Lecture 2
Constitutive Relations

Conservation equations

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \]
\[ \rho \frac{D\mathbf{v}}{Dt} = -\nabla p + \nabla \cdot \mathbf{\Sigma} + \rho \mathbf{g} \]
\[ \rho \frac{DY_i}{Dt} + \nabla \cdot (\rho Y_i \mathbf{V}_i) = \omega_i \quad i = 1, 2, \ldots, N \]
\[ \rho \frac{Dc}{Dt} = -p \nabla \cdot \mathbf{v} + \Phi - \nabla \cdot \mathbf{q} \]
\[ \rho \frac{Dh}{Dt} = \frac{Dp}{Dt} + \Phi - \nabla \cdot \mathbf{q} \]
\[ p = \rho RT \sum_{i=1}^{N} \frac{Y_i}{W_i} \quad h = \sum_{i=1}^{N} Y_i h_i^0 + \int_{T_0}^{T} c_p dT \]

We already have expressions for the viscous stress tensor \( \mathbf{\Sigma} \) and the dissipation function \( \Phi \). We need constitutive relations for the heat flux vector \( \mathbf{q} \), the diffusion velocities \( \mathbf{V}_i \) and the rates of consumption/production \( \omega_i \).
Heat flux vector

The total energy flux $q$ is the sum of the separate energy fluxes, including the fluxes due to diffusion and the radiant flux $q_r$, but neglecting the Dufour heat flux (due to difference in diffusion velocities)

$$q = -\lambda \nabla T + \rho \sum_{i=1}^{N} Y_i h_i V_i + q_r$$

$$\rho \frac{Dh}{Dt} = \frac{Dp}{Dt} + \Phi + \nabla \cdot (\lambda \nabla T) - \nabla \cdot \sum_{i=1}^{N} \rho Y_i V_i h_i - \nabla \cdot q_r$$

the energy transfer is not just by conduction, but also through diffusion fluxes of the different species

Radiative heat transfer will also be removed and added only when necessary.

$$\rho \frac{Dh}{Dt} = \frac{Dp}{Dt} + \Phi + \nabla \cdot (\lambda \nabla T) - \nabla \cdot \sum_{i=1}^{N} \rho Y_i V_i h_i$$

$h = \sum_{i=1}^{N} Y_i h_i + \int_{T_{\infty}}^{T} c_p dT$

$$\rho \frac{Dh}{Dt} = \frac{Dp}{Dt} + \Phi + \nabla \cdot (\lambda \nabla T) - \nabla \cdot \sum_{i=1}^{N} \rho Y_i V_i h_i$$

$$\rho \frac{Dh}{Dt} \int_{T_{\infty}}^{T} c_p dT = \frac{Dp}{Dt} + \Phi + \nabla \cdot (\lambda \nabla T) - \sum_{i=1}^{N} \left( \rho Y_i V_i \int_{T_{\infty}}^{T} c_p dT \right) h_i - \nabla \cdot \sum_{i=1}^{N} \rho Y_i V_i \int_{T_{\infty}}^{T} c_p dT$$

$$\rho \frac{Dh}{Dt} \left( \int_{T_{\infty}}^{T} c_p dT \right) = \frac{Dp}{Dt} + \Phi + \nabla \cdot (\lambda \nabla T) - \nabla \cdot \sum_{i=1}^{N} \rho Y_i V_i \int_{T_{\infty}}^{T} c_p dT - \sum_{i=1}^{N} \omega_i h_i$$

