

# Lecture 8

## Scaling dimensions and other issues

## **Scaling dimensions and issues**

Consequences of size reduction for different processes -  
relevance of material properties and behavior, processes, and  
miniaturized devices

1 Material properties

2. Processes

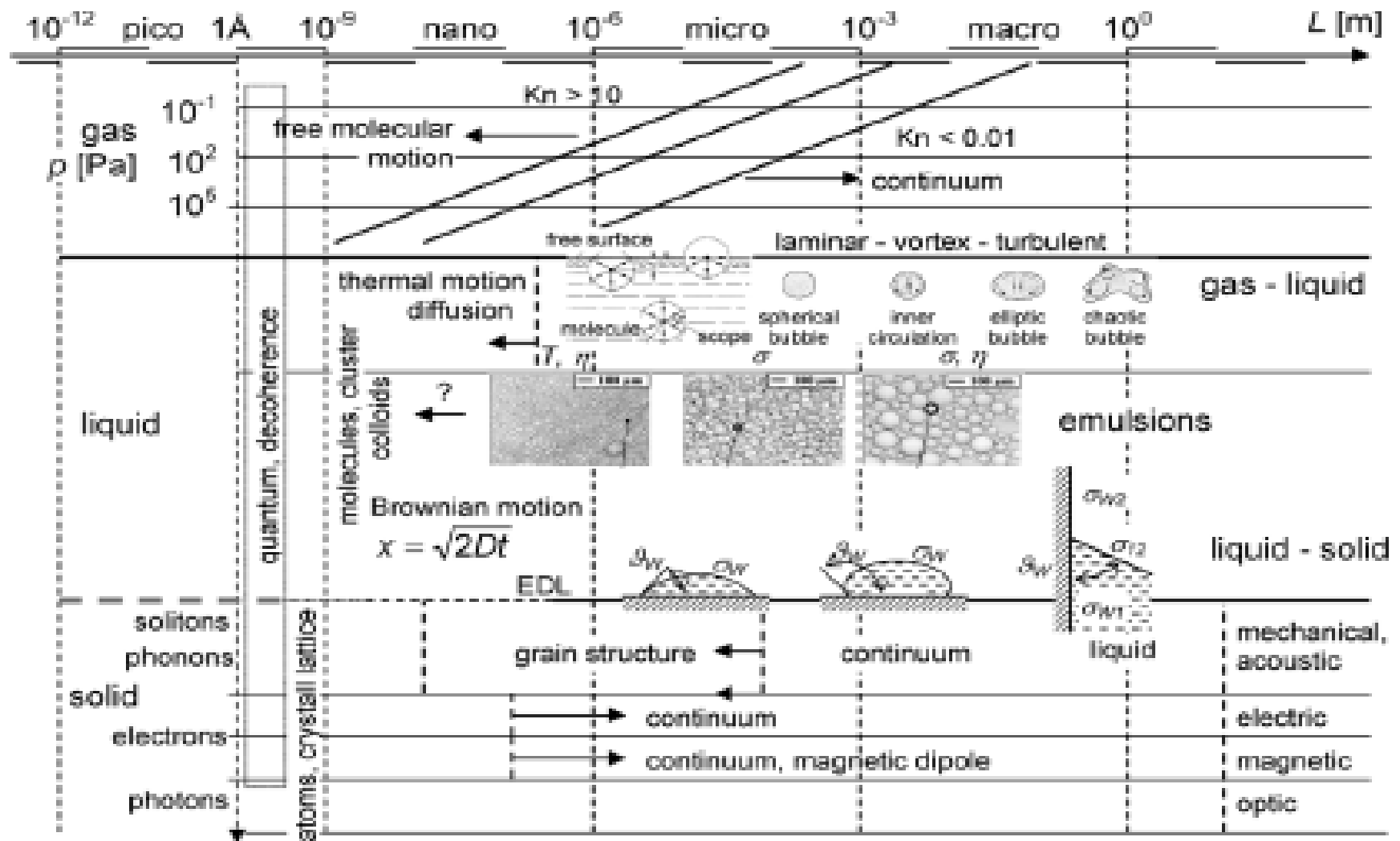
3. Devices

## 1. Material properties

With decreasing length, not only the **material properties change**, e.g., behavior of rarefied gases in pipes and channels, **the operation and efficiency of unit operations are affected** in various ways

