natural broadening. (What is not neglected is the opportunity to increase confusion through terminology; many texts and papers refer to "Lorenz" broadening or "Lorenz" lines even when only the collision, not natural broadening part is included.)

3. Doppler broadening, due to the motion of the molecules toward and away from the observer. This is the same effect that causes sound emitted by a car to appear higher in frequency when the car is approaching, and lower when the car is going away. In this case κ_η varies with η according to

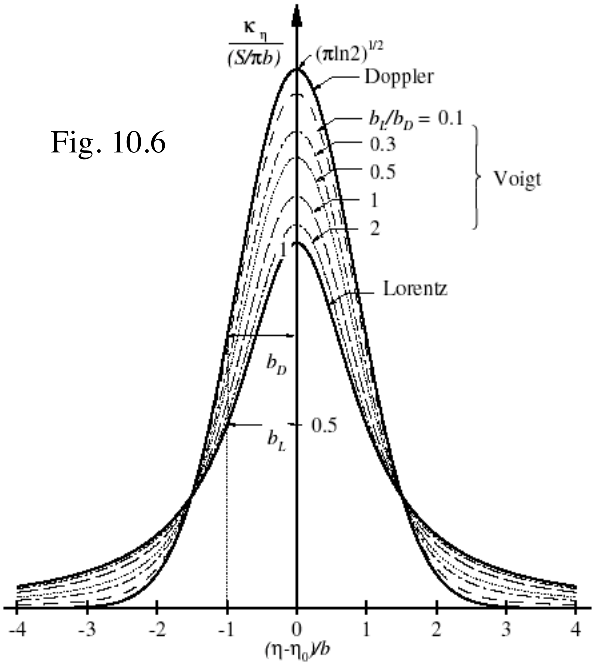
$$\kappa_\eta = \sqrt{\frac{\ln 2}{\pi}}\left(\frac{S}{b_D}\right)\exp\left[-(\ln 2)\left(\frac{\eta-\eta_0}{b_D}\right)^2\right], \tag{10.29}$$

where in this case the line width b_D is given by

$$b_D = \frac{\eta_0}{c_0}\sqrt{\frac{2kT}{m}\ln 2}. \tag{10.30}$$

This can be interpreted physically as follows. The term inside the square root is proportional to the sound speed c_s. The Doppler frequency shift $\Delta\nu = \nu_0 c_s/c_0$, and thus the wavenumber shift $\Delta\eta$ is $\Delta\nu/c_0 = (\nu_0 c_s/c_0)/c_0 = (\nu_0/c_0)(c_s/c_0) = \eta_0 c_s/c_0$ as Eq. (10.30) shows. Note that, unlike collision broadening, the line width depends on the line center wavenumber η_o. For CO at 300K, 1 atm and $\eta_o = 1/4.7\ \mu m = 2130\ cm^{-1}$ (where its strongest absorption band is located), Eq. (10.30) predicts $b_D = 0.0025\ cm^{-1}$, which is 18 times smaller than the collision broadening width b_c. Since Doppler broadening line widths increase with T but are independent of P, whereas collision broadening line widths decrease with T and increase with P, Doppler broadening may be more important than collision broadening at high T and/or low P, e.g. in solar and plasma physics (high T) or atmospheric (low P) radiation. Figure 10-6 shows the line

Fig. 10.6



shapes for Doppler, Lorentz (collision + natural) and Voight (combined Doppler and Lorentz) broadened lines with the same b and S.

It is important to note that while $\kappa_\eta(\eta)$ changes due to broadening, the integrated line strength S generally does not; in other words, broadening effects redistribute the absorption over range of wavenumbers but does not generally change the total absorption capability of the line. In particular, if S is expressed in units of $\text{cm}^{-2}\text{atm}^{-1}$, pressure will affect the line width through collision broadening and thus the profile of $\kappa_\eta(\eta)$ (units $\text{cm}^{-2}\text{atm}^{-1}$) but not S. Temperature always affects line strengths because it changes the distribution of rotational and vibrational energy states of the molecules, thus the number of molecules in any given state, and thus the relative probability of any particular transition occurring, and thus the strength of any given line.