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Alternative form of the energy equation

\[ h = \sum_{i=1}^{N} h_i Y_i \Rightarrow dh = \sum_{i=1}^{N} dh_i Y_i + \sum_{i=1}^{N} h_i dY_i = \sum_{i=1}^{N} c_p Y_i dT + \sum_{i=1}^{N} h_i dY_i = c_p dT + \sum_{i=1}^{N} h_i dY_i \]

\[ \Rightarrow \frac{Dh}{Dt} = c_p \frac{DT}{Dt} + \sum_{i=1}^{N} \frac{h_i}{\omega_i} \frac{DY_i}{Dt} \]

\[ \rho \frac{Dh}{Dt} = \frac{Dp}{Dt} + \Phi + \nabla \cdot (\lambda \nabla T) - \nabla \cdot \left( \sum_{i=1}^{N} \rho Y_i V_i h_i \right) \]

\[ \rho c_p \frac{DT}{Dt} + \sum_{i=1}^{N} h_i \rho \frac{DY_i}{Dt} = \frac{Dp}{Dt} + \Phi + \nabla \cdot (\lambda \nabla T) - \nabla \cdot \left( \sum_{i=1}^{N} \rho Y_i V_i h_i \right) \]

\[ \rho c_p \frac{DT}{Dt} = \frac{Dp}{Dt} + \Phi + \nabla \cdot (\lambda \nabla T) - \sum_{i=1}^{N} \rho c_p Y_i V_i \cdot \nabla h_i - \sum_{i=1}^{N} h_i \frac{h_i}{\omega_i} \]

and it can be shown that the two versions are equivalent. Moreover, when all the \( c_{p_i} \) are the same, i.e., \( c_{p_i} = c_p \) for all \( i \), the energy equation reduces to

\[ \rho c_p \frac{DT}{Dt} = \frac{Dp}{Dt} + \Phi + \nabla \cdot (\lambda \nabla T) - \sum_{i=1}^{N} h_i \frac{h_i}{\omega_i} \]

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**Diffusion**

Fick’s law of **binary diffusion**

In a *binary mixture* Fick’s law of diffusion states that the diffusion mass flux of a given species is proportional to its concentration gradient

\[ \rho Y_1 \mathbf{V}_1 = -\rho D_{12} \nabla Y_1 \]

\[ \rho Y_2 \mathbf{V}_2 = -\rho D_{21} \nabla Y_2 \]

The constrains \( Y_1 \mathbf{V}_1 + Y_2 \mathbf{V}_2 = 0 \), and \( Y_1 + Y_2 = 1 \), imply that \( D_{12} = D_{21} \equiv D \)

\[ \rho Y_i \mathbf{V}_i = -\rho D \nabla Y_i \]

\[ \rho \frac{DY_i}{Dt} + \nabla \cdot (\rho Y_i \mathbf{V}_i) = \omega_i \quad i = 1, 2 \]

\[ \rho \frac{DY_i}{Dt} + \nabla \cdot (\rho D \nabla Y_i) = \omega_i \quad i = 1, 2 \]

For \( \rho D = \text{const.} \) \( \Rightarrow \frac{DY_i}{Dt} + D \nabla^2 Y_i = \omega_i \quad i = 1, 2 \)

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For **multicomponent diffusion** in gases (Curtiss & Hirschfelder 1949)

\[ \nabla X_i = \sum_{j=1}^{N} \frac{X_i X_j}{D_{ij}} (\mathbf{V}_j - \mathbf{V}_i) + \frac{\nabla \rho}{\rho} \sum_{j=1}^{N} \frac{X_i X_j}{\rho D_{ij}} \left( \frac{\nabla T}{T} - \frac{\nabla T}{T} \right) + \frac{\rho}{p} \sum_{j=1}^{N} Y_j (f_i - f_j) \]

The effects of pressure gradients, and temperature gradients (known as Soret effect) on diffusion are typically small. If, in addition, there are no significant unequal forces acting on the species (often relevant for ions and electrons where \( f \) is due to an electrical field), then

\[ \nabla X_i = \sum_{j=1}^{N} \frac{X_i X_j}{D_{ij}} (\mathbf{V}_j - \mathbf{V}_i) \]

