

Compressible Flow - TME085

Lecture 15

Niklas Andersson

Chalmers University of Technology
Department of Mechanics and Maritime Sciences
Division of Fluid Mechanics
Gothenburg, Sweden

`niklas.andersson@chalmers.se`

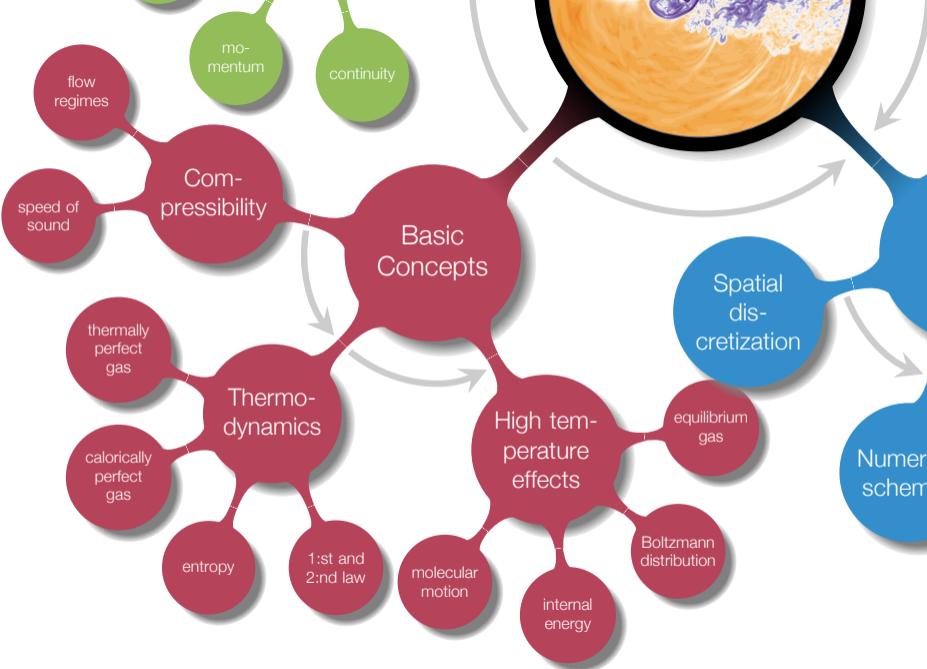


Chapter 16

Properties of High-Temperature Gases



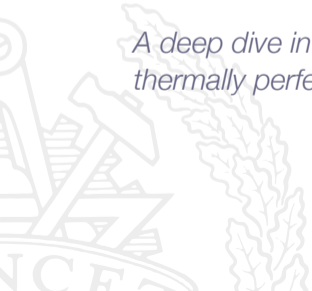
Overview



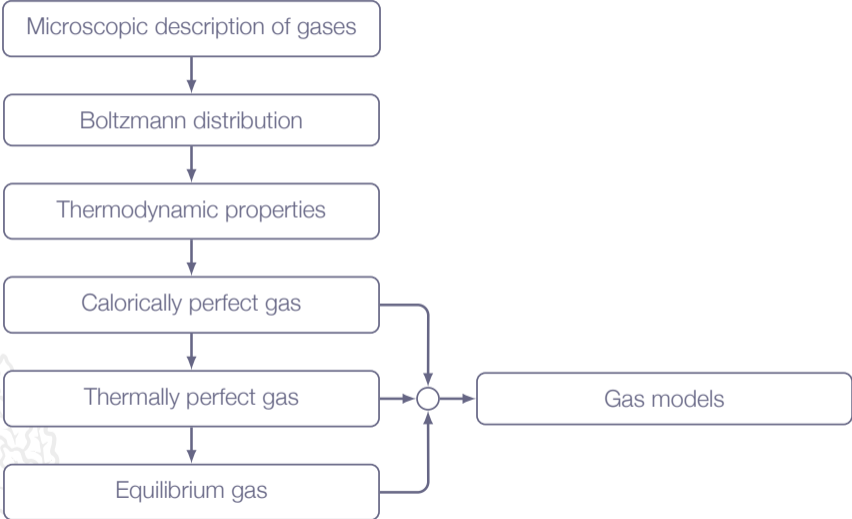
Learning Outcomes

- 6 **Define** the special cases of calorically perfect gas, thermally perfect gas and real gas and **explain** the implication of each of these special cases