For an individual line, with κ_η at a particular wavenumber η known from the broadening expressions given above, the increase or decrease in intensity along a ray of length s can be calculated using Eq. (9.13). To get the effect of this line on the total intensity, Eq. (9.13) must be integrated over the entire line width $\Delta\eta$. (Technically the line width is infinite, but since κ_η tails off quickly on either side of the line center η_0, one can truncate the integral over a few units of the line width parameter b.) Since the line is narrow compared to the whole blackbody spectrum, over the entire line width $\Delta\eta$ the blackbody intensity $I_{b\eta}$ does not change significantly thus $I_{b\eta}$ can be taken out of the integral. For no scattering ($\sigma_{s\eta} = 0$, thus $\beta_\eta = \kappa_\eta$) and assuming that κ_η does not vary along the path s (i.e. the gas is homogenous and isothermal) so that $\tau_\eta = \kappa_\eta s$, Eq. (9.13) can be integrated over entire line width $\Delta\eta$ to obtain

$$I(X) - I(0) = \int_{\Delta\eta} [I_\eta(X) - I_\eta(0)]\, d\eta \approx [I_{b\eta} - I_\eta(0)] \int_{\Delta\eta} \left(1 - e^{-\kappa_\eta X}\right) d\eta, \tag{10.34}$$

where X is just the path length s if κ_η is in units of cm^{-1}, X is sP if κ_η is in units of $\text{cm}^{-1}\text{atm}^{-1}$, or X is $s\rho$, where ρ is the partial density of the gas of interest, if κ_η is in units of $\text{cm}^{-1}(\text{kg/m}^3)^{-1}$. The integral on the right hand side of Eq. (10.34) is called the *equivalent line width* (W):

$$W = \int_{\Delta\eta} \left(1 - e^{-\kappa_\eta X}\right) d\eta \tag{10.35}$$

because physically it corresponds to the width $\Delta\eta$ of a line of infinite absorption coefficient (thus emittance and absorptance of 1) across the entire line ($\kappa_\eta \to \infty$ for $\eta_o - W/2 < \eta < \eta_o + W/2$, $\kappa_\eta = 0$ otherwise) with line that would have the same effect as the actual line. In other words, the actual line is equivalent to a line that is "black" but only for wavenumbers corresponding to $\eta_o - W/2 < \eta < \eta_o + W/2$, not black across the entire wavenumber spectrum. To see this, note that if $\kappa_\eta \to \infty$, $1 - \exp(-\kappa_\eta X) = 1 - 0 = 1$, and if $\kappa_\eta = 0$, $1 - \exp(-\kappa_\eta X) = 1 - 1 = 0$, thus $\int_{\Delta\eta}\{1-\exp(-\kappa_\eta X)\}d\eta = 1*W + 0*(\Delta\eta - W) = W$.

Equation (10.35) can be integrated over a Lorentz line profile (Eq. 10.23) with b_L replacing b_c to obtain

$$W = 2\pi b_L x e^{-x}[I_0(x) + I_1(x)] = 2\pi b_L L(x), \tag{10.36}$$

where I_n is the modified Bessel function of the n^{th} kind and $x = SX/2\pi b_L$ is the dimensionless optical path length. This plot is shown in Fig. PDR-1 (if you have the electronic version, you can double-click the figure to open the Excel spreadsheet that generated the plot.) W(x) is linear (W ~ x) at x << 1 and has a square-root behavior (W ~ $x^{1/2}$) for x >> 1. Note that Eq. (10.36) and Fig. PDR-1 are valid only for Lorenz line shapes; as previously mentioned this is the most important line shape (due to the collision broadening) for most engineering applications.

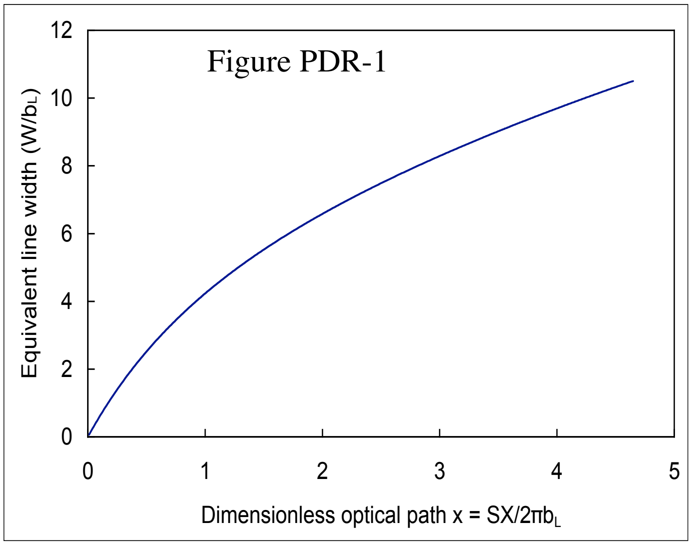


Figure PDR-1

Modeling of emission and absorption of gases with many lines

As a net result of the inherent quantization of energy states plus line broadening, a plot of κ_η vs. η has sharp peaks (lines) with much lower values of κ_η between lines (e.g. Fig. 10-8). As a result of collision broadening, the spectrum is much more "spiky" (narrower lines) at low pressures (Fig. 10-9, top) than at higher pressures (Fig. 10-9, middle), and is more spiky at high temperatures (Fig. 10-9, bottom.)

