Compressible Flow - TME085 Lecture 14

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

Chapter 17 High-Temperature Flows: Basic Examples



Addressed 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 Effects



Properties of High-Temperature Gases

Applications:

- Rocket nozzle flows
- Reentry vehicles
 - Shock tubes / Shock tunnels
 - Internal combustion engines

Properties of High-Temperature Gases

Example: Reentry vehicle

Mach 32.5 Air Calorically perfect gas $T_{\infty} = 283$

Table A.2 \Rightarrow $T_s/T_{\infty} = 206$

 $T_{\infty} = 283 \Rightarrow T_s = 58\ 300\ {\rm K}$

Properties of High-Temperature Gases

Example: Reentry vehicle

Mach 32.5 Air Calorically perfect gas $T_{\infty} = 283$

Table A.2 \Rightarrow T_s/T_{∞} = 206

 $T_{\infty} = 283 \Rightarrow T_s = 58\ 300\ {\rm K}$

A more correct value is $T_s = 11600$ K

Something is fishy here!

Roadmap - High Temperature Effects



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

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

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

Not continuous! Might seem unintuitive

Molecular Energy

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

- ▶ for rotational energy the zero-point energy is exactly zero
- $\blacktriangleright \ \varepsilon'_{o_{\rm trans}}$ is very small but finite at absolute zero, molecules still moves but not much



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

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) ⇒ 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 ⇒ possible to find the most probable macrostate by counting microstates



17/83





$$N = \sum_{j} N_{j}$$



$$E = \sum_{j} \varepsilon'_{j} N_{j}$$

Niklas Andersson - Chalmers

Roadmap - High Temperature Effects



Chapter 16.5 The Limiting Case: Boltzmann Distribution

Boltzmann Distribution

The Boltzmann distribution:

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

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

$$Q \equiv \sum_{j} g_{j} \mathrm{e}^{-\varepsilon_{j}/k7}$$

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

Boltzmann Distribution

The Boltzmann distribution:

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

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_i .

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 ~ 5K, molecules are distributed over many energy levels, and therefore the states are generally sparsely populated ($N_i \ll g_i$)
- Higher energy levels become more populated as temperature increases

Roadmap - High Temperature Effects



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

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

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

$$\Rightarrow \cdots \Rightarrow$$

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

Internal Energy - Translation

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

$$\ln Q_{trans} = \frac{3}{2} \ln 7 + \frac{3}{2} \ln \frac{2\pi m k}{h^2} + \ln V \Rightarrow$$

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

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

Internal Energy - Rotation

$$\varepsilon_{rot}' = \frac{h^2}{8\pi^2 l} J(J+1)$$

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

$$\Rightarrow \cdots \Rightarrow$$

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

Niklas Andersson - Chalmers

Internal Energy - Rotation

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

$$\ln Q_{rot} = \ln \mathbf{7} + \ln \frac{8\pi^2 l k}{h^2} \Rightarrow$$

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

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

Internal Energy - Vibration

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

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

$$\Rightarrow \cdots \Rightarrow$$

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

Internal Energy - Vibration

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

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

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

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

Specific Heat

$$e = e_{trans} + e_{rot} + e_{vib} + e_{el}$$

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

$$C_{v} \equiv \left(\frac{\partial e}{\partial T}\right)_{v}$$
Specific Heat

Molecules with only translational and rotational energy

$$e = \frac{3}{2}RT + RT = \frac{5}{2}RT \Rightarrow C_v = \frac{5}{2}R$$
$$C_p = C_v + R = \frac{7}{2}R$$
$$\gamma = \frac{C_p}{C_v} = \frac{7}{5} = 1.4$$

Mono-atomic gases with only translational and rotational energy

$$e = \frac{3}{2}RT \Rightarrow C_{\nu} = \frac{3}{2}R$$
$$C_{\rho} = C_{\nu} + R = \frac{5}{2}R$$
$$\gamma = \frac{C_{\rho}}{C_{\nu}} = \frac{5}{3} = 1\frac{2}{3} \simeq 1.67$$