A deep dive into the theory behind the definitions of calorically perfect gas, thermally perfect gas, and other models



Roadmap - High-Temperature Gases

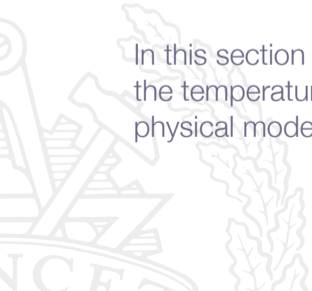


Motivation

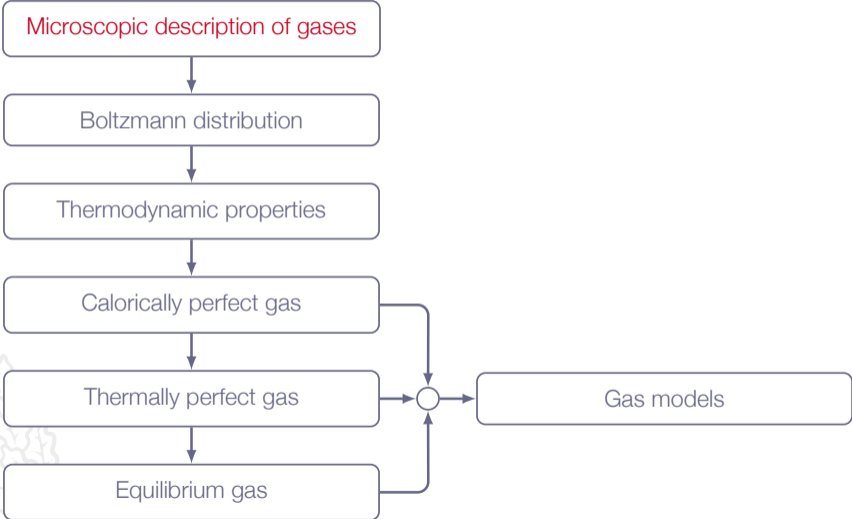
Explosions and combustion are two examples of cases where high-temperature effects must be taken into account

The temperature does not have to be extremely high in order for temperature effects to appear, 600 K is enough

In this section you will learn what happens in a gas on a molecular level when the temperature increases and what implications that has on applicability of physical models



Roadmap - High-Temperature Gases



Chapter 16.2

Microscopic Description of Gases

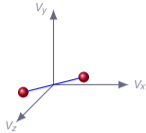


Microscopic Description of Gases

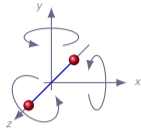
- ▶ Hard to make measurements
- ▶ Accurate, reliable theoretical models needed
- ▶ Available models do work quite well



Molecular Energy



Translational kinetic energy
thermal degrees of freedom: 3



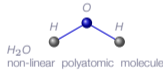
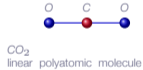
Rotational kinetic energy
thermal degrees of freedom:
2 for diatomic gases
2 for linear polyatomic gases
3 for non-linear polyatomic gases



Vibrational energy
(kinetic energy + potential energy)
thermal degrees of freedom: 2



Electronic energy of electrons in orbit
(kinetic energy + potential energy)



- ▶ Translational energy
- ▶ Rotational energy
(only for molecules - not for mono-atomic gases)
- ▶ Vibrational energy
- ▶ Electronic energy

Molecular Energy

The energy for one molecule can be described by

$$\epsilon' = \epsilon'_{trans} + \epsilon'_{rot} + \epsilon'_{vib} + \epsilon'_{el}$$

Results of quantum mechanics have shown that **energy is quantized** *i.e.* they can **exist only at discrete values**

Energy is **not** continuous! Might seem unintuitive

Molecular Energy

The lowest quantum numbers defines the **zero-point energy** for each mode

- ▶ $\epsilon'_{0rot} = 0$ the rotational energy at **absolute zero** is exactly zero
- ▶ ϵ'_{0trans} is very small but finite - at **absolute zero**, molecules still moves but not much