Stefan-Maxwell equations

where \( D_{ij} \) are the **binary diffusivities**, which have been proven to be symmetric, i.e., \( D_{ij} = D_{ji} \). For a dilute ideal gas mixture they are independent of composition, and determined by a simple two-components experiment where a species in low concentration diffuses through a second species that is in abundance.
For a binary mixture
\[
\nabla X_1 = \frac{X_1X_2}{D_{12}}(V_2 - V_1) \\
\nabla X_2 = \frac{X_2X_1}{D_{21}}(V_1 - V_2)
\]
\[
\Rightarrow \\
\frac{\nabla(X_1 + X_2)}{X_1X_2} = (V_2 - V_1) \left( \frac{1}{D_{12}} - \frac{1}{D_{21}} \right) = 0
\]
\[
D_{12} = D_{21} \equiv D
\]
and the Stefan-Maxwell equations reduce to Fick’s law of diffusion
\[
Y_1V_1 = -D\nabla Y_1 \\
Y_2V_2 = -D\nabla Y_2
\]
More generally, Fick’s law is recovered if one assumes that the binary diffusion coefficients are all equal, i.e., \(D_{ij} = D\).
\[
Y_iV_i = -D\nabla Y_i \quad \text{for } i = 1, \ldots, N
\]

If the binary diffusion coefficients are all equal, i.e., \(D_{ij} = D\), we again cover Fick’s law.
\[
\nabla X_i = \sum_{j=1}^{N} \frac{X_iX_j}{D_{ij}}(V_j - V_i) = \frac{X_i}{D} \sum_{j=1}^{N} X_j(V_j - V_i) = \frac{X_i}{D} \sum_{j=1}^{N} X_jV_j - \frac{X_i}{D}V_i
\]
\[
D\frac{\nabla X_i}{X_i} = \sum_{j=1}^{N} X_jV_j - V_i
\]
it can be shown, after some algebraic manipulations that
\[
\sum_{j=1}^{N} X_jV_j = D(\nabla W/W)
\]
\[
D\frac{\nabla X_i}{X_i} = D\frac{\nabla W}{W} - V_i
\]
and, since
\[
X_i = WY_i/W_i \quad \Rightarrow \quad \frac{\nabla X_i}{X_i} = \frac{\nabla Y_i}{Y_i} + \frac{\nabla W}{W}
\]
\[
D \left( \frac{\nabla Y_i}{Y_i} + \frac{\nabla W}{W} \right) = D \frac{\nabla W}{W} - \nabla V_i
\]
\[
Y_iV_i = -D\nabla Y_i
\]
The use of the Stefan-Maxwell equations is quite complicated because the diffusion velocities $V_i$ are not expressed explicitly in terms of the concentration gradients.

**Generalized Fick equations**

$$ V_i = \sum_{j=1}^{N} D_{ij} \nabla X_j $$

would be more convenient for the evaluation of the diffusion term in the species equations, but the "Fick diffusivities" $D_{ij}$ are not simply related to the binary diffusivities $D_{ij}$, and they are concentration-dependent.

The coefficients $D_{ij}$, which don’t have to be necessarily positive, satisfy

$$ D_{ij} = D_{ji}, \quad \text{for all } i, j $$

$$ \sum_{i=1}^{N} Y_i D_{ij} = 0 \quad \text{for all } j $$

Note that there are many definitions for multicomponent diffusivities; the one quoted here (with the $D_{ij}$ symmetric) follow Curtiss & Bird (1999).

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One can find the relation between the multi-component diffusivities $D_{ij}$ and the binary diffusivities $D_{ij}$. For a binary mixture

**Stefan-Maxwell**

$$ \nabla X_1 = \frac{X_1 X_2}{D_{12}} (V_2 - V_1) \quad D_{12} = D_{21} $$

$$ \nabla X_2 = \frac{X_1 X_2}{D_{21}} (V_1 - V_2) $$

**Multi-component diffusion**

$$ V_1 = D_{11} \nabla X_1 + D_{12} \nabla X_2 $$

$$ V_2 = D_{21} \nabla X_1 + D_{22} \nabla X_2 $$

$$ D_{12} = D_{21} $$

$$ D_{11} Y_1 + D_{12} Y_2 = 0 $$

$$ D_{12} Y_1 + D_{22} Y_2 = 0 $$

$$ \Rightarrow $$

$$ D_{11} = \frac{Y_2^2}{X_1 X_2} D_{12} $$

$$ D_{22} = \frac{Y_1^2}{X_1 X_2} D_{12} $$

$$ D_{12} = D_{21} = \frac{Y_1 Y_2}{X_1 X_2} D_{12} $$
Expressions for ternary and quaternary mixtures are available, but are more complicated.