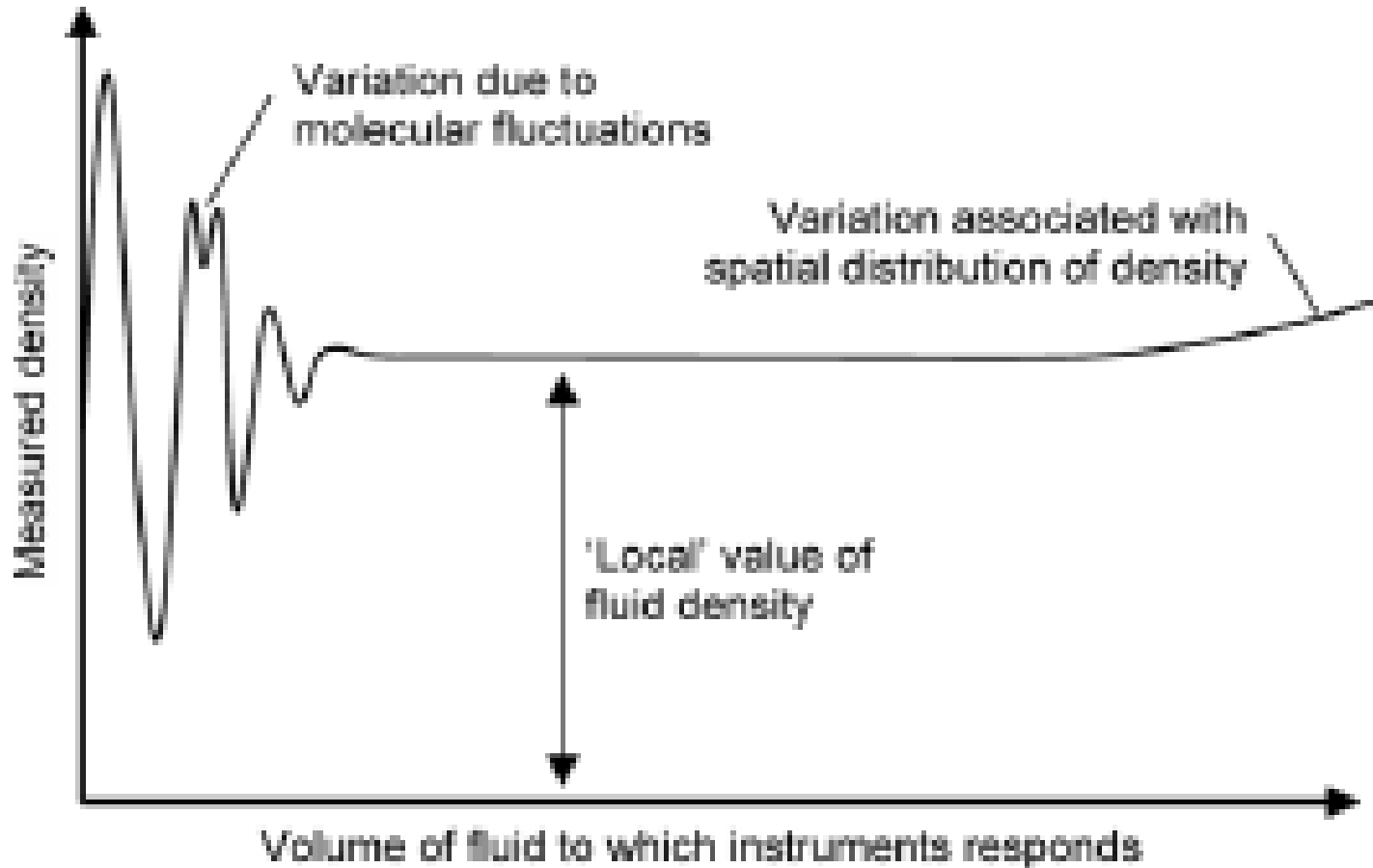
The miniaturization of chemical equipment mostly emphasizes the length reduction of the main dimensions.