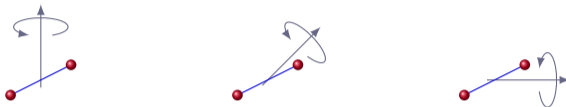
$$\epsilon_{jtrans} = \epsilon'_{jtrans} - \epsilon'_{0trans}$$

$$\epsilon_{lvib} = \epsilon'_{lvib} - \epsilon'_{0vib}$$

$$\epsilon_{krot} = \epsilon'_{krot}$$

$$\epsilon_{mel} = \epsilon'_{mel} - \epsilon'_{0el}$$

Energy States



- ▶ three cases with the **same rotational energy**
- ▶ different direction of angular momentum
- ▶ quantum mechanics \Rightarrow different **distinguishable states**
- ▶ a finite number of possible states for each energy level

Macrostates and Microstates

Macrostate:

- ▶ molecules collide and exchange energy \Rightarrow the N_j distribution (the macrostate) will change over time
- ▶ some macrostates are more probable than other
- ▶ most probable macrostates (distribution) \Rightarrow **thermodynamic equilibrium**

Microstate:

- ▶ same number of molecules in each energy level but different states
- ▶ the most probable macrostate is the one with the most possible microstates \Rightarrow possible to find the most probable macrostate by counting microstates

Macrostates and Microstates

Macrostate I Microstate I

ε'_0 : ● ● ○ ○ ○ ($N_0 = 2, g_0 = 5$)

ε'_1 : ● ● ● ○ ● ● ($N_1 = 5, g_1 = 6$)

ε'_2 : ● ● ● ○ ○ ($N_2 = 3, g_2 = 5$)

⋮

ε'_j : ○ ● ● ($N_j = 2, g_j = 3$)



Macrostates and Microstates

Macrostate I Microstate II

ε'_0 : ○ ● ○ ○ ● ($N_0 = 2, g_0 = 5$)

ε'_1 : ● ○ ● ● ● ● ($N_1 = 5, g_1 = 6$)

ε'_2 : ○ ○ ● ● ● ($N_2 = 3, g_2 = 5$)

⋮

ε'_j : ○ ● ● ($N_j = 2, g_j = 3$)



Macrostates and Microstates

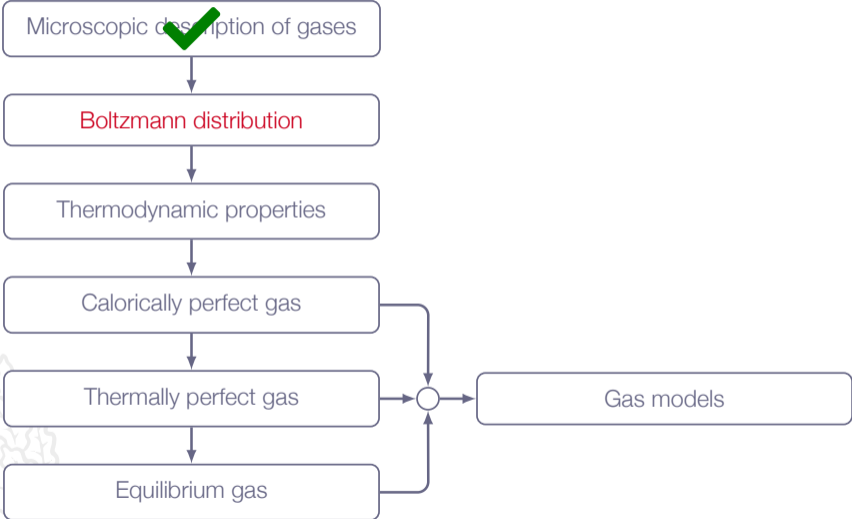
$$N = \sum_j N_j$$

N is the total number of molecules and N_j is the number of molecules at energy level j

$$E = \sum_j \epsilon'_j N_j$$

E is the total energy and ϵ'_j is the energy per molecule at energy level j

Roadmap - High-Temperature Gases



Chapter 16.5

The Limiting Case: Boltzmann Distribution



Boltzmann Distribution

The Boltzmann distribution:

$$N_j^* = N \frac{g_j e^{-\varepsilon_j/kT}}{Q}$$

where $Q = f(T, V)$ is the state sum defined as

$$Q \equiv \sum_j g_j e^{-\varepsilon_j/kT}$$

g_j is the number of **degenerate states**, ε_j is the energy above zero-level ($\varepsilon_j = \varepsilon_j' - \varepsilon_0$), and k is the **Boltzmann constant**

