

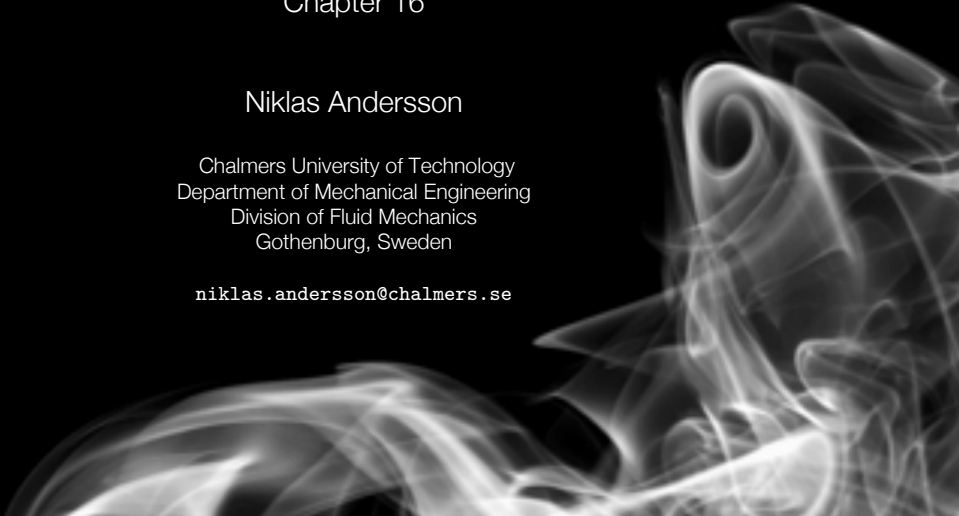
# Compressible Flow - TME085

## Chapter 16

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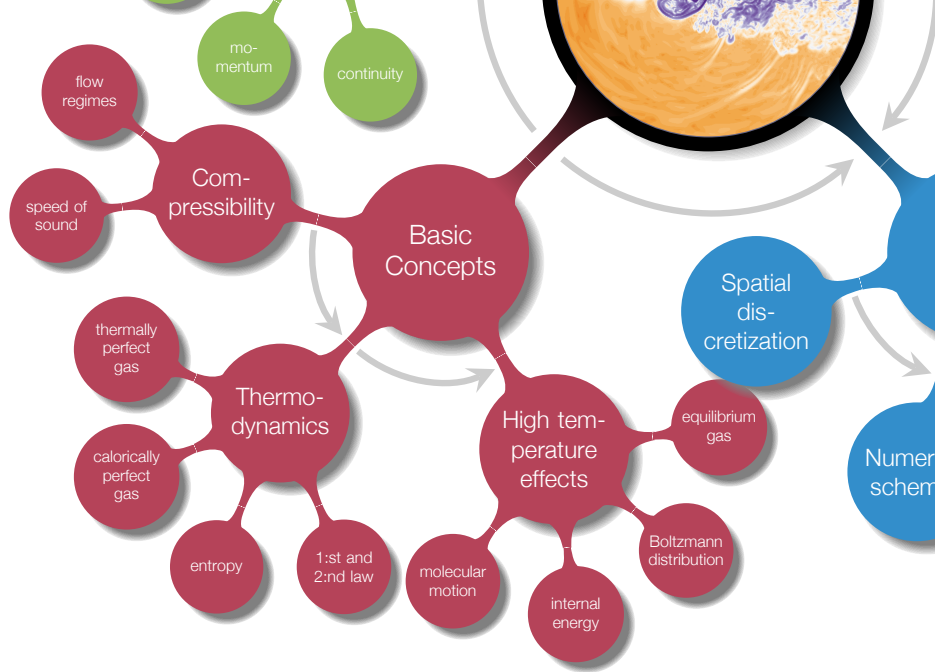
`niklas.andersson@chalmers.se`