Roadmap - High Temperature Effects



Calorically Perfect Gas

- 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)
 - 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 ($\gamma = 5/3$)
 - H_2 , O_2 , N_2 , ... di-atomic gases ($\gamma = 7/5$)
 - H_2O (gaseous), CO_2 , ... tri-atomic gases ($\gamma < 7/5$)

Calorically Perfect Gas

$$p = \rho RT \quad e = C_v T$$
$$h = C_p T$$
$$h = e + p/\rho$$







 γ , R, C_v, and C_p are constants

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

Thermally Perfect Gas

- 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

$$p = \rho RT \quad e = e(T) \qquad C_v = de/dT \qquad C_p - C_v = R$$

$$h = h(T) \qquad C_p = dh/dT \qquad$$

$$h = e + p/\rho \qquad \gamma = C_p/C_v$$



$$C_{\rho} = \frac{\gamma R}{\gamma - 1}$$

R is constant γ , C_{ν} , and C_{ρ} are variable (functions of *T*)

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



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

$$\lim_{T\to\infty} e_{\text{vib}} = RT \Rightarrow C_{\text{v}} = \frac{7}{2}R$$

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

- \blacktriangleright Translational and rotational energy fully excited above ${\sim}5~{\rm K}$
- Vibrational energy is non-negligible above 600 K
- Chemical reactions begin to occur above ~2000 K

As temperature increase further vibrational energy becomes less important

Why is that so?

Example: properties of air (continued)



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

Equilibrium Gas

For temperatures $T > \sim 2500 K$

- 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

How do we obtain a thermodynamic description?

$$p = p(R,T) \qquad e = e(\nu,T) \qquad C_{\nu} = \left(\frac{\partial e}{\partial T}\right)_{\nu} \\ h = h(p,T) \qquad h = e + \frac{p}{\rho} \qquad C_{\rho} = \left(\frac{\partial h}{\partial T}\right)_{\rho} \\ a_{e}^{2} = \gamma RT \frac{1 + \frac{1}{p} \left(\frac{\partial e}{\partial \nu}\right)_{T}}{1 - \rho \left(\frac{\partial h}{\partial \rho}\right)_{T}} \qquad \gamma = \frac{C_{\rho}}{C_{\nu}} = \frac{\left(\frac{\partial h}{\partial T}\right)_{\rho}}{\left(\frac{\partial e}{\partial T}\right)_{\nu}} \qquad RT = \frac{p}{\rho} \\ Nter R \text{ is not a constant here} \\ l.e. \text{ this is not the ideal gas law}} \\ Nter Andersson - Chalmers \qquad Weights are descent as the second second$$

Roadmap - High Temperature Effects



Chapter 17.1 Thermodynamic and Chemical Equilibrium

Thermodynamic Equilibrium

Molecules are distributed among their possible energy states according to the Boltzmann distribution (which is a statistical equilibrium) for the given temperature of the gas

 extremely fast process (time and length scales of the molecular processes)

much faster than flow time scales in general (not true inside shocks)

Thermodynamic Equilibrium

Global thermodynamic equilibrium:

- ▶ there are no gradients of p, T, ρ , \mathbf{v} , species concentrations
- "true thermodynamic equilibrium"

Local thermodynamic equilibrium:

- gradients can be neglected locally
- his requirement is fulfilled in most cases (hard not to get)

Composition of gas (species concentrations) is fixed in time

- forward and backward rates of all chemical reactions are equal
- zero net reaction rates

chemical reactions may be either slow or fast in comparison to flow time scale depending on the case studied

Chemical Equilibrium

Global chemical equilibrium:

- there are no gradients of species concentrations
- ► together with global thermodynamic equilibrium ⇒ all gradients are zero

Local chemical equilibrium

- gradients of species concentrations can be neglected locally
- not always true depends on reaction rates and flow time scales

Thermodynamic and Chemical Equilibrium

Most common cases:

	Thermodynamic Equilibrium	Chemical Equilibrium	Gas Model
1	local thermodynamic equilibrium	local chemical equilibrium	equilibrium gas
2	local thermodynamic equilibrium	chemical non-equilibrium	finite rate chemistry
3	local thermodynamic equilibrium	frozen composition	frozen flow
4	thermodynamic non-equilibrium	frozen composition	vibrationally frozen flow

- length and time scales of flow decreases from 1 to 4
- Frozen composition \Rightarrow no (or slow) reactions
- vibrationally frozen flow gives the same gas relations as calorically perfect gas!

no chemical reactions and unchanged vibrational energyexample: small nozzles with high-speed flow

Roadmap - High Temperature Effects



Chapter 17.2 Equilibrium Normal Shock Wave Flows

Question: Is the equilibrium gas assumption OK?