Boltzmann Distribution

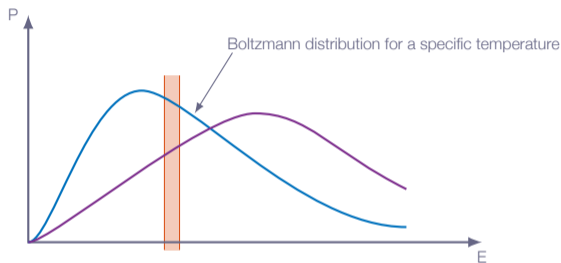
The Boltzmann distribution:

$$N_j^* = N \frac{g_j e^{-\varepsilon_j/kT}}{Q}$$

For molecules or atoms of a given species, quantum mechanics says that a set of well-defined energy levels ε_j exists, over which the molecules or atoms can be distributed at any given instant, and that each energy level has a certain number of energy states, g_j .

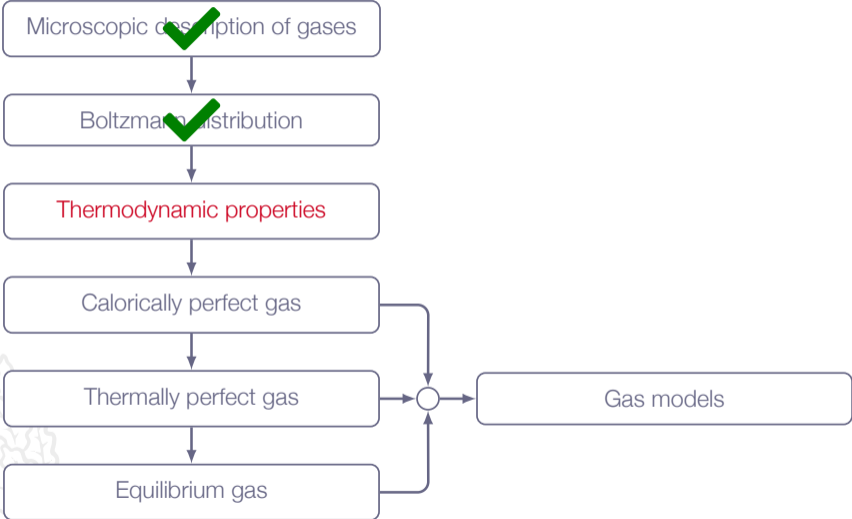
For a system of N molecules or atoms at a given T and V , N_j^ are the number of molecules or atoms in each energy level ε_j when the system is in **thermodynamic equilibrium**.*

Boltzmann Distribution



- ▶ At temperatures above $\sim 5\text{K}$, molecules are distributed over many energy levels, and therefore the states are generally **sparsely populated** ($N_j \ll g_j$)
- ▶ Higher energy levels become more populated as temperature increases

Roadmap - High-Temperature Gases



Chapter 16.6 - 16.8

Evaluation of Gas Thermodynamic Properties



Internal Energy

The internal energy is calculated as

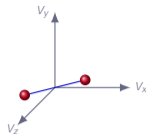
$$E = NkT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V$$

The internal energy per unit mass is obtained as

$$e = \frac{E}{M} = \frac{NkT^2}{Nm} \left(\frac{\partial \ln Q}{\partial T} \right)_V = \left\{ \frac{k}{m} = R \right\} = RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V$$

Internal Energy - Translation

$$\epsilon'_{trans} = \frac{h^2}{8m} \left(\frac{n_1^2}{a_1^2} + \frac{n_2^2}{a_2^2} + \frac{n_3^2}{a_3^2} \right)$$

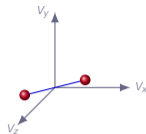


$n_1 - n_3$	quantum numbers (1,2,3,...)
$a_1 - a_3$	linear dimensions that describes the size of the system
h	Planck's constant
m	mass of the individual molecule