Ultimately one wants to determine the effective emittance $\bar{\varepsilon}$ of the gas through the integration of (9.14) over the entire spectrum, e.g.

$$\bar{\varepsilon} = \frac{\int_0^\infty \varepsilon_\eta I_{b\eta} d\eta}{\int_0^\infty I_{b\eta} d\eta} = \frac{\int_0^\infty (1-e^{-\tau_\eta}) d\eta}{\frac{1}{\pi}\sigma T^4} = \frac{\int_0^\infty (1-e^{-\kappa_\eta X}) d\eta}{\frac{1}{\pi}\sigma T^4} \quad \text{(PDR-4)}$$

where in the last equality again it has been assumed that there is no scattering and the path length is homogeneous. *Relations such as (10.23) and (10.29) provide $\kappa_\eta(\eta)$ only for one individual line; to determine the physically observed $\kappa_\eta(\eta)$ and the resulting radiant intensity I and effective emissivity, the individual contributions of all lines must be considered.* The difficulty arises because the "tails" of the lines overlap, particularly for Lorentz lines with slower decaying algebraic ($b_c/(\eta_0-\eta)^2$) tails than the exponential tails of Doppler lines. Thus one cannot merely sum up the contributions of the individual lines to the total intensity using Eq. (10-36) with Eqs. (10.34) and (10-35). This overlapping character of the lines is readily seen in Fig. 10-9. Evaluating the emission and absorption due to each individual line (Eq. 10.36) is usually implausible (except to

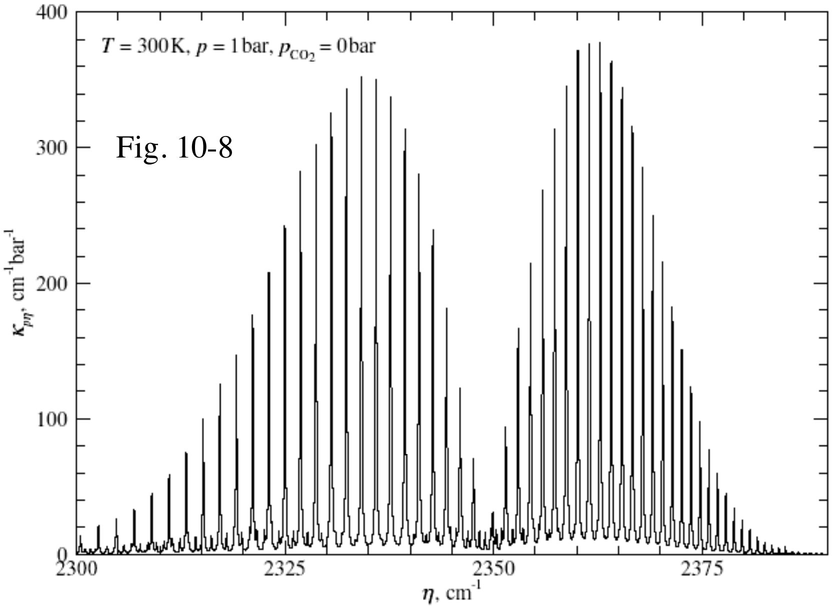


Fig. 10-8

calibrate simplified models) since there are about *1 million* known lines *each* for H_2O and CO_2!

As a result, one resorts to either (1) *narrow band*, (2) *wide band* or (3) *global* models. (1) – (3) represent models of decreasing complexity and of course decreasing accuracy and flexibility.