## Chapter 16 - Properties of High-Temperature Gases

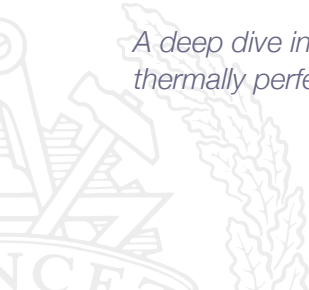
# Overview



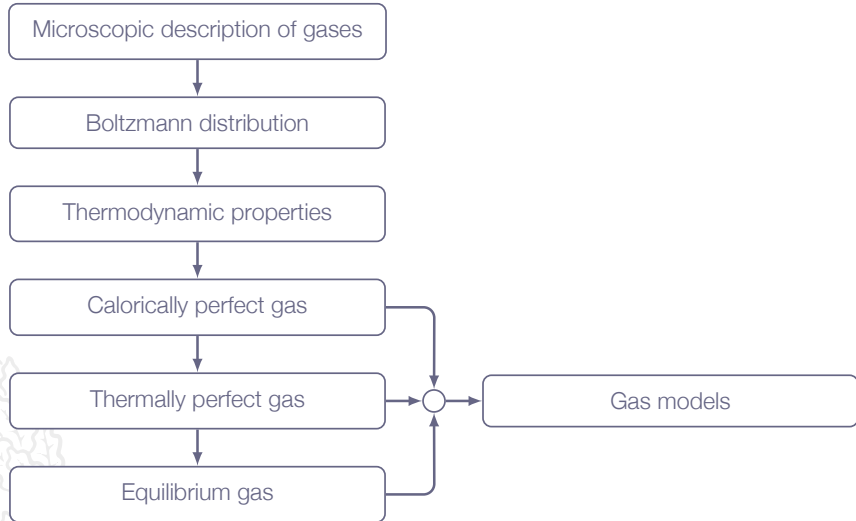
# Learning Outcomes

- 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



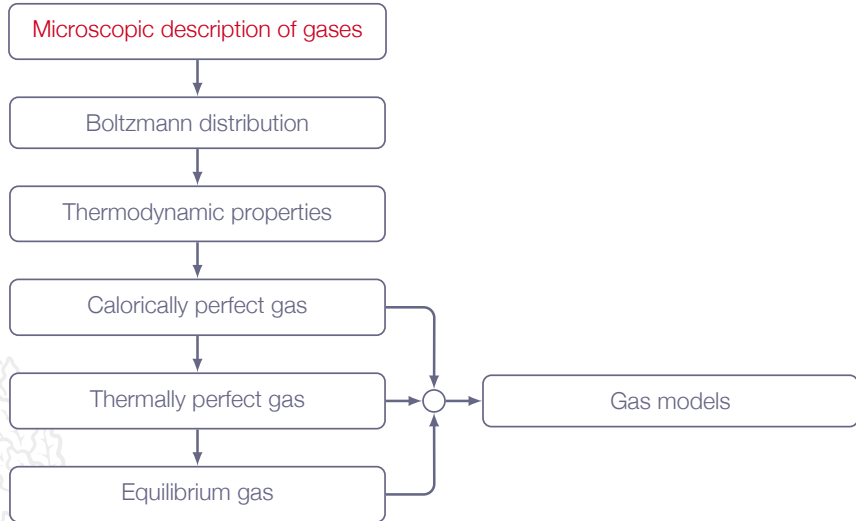
# Motivation

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

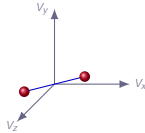
Accurate, reliable theoretical models needed

Available models do work quite well



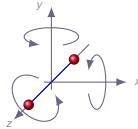
# Molecular Energy

## Translation



Translational kinetic energy  
thermal degrees of freedom: 3

## Rotation



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

## Vibration

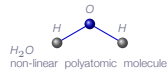
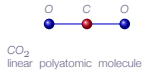


Vibrational energy  
(kinetic energy + potential energy)  
thermal degrees of freedom: 2

## Electronic energy



Electronic energy of electrons in orbit  
(kinetic energy + potential 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.* energy can **exist only at specific discrete values**