$\Rightarrow \dots \Rightarrow$

$$Q_{trans} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V$$

Internal Energy - Translation



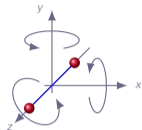
$$Q_{trans} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V$$

$$\ln Q_{trans} = \frac{3}{2} \ln T + \frac{3}{2} \ln \frac{2\pi mk}{h^2} + \ln V \Rightarrow$$

$$\left(\frac{\partial \ln Q_{trans}}{\partial T} \right)_V = \frac{3}{2} \frac{1}{T} \Rightarrow$$

$$e_{trans} = RT^2 \left(\frac{\partial \ln Q_{trans}}{\partial T} \right)_V = RT^2 \frac{3}{2T} = \frac{3}{2} RT$$

Internal Energy - Rotation



$$\epsilon'_{rot} = \frac{h^2}{8\pi^2 I} J(J + 1)$$

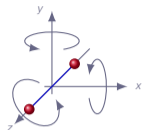
J rotational quantum number (0,1,2,...)
 I moment of inertia (tabulated for common molecules)
 h Planck's constant

$\Rightarrow \dots \Rightarrow$

$$Q_{rot} = \frac{8\pi^2 I k T}{h^2}$$

Internal Energy - Rotation

$$Q_{rot} = \frac{8\pi^2 I k T}{h^2}$$

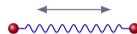


$$\ln Q_{rot} = \ln T + \ln \frac{8\pi^2 I k}{h^2} \Rightarrow$$

$$\left(\frac{\partial \ln Q_{rot}}{\partial T} \right)_V = \frac{1}{T} \Rightarrow$$

$$e_{rot} = RT^2 \left(\frac{\partial \ln Q_{rot}}{\partial T} \right)_V = RT^2 \frac{1}{T} = RT$$

Internal Energy - Vibration



$$\epsilon'_{vib} = h\nu \left(n + \frac{1}{2} \right)$$

- n vibrational quantum number (0,1,2,...)
- ν fundamental vibrational frequency (tabulated for common molecules)
- h Planck's constant

$\Rightarrow \dots \Rightarrow$

$$Q_{vib} = \frac{1}{1 - e^{-h\nu/kT}}$$

Internal Energy - Vibration

$$Q_{vib} = \frac{1}{1 - e^{-h\nu/kT}}$$



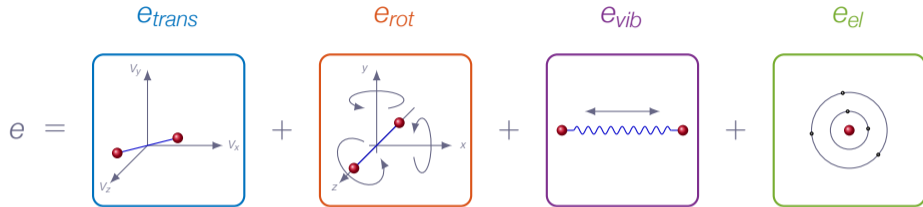
$$\ln Q_{vib} = -\ln(1 - e^{-h\nu/kT}) \Rightarrow$$

$$\left(\frac{\partial \ln Q_{vib}}{\partial T}\right)_V = \frac{h\nu/kT^2}{e^{h\nu/kT} - 1} \Rightarrow$$

$$e_{vib} = RT^2 \left(\frac{\partial \ln Q_{vib}}{\partial T}\right)_V = RT^2 \frac{h\nu/kT^2}{e^{h\nu/kT} - 1} = \frac{h\nu/kT}{e^{h\nu/kT} - 1} RT$$

$$\lim_{T \rightarrow \infty} \frac{h\nu/kT}{e^{h\nu/kT} - 1} = 1 \Rightarrow e_{vib} \leq RT$$

Specific Heat



$$e = \frac{3}{2}RT + RT + \frac{h\nu/kT}{e^{h\nu/kT}-1}RT + e_{el}$$

From before, we know that the specific heat is defined as follows:

$$C_v \equiv \left(\frac{\partial e}{\partial T} \right)_v$$

Specific Heat

$$e = e_{trans} + e_{rot} + e_{vib} + e_{el} = \frac{3}{2}RT + RT + \frac{h\nu/kT}{e^{h\nu/kT}-1}RT + e_{el}$$