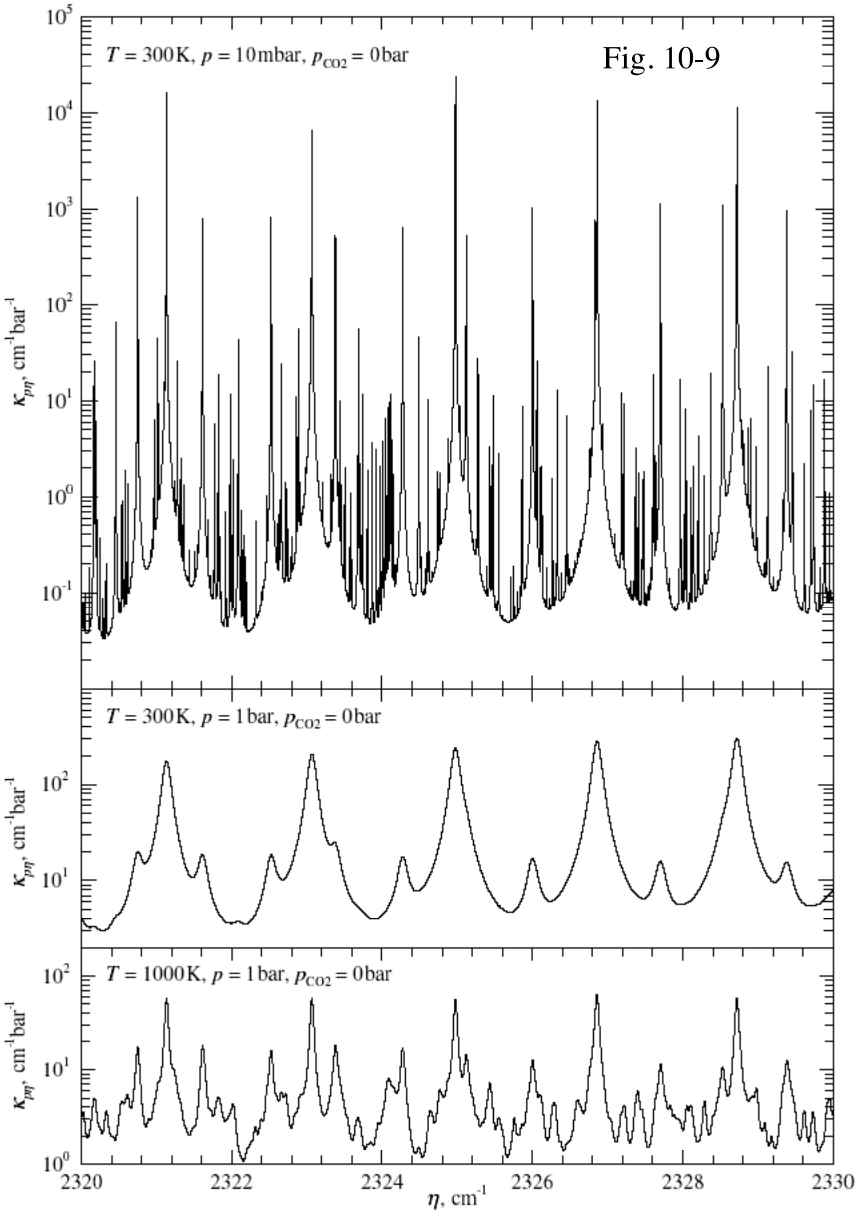


Fig. 10-9

Narrow-band models break up the entire spectrum into a number of individual bands, *each band corresponding to a range of wavenumbers ($\Delta\eta_{band}$) that is much larger than the line width (b_L or b_D) and large enough that there will be many lines within the band, but still $\Delta\eta_{band}$ is small enough that the spectral blackbody intensity $I_{b\eta}$ can be assumed constant over the band.* Over each narrow band, every line is assumed to have the same broadening parameter b_L or b_D and is assumed to follow the same broadening function (Lorenz or Doppler). A particular distribution of line center wavenumbers η_0 and line strengths S are assumed. In some models (e.g. Elsasser, Fig. 10-10, left) the spacing between lines and line strength are assumed constant, whereas in other models, called *statistical narrow band* models, the lines are assumed to be randomly distributed across the band and have randomly distributed strengths that follow a presumed probability distribution function (Fig. 10-10, right). In the case of the popular Malkmus model, this probability distribution is $p(S) = S^{-1}\exp(-S/\overline{S})$, where $\overline{S}$ is an average line strength. The combined effect of all these individual lines is then summed to obtain the effective emissivity for each range of wavenumbers $\Delta\eta_{band}$. The first step in doing this is determining $\kappa_\eta(\eta)$ across the entire narrow band due to the effect of all the lines, each with its own individual $\kappa_\eta(\eta)$. Then Eq. (PDR-4) is integrated across $\Delta\eta_{band}$ to get the effective emittance for the band. For the Elsasser model this leads to

$$\overline{\epsilon}_\eta = \mathrm{erf}\left(\frac{\sqrt{\pi}}{2}\frac{W}{d}\right) = \mathrm{erf}\left(\frac{\sqrt{\pi}}{2}\frac{S}{d}Xe^{-x}[I_0(x)+I_1(x)]\right) = \mathrm{erf}\left(\sqrt{\pi}\beta L(x)\right) \tag{10.58}$$

where $\beta = \pi b_L/d$ is the ratio of line width (b_L) to line spacing (d). For the Malkmus model this leads to

$$\varepsilon_\eta = 1-\exp\left(\frac{-\beta}{2}\left(\sqrt{1+\frac{4\tau}{\beta}}-1\right)\right) \quad \text{(PDR-5)}$$

where $\tau = 2\beta x$. The predictions of four models are shown in Fig. 10-11 in terms of the effect of the dimensionless optical depth τ. Note that