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

# Molecular Energy

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

$$\varepsilon'_{0rot} = 0$$

$$\varepsilon'_{0trans} > 0 \text{ (very small but finite)}$$

At **absolute zero**, molecules still moves but not much. The rotational energy is, however, exactly zero.

$$\varepsilon_{jtrans} = \varepsilon'_{jtrans} - \varepsilon'_{0trans}$$

$$\varepsilon_{lvib} = \varepsilon'_{lvib} - \varepsilon'_{0vib}$$

$$\varepsilon_{krot} = \varepsilon'_{krot}$$

$$\varepsilon_{mel} = \varepsilon'_{mel} - \varepsilon'_{0el}$$

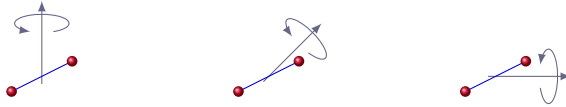
# Molecular Energy

Thus the total energy of a specific molecule may be expressed as

$$\varepsilon'_i = \varepsilon_{j_{trans}} + \varepsilon_{k_{rot}} + \varepsilon_{l_{vib}} + \varepsilon_{m_{el}} + \varepsilon'_o$$

**Note!** since  $\varepsilon'_i$  is the sum of individually quantized energy levels,  $\varepsilon'_i$  itself is also quantized

# Energy States - Example



three cases with the **same rotational energy**

different direction of angular momentum

quantum mechanics  $\Rightarrow$  different **distinguishable states**

a finite number of possible **degenerate states**  $g_j$  at each energy level  $j$

# Macrostates and Microstates

## Macrostate:

molecules collide and exchange energy  $\Rightarrow$  the number of molecules at each energy level  $j$  (the macrostate or the  $N_j$  distribution) will change over time

some macrostates are more probable than other

most probable macrostates (energy distributions)  $\Rightarrow$  **thermodynamic equilibrium**

## Microstate:

different microstates constitute the same number of molecules in each energy level (same macrostate) but molecules are in **different degenerate 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

$\varepsilon_j$  molecular energy at energy level  $j$   
 $N_j$  the number of molecules at energy level  $j$   
 $g_j$  the number of possible degenerate states at energy level  $j$

Macrostate I    Microstate I

$\varepsilon'_0 :$     ●    ●    ○    ○    ○    (  $N_0 = 2, g_0 = 5$  )

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

$\varepsilon'_2 :$     ●    ●    ●    ○    ○    (  $N_2 = 3, g_2 = 5$  )

⋮

$\varepsilon'_j :$     ○    ●    ●    (  $N_j = 2, g_j = 3$  )



# Macrostates and Microstates

$\varepsilon_j$  molecular energy at energy level  $j$   
 $N_j$  the number of molecules at energy level  $j$   
 $g_j$  the number of possible degenerate states at energy level  $j$

Macrostate I    Microstate II

$\varepsilon'_0 :$     ○    ●    ○    ○    ●    (  $N_0 = 2, g_0 = 5$  )

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

$\varepsilon'_2 :$     ○    ○    ●    ●    ●    (  $N_2 = 3, g_2 = 5$  )

⋮

$\varepsilon'_j :$     ○    ●    ●    (  $N_j = 2, g_j = 3$  )

# Macrostates and Microstates

$\varepsilon_j$  molecular energy at energy level  $j$   
 $N_j$  the number of molecules at energy level  $j$   
 $g_j$  the number of possible degenerate states at energy level  $j$

Macrostate II    Microstate I

$\varepsilon'_0 :$     ○    ●    ○    ○    ○    ○    ( $N_0 = 1, g_0 = 5$ )

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

$\varepsilon'_2 :$     ●    ○    ●    ●    ●       ( $N_2 = 4, g_2 = 5$ )

⋮

$\varepsilon'_j :$     ○    ○    ●       ( $N_j = 1, g_j = 3$ )