For molecules with only translational and rotational energy

$$e = \frac{3}{2}RT + RT = \frac{5}{2}RT \Rightarrow C_v \equiv \left(\frac{\partial e}{\partial T} \right)_v = \frac{5}{2}R$$

$$C_p = C_v + R = \frac{7}{2}R$$

$$\gamma = \frac{C_p}{C_v} = \frac{7}{5} = 1.4$$



Specific Heat

$$e = e_{trans} + e_{rot} + e_{vib} + e_{el} = \frac{3}{2}RT + RT + \frac{h\nu/kT}{e^{h\nu/kT}-1}RT + e_{el}$$

For mono-atomic gases with only translational and (rotational) energy

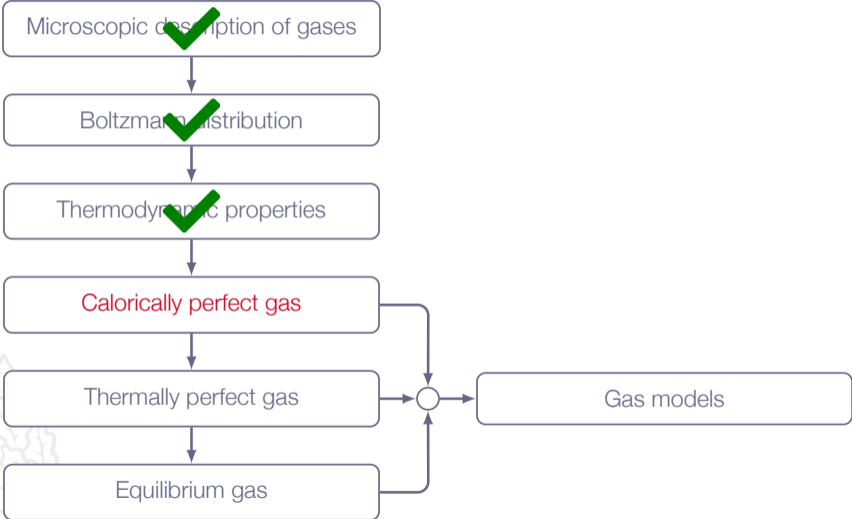
$$e = \frac{3}{2}RT + 0 \Rightarrow C_v \equiv \left(\frac{\partial e}{\partial T} \right)_v = \frac{3}{2}R$$

$$C_p = C_v + R = \frac{5}{2}R$$

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3} = 1\frac{2}{3} \simeq 1.67$$



Roadmap - High-Temperature Gases



Calorically Perfect Gas

$$e = e_{trans} + e_{rot} + e_{vib} + e_{el} = \frac{3}{2}RT + RT + \frac{h\nu/kT}{e^{h\nu/kT}-1}RT + e_{el}$$

- ▶ In general, only **translational** and **rotational** modes of molecular excitation
- ▶ **Translational** and **rotational** energy levels are sparsely populated, according to Boltzmann distribution (the Boltzmann limit)
- ▶ **Vibrational** energy levels are practically unpopulated (except for the zero level)

Calorically Perfect Gas

$$e = e_{trans} + e_{rot} + e_{vib} + e_{el} = \frac{3}{2}RT + RT + \frac{h\nu/kT}{e^{h\nu/kT}-1}RT + e_{el}$$

Characteristic values of γ for each type of molecule, e.g. mono-atomic gas, di-atomic gas, tri-atomic gas, etc

He, Ar, Ne, ... - mono-atomic gases ($\gamma = 5/3$)

H₂, O₂, N₂, ... - di-atomic gases ($\gamma = 7/5$)

H₂O (gaseous), CO₂, ... - tri-atomic gases ($\gamma < 7/5$)