For example, for a ternary mixture

\[ D_{11} = -\frac{(Y_2 + Y_3)^2}{X_1 D_{23}} + \frac{Y_2^2}{X_2 D_{13}} + \frac{Y_3^2}{X_3 D_{12}} \]

\[ D_{12} = \frac{Y_1 (Y_2 + Y_3)}{X_1 D_{23}} + \frac{Y_2 (Y_1 + Y_3)}{X_2 D_{13}} - \frac{Y_3^2}{X_3 D_{12}} \]

with the additional entries generated by cyclic permutation of the indices.

For the general case, one can write a relation between the matrix of Fick diffusivities \( D_{ij} \) and that of binary (Stefan-Maxwell) diffusivities \( D_{ij} \); see Curtiss & Bird Ind. Eng. Chem. Res. 38:2515-2522 (1999).

We are interested in rewriting the generalized Fick equations in terms of the mass fraction

\[ V_i = \sum_{j=1}^{N} \hat{D}_{ij} \nabla Y_j \]

which requires expressing \( \nabla X_i \) in terms of \( \nabla Y_i \), or using the differential relation (Bird, Stewart & Lightfoot)

\[ \nabla X_i = -\frac{W_i}{W_i^2} \sum_{j=1}^{N} \left[ \frac{1}{W_i} + Y_i \left( \frac{1}{W_j} - \frac{1}{W_i} \right) \right] \nabla Y_j . \]

This leads, in general to complicated expressions for the \( \hat{D}_{ij} \).

For a binary mixture,

\[ \hat{D}_{11} = -\frac{Y_2}{Y_1 D} \quad \hat{D}_{22} = -\frac{Y_1}{Y_2 D} \quad \hat{D}_{12} = \hat{D}_{21} = \hat{D} \]

\[ Y_i V_1 = -D Y_2 \nabla Y_1 + D Y_1 \nabla Y_2 = -D (Y_2 + Y_1) \nabla Y_1 = -D \nabla Y_1 \]

and we recover Fick’s law, as we should.
### Dilute mixture

There is an abundant species in the mixture, denoted by $N$, while all other species may be treated as trace species (for combustion in air, nitrogen is abundant)

\[
Y_i \ll 1 \text{ for } i = 1, \ldots, N - 1, \quad Y_N \sim 1
\]

\[
X_i \ll 1 \text{ for } i = 1, \ldots, N - 1, \quad X_N \sim 1
\]

\[
\sum_{i=1}^{N} Y_i V_i = 0, \quad \Rightarrow \quad V_N \ll 1
\]

\[
W = \sum_{i=1}^{N} X_i W_i \sim W_N
\]

\[
\nabla X_i = \sum_{j=1}^{N} \frac{X_i X_j}{D_{i,j}} (V_j - V_i) \sim -\frac{X_i}{D_{i,N}} V_i \quad \text{for } i = 1, 2, \ldots, N - 1
\]

\[
\nabla Y_i \sim -\frac{Y_i V_i}{D_{i,N}} \quad \text{for } i = 1, 2, \ldots, N - 1
\]

\[
Y_i V_i = -D_{i} \nabla Y_i \quad \text{for } i = 1, 2, \ldots, N - 1
\]

Fick’s law may be used as an approximation with the diffusion coefficient interpreted as the binary diffusion coefficient with respect to the abundant species, i.e., $D_i = D_{i,N}$. The equation for $N$ is still complicated, but is not needed because $Y_N = 1 - \sum_{i=1}^{N-1} Y_i$. 