Answer:

- ► for hypersonic flows with very little ionization in the shock region, it is a fair approximation
 - not perfect, since the assumption of local thermodynamic and chemical equilibrium is not really true around the shock
- however, it gives a significant improvement compared to the calorically perfect gas assumption

Basic relations (for all gases), stationary normal shock:

$$\begin{cases} \rho_1 u_1 = \rho_2 u_2 \\ \rho_1 u_1^2 + \rho_1 = \rho_2 u_2^2 + \rho_2 \\ h_1 \frac{1}{2} u_1^2 = h_2 + \frac{1}{2} u_2^2 \end{cases}$$

For equilibrium gas we have:

$$\begin{cases} \rho = \rho(\rho, h) \\ T = T(\rho, h) \end{cases}$$

(we are free to choose any two states as independent variables)

Niklas Andersson - Chalmers

Assume that ρ_1 , u_1 , p_1 , T_1 , and h_1 are known

$$U_{2} = \frac{\rho_{1}U_{1}}{\rho_{2}} \Rightarrow \rho_{1}U_{1}^{2} + \rho_{1} = \rho_{2}\left(\frac{\rho_{1}}{\rho_{2}}U_{1}\right)^{2} + \rho_{2} \Rightarrow$$
$$\rho_{2} = \rho_{1} + \rho_{1}U_{1}^{2}\left(1 - \frac{\rho_{1}}{\rho_{2}}\right)$$

Also

$$h_{1} + \frac{1}{2}u_{1}^{2} = h_{2} + \frac{1}{2}\left(\frac{\rho_{1}}{\rho_{2}}u_{1}\right)^{2} \Rightarrow$$
$$h_{2} = h_{1} + \frac{1}{2}u_{1}^{2}\left(1 - \left(\frac{\rho_{1}}{\rho_{2}}\right)^{2}\right)$$



when converged:

$$\left.\begin{array}{l} \rho_2 = \rho(\rho_2, h_2) \\ \\ T_2 = T(\rho_2, h_2) \end{array}\right\} \Rightarrow$$

 $\rho_2, u_2, p_2, T_2, h_2$ known

Equilibrium Air - Normal Shock

Tables of thermodynamic properties for different conditions are available

For a very strong shock case ($M_1 = 32$), the table below (Table 17.1) shows some typical results for equilibrium air

	calorically perfect gas $(\gamma = 1.4)$	equilibrium air
$p_2/p_1 \ ho_2/ ho_1 \ h_2/h_1 \ T_2/T_1$	1233 5.97 206.35 206.35	1387 15.19 212.80 41.64
573)	2	

Equilibrium Air - Normal Shock

Analysis:

- Pressure ratio is comparable
- Density ratio differs by factor of 2.5
- Temperature ratio differs by factor of 5

Explanation:

- Using equilibrium gas means that vibration, dissociation and chemical reactions are accounted for
- The chemical reactions taking place in the shock region lead to an "absorption" of energy into chemical energy
 - drastically reducing the temperature downstream of the shock
 - this also explains the difference in density after the shock

Equilibrium Air - Normal Shock

Additional notes:

- ▶ For a normal shock in an equilibrium gas, the pressure ratio, density ratio, enthalpy ratio, temperature ratio, etc all depend on three upstream variables, e.g. u₁, p₁, T₁
- ► For a normal shock in a thermally perfect gas, the pressure ratio, density ratio, enthalpy ratio, temperature ratio, etc all depend on two upstream variables, *e.g.* M₁, T₁
- For a normal shock in a calorically perfect gas, the pressure ratio, density ratio, enthalpy ratio, temperature ratio, etc all depend on one upstream variable, *e.g.* M_1

Equilibrium Gas - Detached Shock



What's the reason for the difference in predicted shock position?