Calorically Perfect Gas - Thermodynamic Relations

$$p = p(R, T)$$

$$e = C_v T$$

$$C_p - C_v = R$$

$$h = C_p T$$

$$\gamma = C_p / C_v$$

$$h = e + p/\rho$$

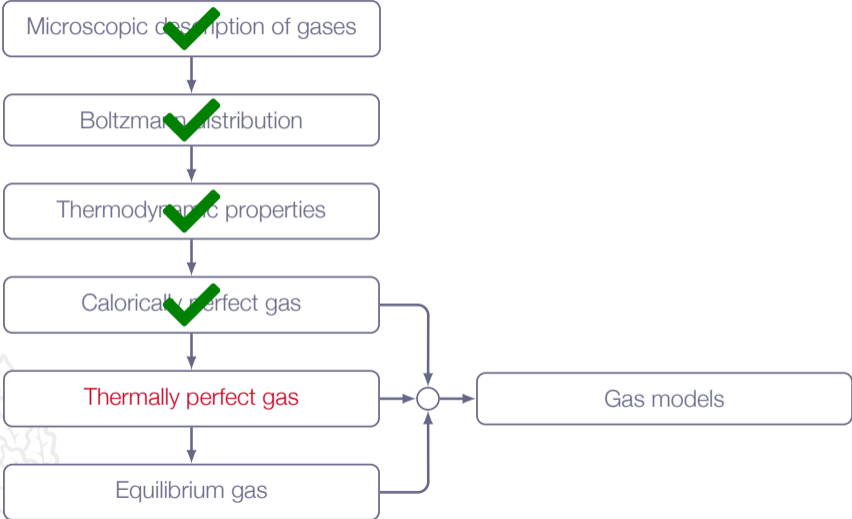
$$C_v = \frac{R}{\gamma - 1}$$

$$a = \sqrt{\frac{\gamma p}{\rho}} = \sqrt{\gamma R T}$$

$$C_p = \frac{\gamma R}{\gamma - 1}$$

γ , R , C_v , and C_p are constants

Roadmap - High-Temperature Gases



Thermally Perfect Gas

$$e = e_{trans} + e_{rot} + e_{vib} + e_{el} = \frac{3}{2}RT + RT + \frac{h\nu/kT}{e^{h\nu/kT}-1}RT + e_{el}$$

- ▶ In general, only translational, rotational and vibrational modes of molecular excitation
- ▶ Translational and rotational energy levels are sparsely populated, according to Boltzmann distribution (the Boltzmann limit)
- ▶ The population of the vibrational energy levels approaches the Boltzmann limit as temperature increases
- ▶ Temperature dependent values of γ for all types of molecules except mono-atomic (no vibrational modes possible)

Thermally Perfect Gas - Thermodynamic Relations

$$p = p(R, T)$$

$$e = e(T)$$

$$C_v = de/dT$$

$$C_p - C_v = R$$

$$h = h(T)$$

$$C_p = dh/dT$$

$$\gamma = C_p/C_v$$

$$h = e + p/\rho$$

$$C_v = \frac{R}{\gamma - 1}$$

$$a = \sqrt{\frac{\gamma p}{\rho}} = \sqrt{\gamma RT}$$

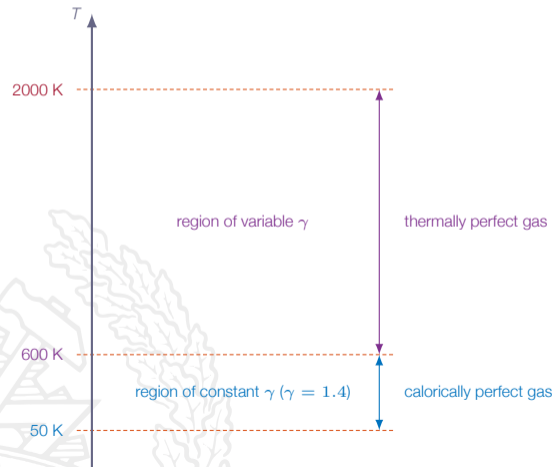
$$C_p = \frac{\gamma R}{\gamma - 1}$$

γ , C_v , and C_p are variable (functions of T)

R is constant

High-Temperature Effects

Example: properties of air



Thermally perfect gas:
 e and h are non-linear functions of T

the temperature range represents standard atmospheric pressure (lower pressure gives lower temperatures)

High-Temperature Effects

$$e = e_{trans} + e_{rot} + e_{vib} + e_{el} = \frac{3}{2}RT + RT + \frac{h\nu/kT}{e^{h\nu/kT}-1}RT + e_{el}$$

For cases where the vibrational energy is not negligible (*at high temperatures*)

$$\lim_{T \rightarrow \infty} e_{vib} = RT \Rightarrow C_v = \frac{7}{2}R$$

However, chemical reactions and ionization will take place long before that ...