1. For very small τ, the emissivity approaches zero
2. For large τ, the emissivity approaches one
3. For large β, that is, very strong narrow lines without overlap, all models yield the same emissivity, and for $\tau = 1$, this emissivity is $0.63 = 1 - e^{-1}$.
4. The Elsasser model gives the most emissivity, i.e. the least transmissivity, because the lines are equally spaced so there are fewer "holes" in the spectra where lines overlap.

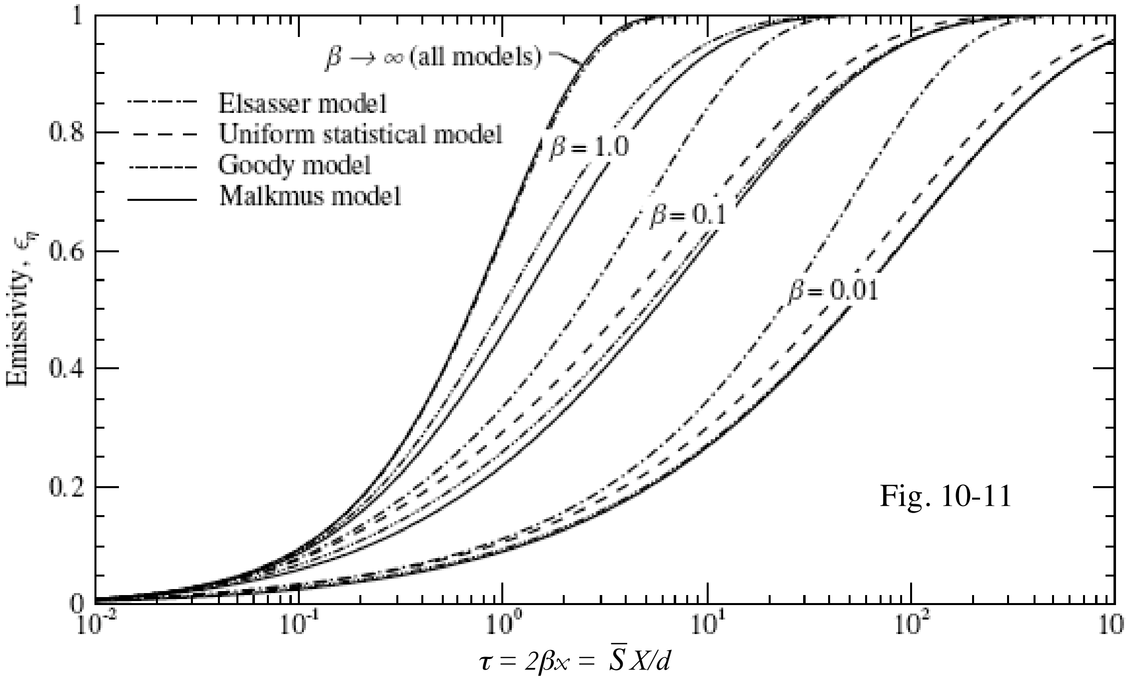


Fig. 10-11

Of course this **still** begs the question of how to determine the appropriate values of the key parameters b_L (Lorentz line width), S (line strength) and d (mean line spacing) for real gases. Probably the most commonly used data set for CO, CO_2 and H_2O is that by A. Soufiani and J. Taine (*Int. J. Heat Mass Trans.* Vol. 40, pp. 987-991 (1997)). In this work the line widths as a function of temperature, pressure and mole fractions are given by empirical formulas (which are independent of wavenumber η), and the effective line strengths and lines spacings are given in tables, one table for each gas which gives the effective line strength and line spacing as a function of η and temperature (T) over the range $150\ cm^{-1} < \eta < 9300\ cm^{-1}$ and $300K < T < 2500K$ in intervals of 25 cm^{-1} and 200 K, respectively. Thus each of the 3 gases has $(9300 - 150)/25 + 1 = 367$ data points in spectral space and $(2500 - 300)/200 = 12$ points in temperature space, for a grand total of 367 (wavenumbers) x 12 (temperatures) x 2 (properties) x 3 (gases) = 26,424 individual values. These data were obtained using the "HITRAN" spectral data base for these gases, which attempts to catalog the millions of individual spectral lines.