Information also needed for the intensive state variables, e.g. whether constant process conditions like pressure, temperature, or concentration remain unchanged when reducing the size of the system.



Typical length scales of material properties and behavior in gas, liquid, and solid phase as well as interfacial phenomena. For comparison, the electron sheath of atoms has a diameter of approx.  $10^{-10}$  m, the nucleus of an atom is approx.  $10^{-15}$  m, electrons are approx.  $10^{-18}$  m in diameter.

# What is continuum?



Effect of size of sensitive volume on the density measured by an instrument. Other macroscopic variables like velocity or temperature show a similar reaction with the observed behavior

## Continuum Hypothesis

- Neglect the fact that real substances are composed of discrete molecules
- Model matter from the start as a smoothed-out **continuum**
- Information about a continuum represents the microscopic information averaged over a volume.
- **Classical thermodynamics** is concerned only with continuum

## Thermodynamic Equilibrium

A system in thermodynamic equilibrium satisfies:

- mechanical equilibrium (no unbalanced forces)
- thermal equilibrium (no temperature differences)
- chemical equilibrium

## Continuum hypothesis

Decreasing the volume may influence the properties of the fluids and the measurement of process parameters like density, velocity, or temperature.

Physical quantities and fluid properties are usually treated as being spread uniformly over a control volume.

Very large control volumes, as in atmospheric systems, show local non-uniformities like depression systems in weather formation.

Variations and fluctuations also occur in small systems, where the behavior of single molecules become important.

With decreasing volume, molecular fluctuations disturb the smooth measurement. If only a few molecules are measured, the single molecule behavior becomes important and varies in an irregular way.

*The fluid can be regarded as a continuum, where the measured fluid property is constant for sensitive volumes, which are small on a macroscopic scale but large on a microscopic scale.*



A  $10\text{ }\mu\text{m}$  cube contains approx.  $3 \times 10^{10}$  molecules of air at normal temperature and pressure, which is large enough to take an average over the molecules.

A microstructured device with dimensions and process conditions in that range can be treated with continuum methods.

However, in some applications the **limits of the continuum hypothesis are reached** and a description of rarefied gases beyond the continuum hypothesis is needed.

## Continuum Assumption

The continuum assumption in fluid mechanics is only valid for sufficient molecules within a given volume to achieve a stable estimate of the macroscopic flow properties.

The ratio of the characteristic length scale  $L$  to the mean molecular spacing  $\delta$  should satisfy to achieve a **statistically stable estimate of the macroscopic properties**.