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A useful approximation is the effective binary diffusivity for the diffusion of species $i$ in the mixture, obtained by assuming that $V_j \approx 0$ for all the species, except for $V_i \neq 0$.

\[
Y_i V_i = -D_{i,\text{eff}} \nabla Y_i \quad \text{or} \quad X_i V_i = -D_{i,\text{eff}} \nabla X_i
\]

\[
\nabla X_i = \sum_{j=1}^{N} \frac{X_i X_j}{D_{i,j}} (V_j - V_i) \approx -\sum_{j=1, j \neq i}^{N} \frac{X_i X_j}{D_{i,j}} V_i = -X_i V_i \left( \frac{X_i}{D_{i,\text{eff}}} + \sum_{j=1, j \neq i}^{N} \frac{X_j}{D_{i,j}} \right)
\]

\[
-\frac{X_i V_i}{D_{i,\text{eff}}} \approx -X_i V_i \left( \frac{X_i}{D_{i,\text{eff}}} + \sum_{j=1, j \neq i}^{N} \frac{X_j}{D_{i,j}} \right)
\]

\[
D_{i,\text{eff}} = \frac{1 - X_i}{\sum_{j=1, j \neq i}^{N} X_j / D_{i,j}}
\]

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note, however, that this can be only used for $N - 1$ species, with the last obtained from the constrain $\sum Y_i V_i = 0$. 

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Introducing the diffusion law $Y_i \nabla_i = -D_i \nabla Y_i$ in the energy equation

$$
\frac{\rho}{\rho} D \left( \int_{T_0}^{T} c_p dT \right) = \frac{Dp}{D} + \Phi + \nabla \cdot (\lambda \nabla T) - \nabla \cdot \left( \rho \sum_{i=1}^{N} \rho Y_i \nabla \int_{T_0}^{T} c_p dT \right) - \omega_i \beta_i
$$

energy transfer due to diffusion fluxes caused by imbalances in the diffusivities and specific heats.

If $D_i = D$ for all $i$

$$
\frac{\rho}{\rho} D \left( \int_{T_0}^{T} c_p dT \right) = \frac{Dp}{D} + \Phi + \nabla \cdot (\lambda \nabla T) + \nabla \cdot (\rho \sum_{i=1}^{N} \rho Y_i \nabla \int_{T_0}^{T} c_p dT) - \omega_i \beta_i
$$

$$
\sum_{i=1}^{N} \nabla Y_i \left( \int_{T_0}^{T} c_p dT \right) = \nabla \cdot \left( \rho \sum_{i=1}^{N} \rho Y_i \nabla \int_{T_0}^{T} c_p dT \right) - \omega_i \beta_i
$$

When all the $c_{p_i}$ are also the same, $c_{p_i} = c_p = c_p(T)$ for all $i$, the energy equation reduces to

$$
\frac{\rho}{\rho} c_p \frac{DT}{Dt} - \nabla \cdot (\lambda \nabla T) = \frac{Dp}{D} + \Phi + \sum_{i=1}^{N} \omega_i \beta_i
$$
Governing Equations

with Fickian diffusion (dilute mixture) and equal $c_{p_i}$

$$\frac{\partial p}{\partial t} + \nabla \cdot \rho \mathbf{v} = 0$$

$$\rho \frac{D \mathbf{v}}{Dt} = -\nabla p + \nabla \cdot \mu \left[ \left( \nabla \mathbf{v} \right) + \left( \nabla \mathbf{v} \right)^T \right] + \nabla \left( \kappa - \frac{2}{3} \mu \right) \left( \nabla \cdot \mathbf{v} \right) + \rho \mathbf{g}$$

$$\rho \frac{D Y_i}{Dt} - \nabla \cdot \left( \rho D_i \nabla Y_i \right) = \omega_i, \quad i = 1, 2, \ldots, N - 1$$

$$\rho c_p \frac{D T}{Dt} - \nabla \cdot \left( \lambda \nabla T \right) = \frac{D p}{Dt} + \Phi = \sum_{i=1}^{N} \omega_i h_i^0$$

Transport Coefficients

The bulk viscosity is negligible in combustion processes; $\kappa \approx 0$.