# Macrostates and Microstates

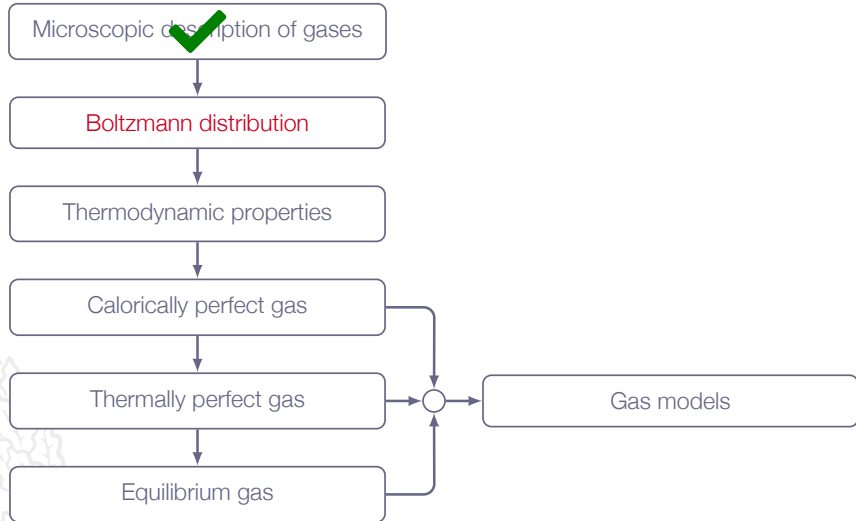
$$N = \sum_j N_j$$

$N$  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  $\epsilon'_j$  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**,  $\varepsilon_j$  is the **energy above zero-level** ( $\varepsilon_j = \varepsilon_j' - \varepsilon_0$ ), and  $k$  is the Boltzmann constant

# Boltzmann Distribution

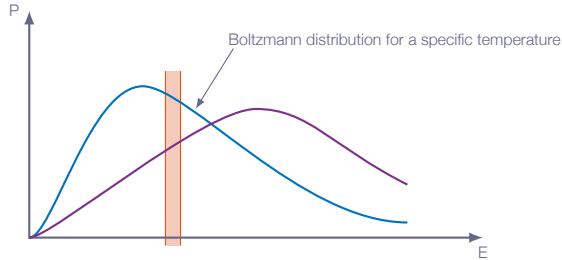
The Boltzmann distribution:

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

*For molecules or atoms of a given species, quantum mechanics says that a set of well-defined energy levels  $\varepsilon_j$  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  $\varepsilon_j$  when the system is in **thermodynamic equilibrium**.*

# Boltzmann Distribution



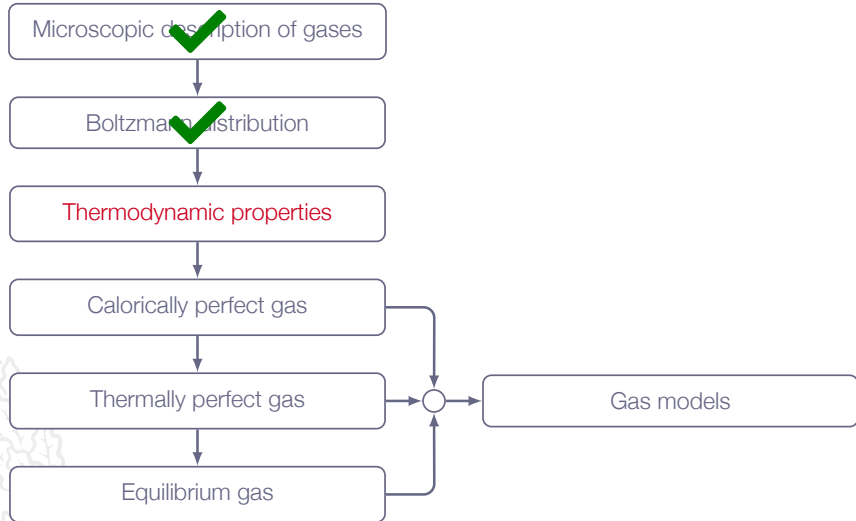
Boltzmann distribution: describes the **probability** ( $P$ ) of population of an **energy level** with the energy ( $E$ )