$$\frac{L}{\delta} > 100$$

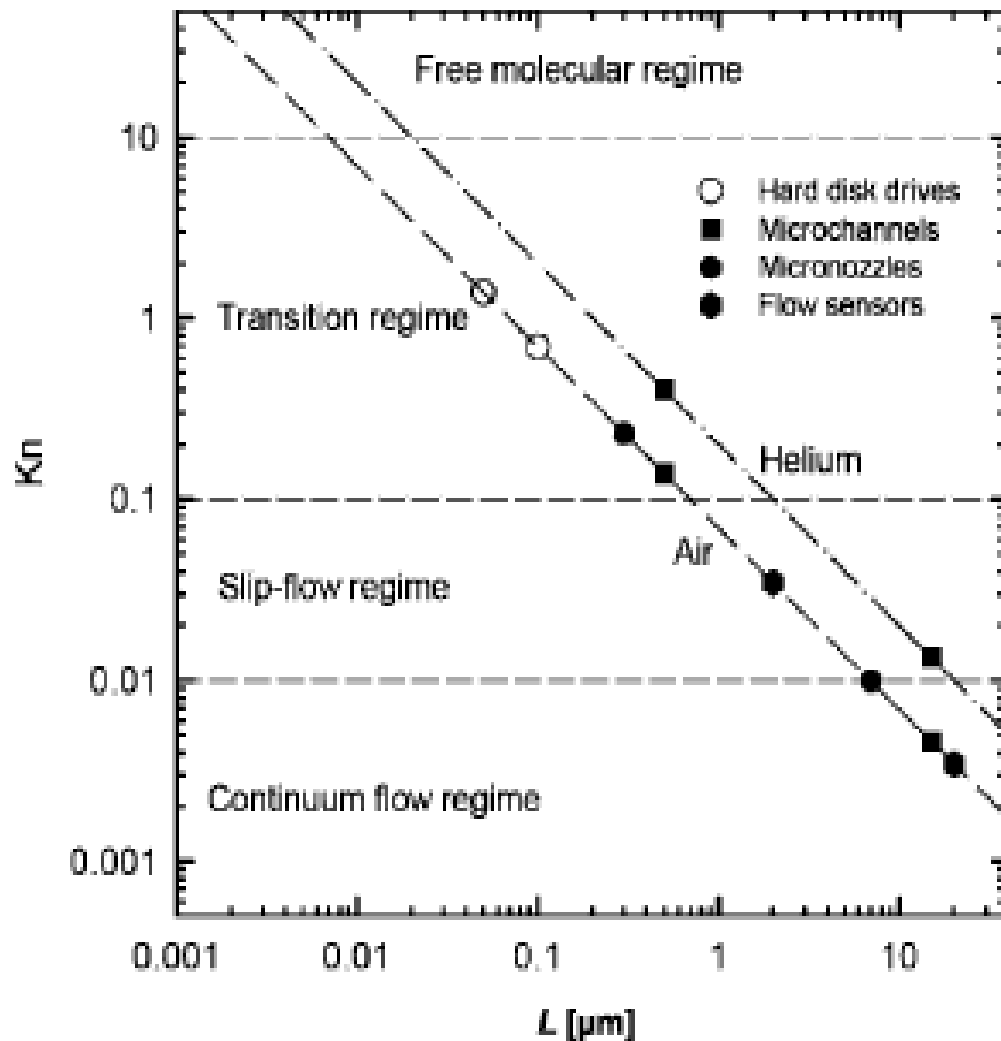
In other words, there should be at least 100 molecular spaces along each face of the sample volume, giving a total of **1 million molecules within the control volume**.

The mean free path  $\lambda$  divided by the characteristic length  $L$  of the system gives the **dimensionless Knudsen number  $Kn$**

$$Kn = \frac{\lambda}{L}$$

*The flow regimes of gases concerning rarefaction effects can be classified according to the range of the  $Kn$  number.*

Generally, rarefied gas behavior is classified into four different regimes according to the range of the  $Kn$  number



Characteristic length scales of typical microfluidic components and the corresponding Knudsen number at standard atmospheric conditions

$$\underline{\mathbf{Kn} < 10^{-2}}$$

The continuum and thermodynamic equilibrium assumptions are appropriate and flow situations can be described by conventional no-slip boundary conditions.

$$10^{-2} < \mathbf{Kn} < 10^{-1}$$

**Slip Flow Regime**

Navier-Stokes equations remain valid provided tangential slip-velocity and temperature-jump boundary conditions are implemented at the walls of the flow domain

$$10^{-1} < \text{Kn} < 10$$

## Transition flow regime

Continuum and thermodynamic equilibrium assumptions of the Navier-Stokes equations begin to break down and alternative analysis methods e.g., particle-based DSMC (direct simulation Monte Carlo) approaches, or molecular dynamics (MD) simulations must be employed.

Stress-strain relationship for the fluid becomes non-linear within a distance of approximately one mean free path from the wall (the so-called Knudsen layer)

# **$Kn > 10$**

## **Free molecular flow**

The mean-free path of the molecules is far greater than the characteristic length scale and, consequently, molecules are reflected from a solid surface and travel, on average, many length scales, before colliding with other molecules.

