Compressible Flow - TME085 Lecture 15

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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



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 **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

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

 $\varepsilon_{\scriptscriptstyle O_{\rm trans}}' > 0$ (very small but finite)

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

$$\begin{aligned} \varepsilon_{j_{trans}} &= \varepsilon'_{j_{trans}} - \varepsilon'_{O_{trans}} \\ \varepsilon_{l_{vib}} &= \varepsilon'_{l_{vib}} - \varepsilon'_{O_{vib}} \\ \varepsilon_{k_{rot}} &= \varepsilon'_{k_{rot}} \\ \end{aligned}$$

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 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) \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







Macrostate II Microstate I

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

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

$$E=\sum_{j}\varepsilon_{j}^{\prime}N_{j}$$

E is the total energy and ε'_i 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:

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

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

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

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

Boltzmann Distribution

The Boltzmann distribution:

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

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_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 ~ 5K, 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

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

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
m	mass of the individual molecule

$$\Rightarrow \cdots \Rightarrow$$

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

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Internal Energy - Translation



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

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

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

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

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Internal Energy - Rotation







- *I* moment of inertia (tabulated for common molecules)
- h Planck's constant

 $\Rightarrow \cdots \Rightarrow$

$$Q_{rot} = \frac{8\pi^2 l k7}{h^2}$$



Internal Energy - Rotation



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

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



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

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

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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

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

 $\Rightarrow \dots \Rightarrow$

Internal Energy - Vibration

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

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

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

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

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

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Specific Heat



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

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

$$C_{\rm V} \equiv \left(\frac{\partial e}{\partial T}\right)_{\rm V}$$

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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

$$e = \frac{3}{2}RT + RT = \frac{5}{2}RT \Rightarrow C_{v} \equiv \left(\frac{\partial e}{\partial T}\right)_{v} = \frac{5}{2}R$$
$$C_{\rho} = C_{v} + R = \frac{7}{2}R$$
$$\gamma = \frac{C_{\rho}}{C_{v}} = \frac{7}{5} = 1.4$$

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

$$\Theta = \frac{3}{2}RT + \mathbf{0} \Rightarrow C_{\nu} \equiv \left(\frac{\partial e}{\partial T}\right)_{\nu} = \frac{3}{2}F$$
$$C_{\rho} = C_{\nu} + R = \frac{5}{2}R$$
$$\gamma = \frac{C_{\rho}}{C_{\nu}} = \frac{5}{3} = 1\frac{2}{3} \simeq 1.67$$

Roadmap - High-Temperature 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 ($\gamma = 5/3$)

 $H_2, O_2, N_2, ... - di-atomic gases (\gamma = 7/5)$

 H_2O (gaseous), CO_2 , ... - tri-atomic gases ($\gamma < 7/5$)

Calorically Perfect Gas - Thermodynamic Relations



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

 $p = p(R,T) \qquad e = e(T) \qquad C_{v} = de/dT \qquad C_{p} - C_{v} = R$ $h = h(T) \qquad C_{p} = dh/dT \qquad \gamma = C_{p}/C_{v}$ $h = e + p/\rho \qquad C_{v} = \frac{R}{\gamma - 1}$

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

 γ , $C_{\rm V}$, and $C_{\rm p}$ are variable (functions of T) R is constant $C_{p} = \frac{\gamma R}{\gamma - 1}$

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)

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

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

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 > 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 tabulated data

Equilibrium Gas - Thermodynamic Relations

How do we obtain a thermodynamic description?

 a_{e}^{2}

$$p = p(R, T) \qquad e = e(\nu, T) \qquad C_{\nu} = \left(\frac{\partial e}{\partial T}\right)_{\nu}$$

$$h = h(p, T) \qquad h = e + \frac{p}{\rho} \qquad C_{p} = \left(\frac{\partial h}{\partial T}\right)_{p}$$

$$P = \gamma RT \frac{1 + \frac{1}{\rho} \left(\frac{\partial e}{\partial \nu}\right)_{T}}{1 - \rho \left(\frac{\partial h}{\partial \rho}\right)_{T}} \qquad \gamma = \frac{C_{p}}{C_{\nu}} = \frac{\left(\frac{\partial h}{\partial T}\right)_{p}}{\left(\frac{\partial e}{\partial T}\right)_{\nu}} \qquad RT = \frac{p}{\rho}$$

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