- ▶ Translational and rotational energy fully excited above ~ 5 K
- ▶ Vibrational energy is non-negligible above 600 K
- ▶ Chemical reactions begin to occur above ~ 2000 K

High-Temperature Effects

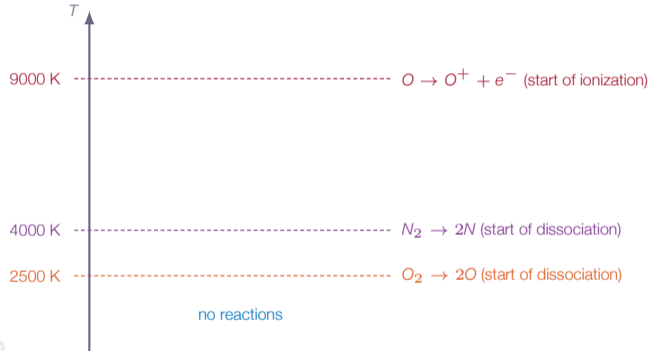
As temperature increase further vibrational energy becomes less important

Why is that so?



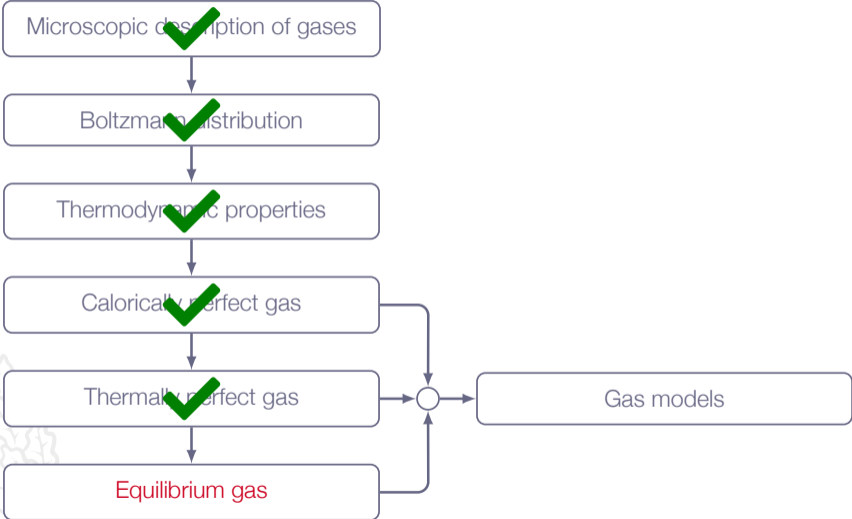
High-Temperature Effects

Example: properties of air (continued)



With increasing temperature, the gas becomes more and more mono-atomic which means that vibrational modes becomes less important

Roadmap - High-Temperature Gases



Equilibrium Gas

For temperatures $T > \sim 2500K$

- ▶ Air may be described as being in **thermodynamic** and **chemical equilibrium** (Equilibrium Gas)
 - ▶ reaction rates (time scales) low compared to flow time scales
 - ▶ reactions in both directions (example: $O_2 \rightleftharpoons 2O$)
- ▶ Tables must be used (Equilibrium Air Data) or special functions which have been made to fit the tabular data

Equilibrium Gas - Thermodynamic Relations

How do we obtain a thermodynamic description?

$$p = p(R, T)$$

$$e = e(\nu, T)$$

$$C_v = \left(\frac{\partial e}{\partial T} \right)_\nu$$

$$h = h(p, T)$$

$$h = e + \frac{p}{\rho}$$

$$C_p = \left(\frac{\partial h}{\partial T} \right)_p$$

$$a_e^2 = \gamma RT \frac{1 + \frac{1}{\rho} \left(\frac{\partial e}{\partial \nu} \right)_T}{1 - \rho \left(\frac{\partial h}{\partial \rho} \right)_T}$$

$$\gamma = \frac{C_p}{C_v} = \frac{\left(\frac{\partial h}{\partial T} \right)_p}{\left(\frac{\partial e}{\partial T} \right)_\nu}$$

Note! R is not a constant here
i.e. this is not the ideal gas law

$$RT = \frac{p}{\rho}$$

Roadmap - High-Temperature Gases