Equilibrium Gas - Detached Shock

Calorically perfect gas:

▶ all energy ends up in translation and rotation ⇒ increased temperature

Equilibrium gas:

energy is absorbed by reactions \Rightarrow does not contribute to the increase of gas temperature

Roadmap - High Temperature Effects



Chapter 17.3 Equilibrium Quasi-One-Dimensional Nozzle Flows

First question: Is chemically reacting gas also isentropic (for inviscid and adiabatic case)?

entropy equation: $Tds = dh - \nu dp$

Quasi-1D equations in differential form (all gases):

momentum equation: $dp = -\rho u du$

energy equation: dh + udu = 0

Equilibrium Quasi-1D Nozzle Flows

$$udu = -\frac{dp}{\rho} = -\nu dp$$

$$Tds = -udu - \nu dp = -udu + udu = 0 \Rightarrow$$

ds = 0

Isentropic flow!

Equilibrium Quasi-1D Nozzle Flows

Second question: Does the area-velocity relation also hold for a chemically reacting gas?

Isentropic process gives

$$\frac{dA}{A} = (M^2 - 1)\frac{du}{u}$$

M = 1 at nozzle throat still holds
For general gas mixture in thermodynamic and chemical equilibrium, we may find tables or graphs describing relations between state variables.

Example: Mollier diagram





For steady-state inviscid adiabatic nozzle flow we have:

$$h_1 + \frac{1}{2}u_1^2 = h_2 + \frac{1}{2}u_2^2 = h_0$$

where h_o is the reservoir enthalpy

s

At point 1 in Mollier diagram we have:

$$\frac{1}{2}u_1^2 = h_0 - h_1 \Rightarrow u_1 = \sqrt{2(h_0 - h_1)}$$

Assume that $u_1 = a_1$ (sonic conditions) gives

$$\rho_1 u_1 A_1 = \rho^* a^* A^*$$

At any point along isentropic line, we have $u = \sqrt{2(h_o - h)}$ and ρ , ρ , T, a etc are all given which means that ρu is given

$$\frac{A}{A^*} = \frac{\rho^* a^*}{\rho u}$$

may be computed for any point along isentropic line

- ► Equilibrium gas gives higher *T* and more thrust
- During the expansion chemical energy is released due to shifts in the equilibrium composition



- ▶ Equilibrium gas gives higher *T* and more thrust
- During the expansion chemical energy is released due to shifts in the equilibrium composition



Chemical and vibrational energy transferred to translation and rotation \Rightarrow increased temperature

Niklas Andersson - Chalmers

Equilibrium Quasi-1D Nozzle Flows - Reacting Mixture

Real nozzle flow with reacting gas mixture:



Equilibrium Quasi-1D Nozzle Flows - Reacting Mixture

Real nozzle flow with reacting gas mixture:



- Space nozzle applications: $u_e \approx 4000$ m/s
- Required prediction accuracy 5 m/s

Equilibrium Quasi-1D Nozzle Flows - Reacting Mixture

Equilibrium gas:

- very fast chemical reactions
- Iocal thermodynamic and chemical equilibrium

Vibrationally frozen gas:

- very slow chemical reactions
 - (no chemical reactions \Rightarrow frozen gas)
- vibrational energy of molecules have no time to change calorically perfect gas!

Large Nozzles

High T_o , high p_o , high reactivity

Real case is close to equilibrium gas results

Example: Ariane 5 launcher, main engine (Vulcain 2)

- ► $H_2 + O_2 \rightarrow H_2O$ in principle, but many different radicals and reactions involved (at least ~10 species, ~20 reactions)
- ▶ $T_o \sim 3600 \text{ K}, p_o \sim 120 \text{ bar}$
- Length scale \sim a few meters
- Gas mixture is quite close to equilibrium conditions all the way through the expansion

Ariane 5

Ariane 5 space launcher

extreme high temperature and high speed flow regime





Vulcain Engine

Vulcain engine:

first stage of the Ariane 5 launcher





Space Shuttle Launcher - SSME







Space Shuttle Launcher - SSME



Small Nozzles

Low T_o , low p_o , lower reactivity

Real case is close to frozen flow results

Example:

Small rockets on satellites (for maneuvering, orbital adjustments, etc)





Small Nozzles







Roadmap - High Temperature Effects