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

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

$k$  is the Boltzmann constant,  $m$  is the molecular weight,  $R$  is the gas constant, and  $Q$  is the state sum

# Internal Energy

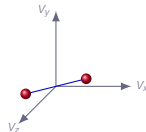
$$e = RT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_V$$

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

In order to be able to calculate the internal energy of a gas at a given temperature, we need an estimate of the state sum  $Q$

# Internal Energy - Translation

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

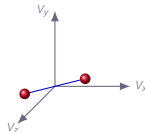


|             |                                                         |
|-------------|---------------------------------------------------------|
| $n_1 - n_3$ | quantum numbers (1,2,3,...)                             |
| $a_1 - a_3$ | linear dimensions that describes the size of the system |
| $h$         | 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



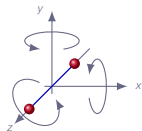
$$Q_{trans} = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V$$

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

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

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

# Internal Energy - Rotation



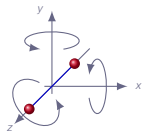
$$\epsilon'_{rot} = \frac{h^2}{8\pi^2 I} J(J+1)$$

|     |                                                    |
|-----|----------------------------------------------------|
| $J$ | 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



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

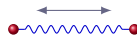
- $n$  vibrational quantum number (0, 1, 2, ...)
- $\nu$  fundamental vibrational frequency (tabulated for common molecules)
- $h$  Planck's constant

$\Rightarrow \dots \Rightarrow$

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

# Internal Energy - Vibration

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



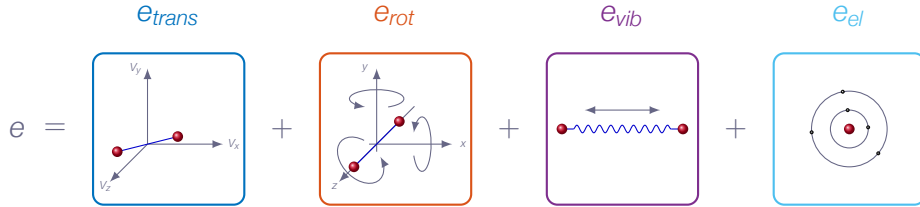
$$\ln Q_{vib} = -\ln(1 - e^{-h\nu/kT}) \Rightarrow$$

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

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

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

# 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

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

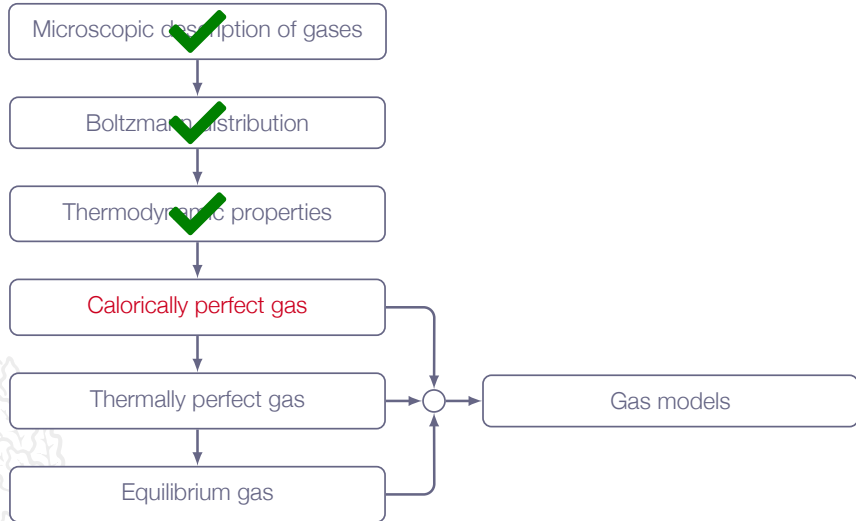
For mono-atomic gases with only translational and (rotational) energy