$$\Sigma = \mu \left[ \left( \nabla \mathbf{v} \right) + \left( \nabla \mathbf{v} \right)^T \right] - \frac{2}{3} \mu \left( \nabla \cdot \mathbf{v} \right) \mathbf{I}$$

$$\Phi = \frac{1}{2} \mu \left( \frac{\partial \rho}{\partial x_j} + \frac{\partial \rho}{\partial x_i} \right)^2 - \frac{2}{3} \mu \left( \nabla \cdot \mathbf{v} \right)^2$$

Although the transport coefficients $\lambda$, $\mu$ in a multicomponent mixture depend in general on the concentrations, this dependence is generally ignored in theoretical studies and average quantities are used; they remain dependent on pressure and temperature.

Similarly $W$ is taken as constant, so that the equation of state reduces to $p = \rho R T / W$. 
The dependence of the binary diffusivities $D_i$ on pressure and temperature is

$$D_i \sim T^\alpha / p \quad 3/2 \leq \alpha \leq 2$$

Typical values at $p = 1$ atm are in the range $0.01 - 10$ cm$^2$/s.

The kinematic viscosity $\mu / \rho$ has the same units and the same pressure and temperature dependence as the molecular diffusivities

$$\mu / \rho \sim T^\alpha / p \quad 3/2 \leq \alpha \leq 2$$

Typical values at $p = 1$ atm are in the range $0.1 - 1$ cm$^2$/s.

The thermal conductivity depends mostly on temperature, and behaves as

$$\lambda \sim T^\alpha / p$$

Typical values at $p = 1$ atm are in the range $0.1 - 1$ cm$^2$/s.

The binary diffusivities $D_i$ on pressure and temperature is

$$D_i \sim T^\alpha / p \quad 3/2 \leq \alpha \leq 2$$

Typical values at $p = 1$ atm are in the range $0.1 - 1$ cm$^2$/s.

Since $\lambda / \rho c_p, \mu / \rho, D_i$ have the same dependence on temperature, their ratios are nearly constant.

$$\frac{\lambda / \rho c_p}{D_i} = Le_i \quad \text{Lewis number}$$

$$\frac{\mu / \rho}{\lambda / \rho c_p} = Pr \quad \text{Prandtl number}$$

$$\frac{\mu / \rho}{D_i} = Sc_i \quad \text{Schmidt number}$$

We can write $\rho D_i = Le_i^{-1}(\lambda / c_p)$ and $\mu = Pr(\lambda / c_p)$ with $\lambda = \lambda(T)$. A good approximation (Smooke & Giovangigli, 1992) for the latter is

$$\frac{\lambda}{c_p} = 2.58 \cdot 10^{-4} \left( \frac{T}{298K} \right)^{0.7} \frac{g}{cm \cdot s}$$

The Prandtl and Lewis numbers are nearly constant; $Pr = 0.75$ and for common combustible mixtures $Le$ varies in the range $0.2 - 1.8$.

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If the transport coefficients $\mu, \lambda, \rho D_i$ assume constant values (an average value, say) the equations simplify to

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} = 0
\]

\[
\rho \frac{D\mathbf{v}}{Dt} = -\nabla p + \mu \left[ \nabla^2 \mathbf{v} + \frac{1}{3} \nabla (\nabla \cdot \mathbf{v}) \right] + \rho g
\]

\[
\rho \frac{D\gamma}{Dt} - \rho D_i \nabla^2 \gamma_i = \omega_i, \quad i = 1 \ldots N - 1
\]

\[
\rho c_p \frac{DT}{Dt} - \lambda \nabla^2 T = \frac{Dp}{Dt} + \Phi - \sum_{i=1}^{N} \omega_i h_i^0
\]

\[
p = \rho RT/W
\]

there are $N + 6$ variables ($\rho, p, T, \mathbf{v}, \gamma_i$) and $N + 5$ equations, supplemented with the constrain $\sum_{i=1}^{N} Y_i = 1$. 

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