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

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

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

# 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  $\gamma$  for each type of molecule, e.g. mono-atomic gas, di-atomic gas, tri-atomic gas, etc

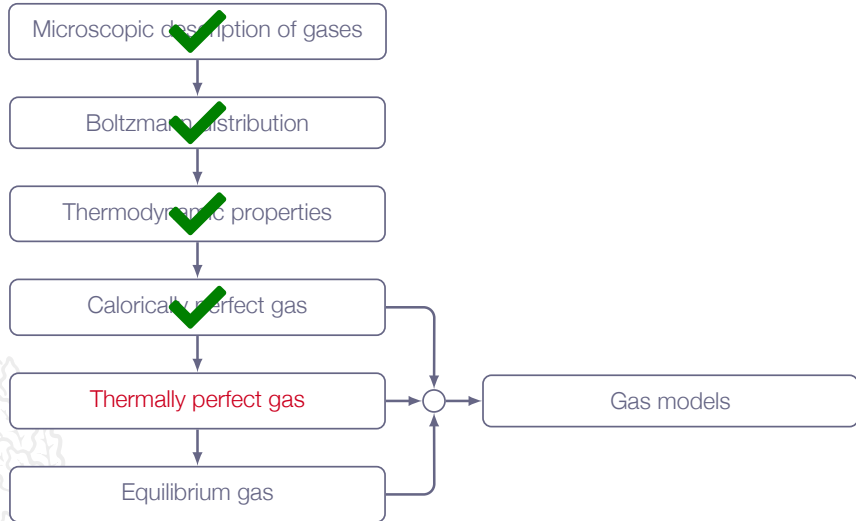
*He, Ar, Ne, ...* - mono-atomic gases ( $\gamma = 5/3$ )

*H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, ...* - di-atomic gases ( $\gamma = 7/5$ )

*H<sub>2</sub>O (gaseous), CO<sub>2</sub>, ...* - tri-atomic gases ( $\gamma < 7/5$ )



# 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

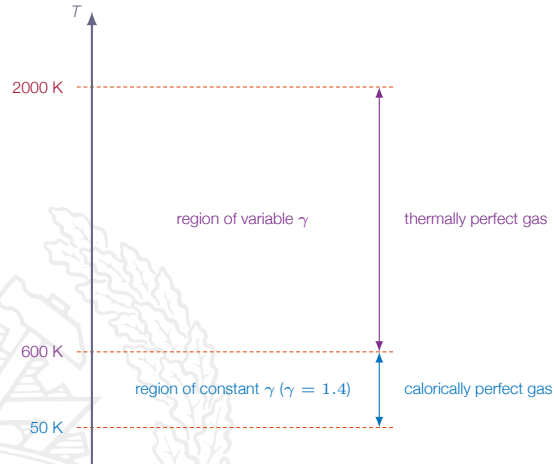
Translational and rotational energy levels are sparsely populated, according to Boltzmann distribution (the **Boltzmann limit**)

The population of the vibrational energy levels **approaches the Boltzmann limit** as temperature increases

**Temperature dependent values of  $\gamma$**  for all types of molecules except mono-atomic (no vibrational modes possible)

# 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  $\sim 5$  K

Vibrational energy is non-negligible above 600 K

Chemical reactions begin to occur above  $\sim 2000$  K

# High-Temperature Effects

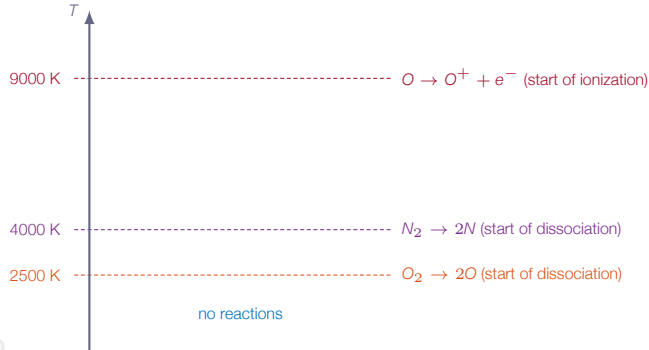
As temperature increase further vibrational energy becomes less important

Why is that so?



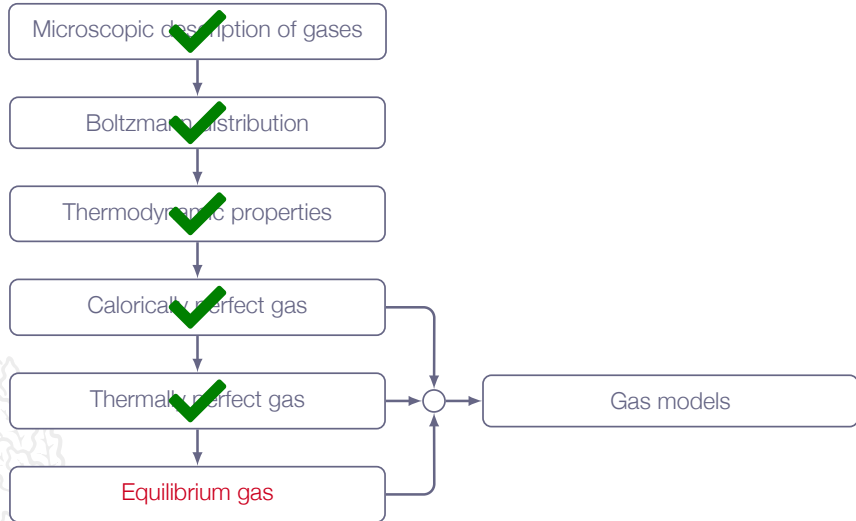
# High-Temperature Effects

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  $T > 2500K$

Air may be described as being in **thermodynamic** and **chemical equilibrium**  
(Equilibrium Gas)

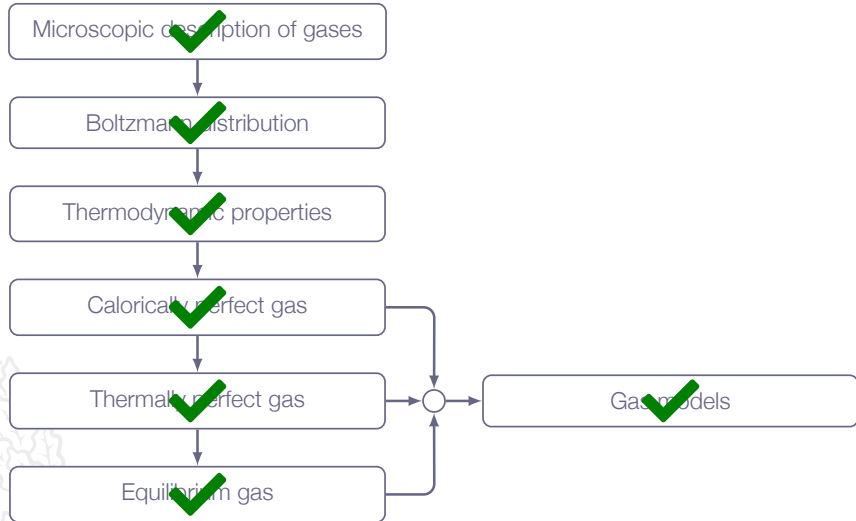
reaction rates (time scales) low compared to flow time scales

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 tabulated data



# Roadmap - High-Temperature Gases



## MODELS OF THE ATOM OVER TIME



1810

SMALL HARD  
BALL MODEL



1904

PLUM PUDDING  
MODEL



1907

TINY BIRD  
MODEL



1911

RUTHERFORD  
MODEL



1913

BOHR MODEL



1928

NUNCHUCK  
MODEL



1932

CHADWICK  
MODEL



2008

538 MODEL



TODAY

QUANTUM  
MODEL



FUTURE

"SMALL HARD  
BALL SURROUNDED  
BY MATH" MODEL