**The above limits are empirical**

**Most microfluidic devices operate in the slip-flow regime or early transition flow regime.**

The characteristic length scale of the device or flow problems are difficult to define. Often the gradient of a macroscopic quantity is used for the definition, for example, of the density:

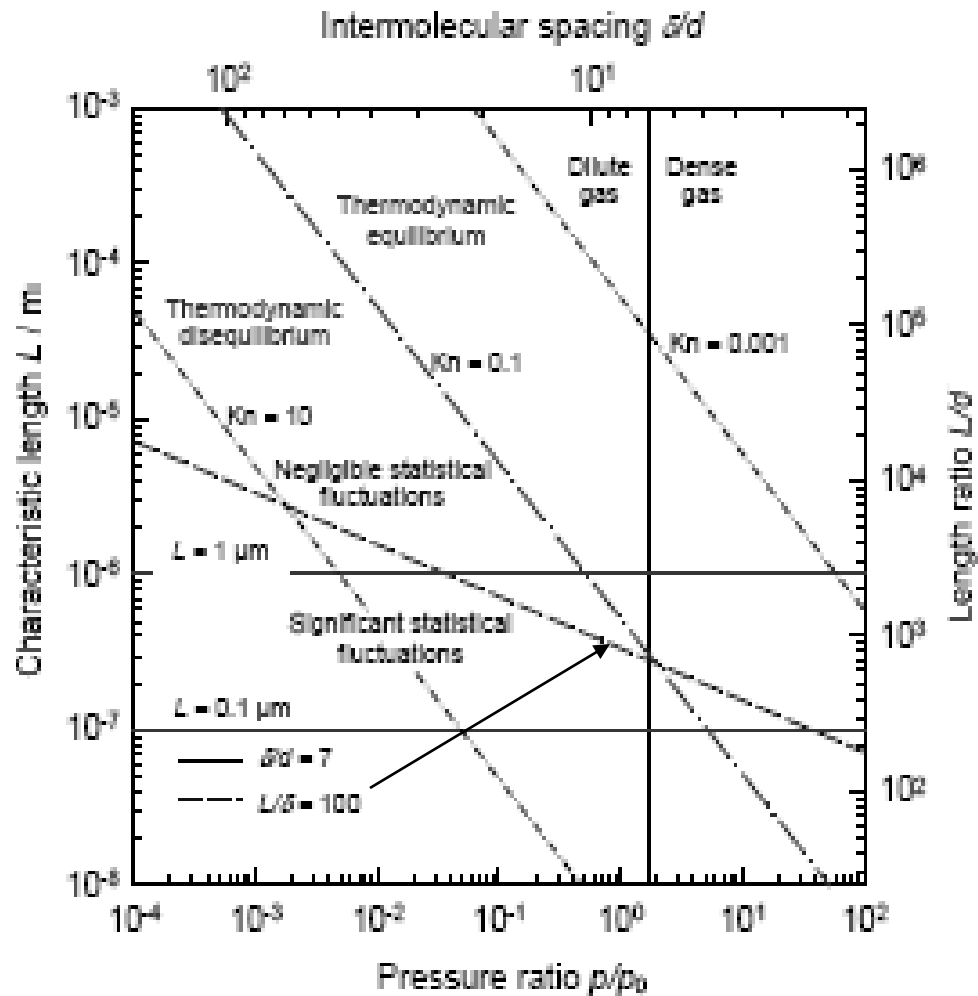
$$L = \frac{\rho}{|\nabla \rho|}$$

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Alternative method to display the transition between continuum behavior and molecular behavior. The conditions of a hard sphere gas are illustrated with a molecular diameter  $d = 4 \times 10^{-10}$  m, which is approximately the molecular diameter of air.



$d$  = mol. dia.  
 $\delta$  = average  
 distance  
 between the  
 molecules  
 $\lambda$  = mean free  
 path



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Limiting criteria for the application of the Navier-Stokes Eqns  
 to air with  $d = 4 \times 10^{-10} m$ , collision cross section  $\sigma = \pi d^2$

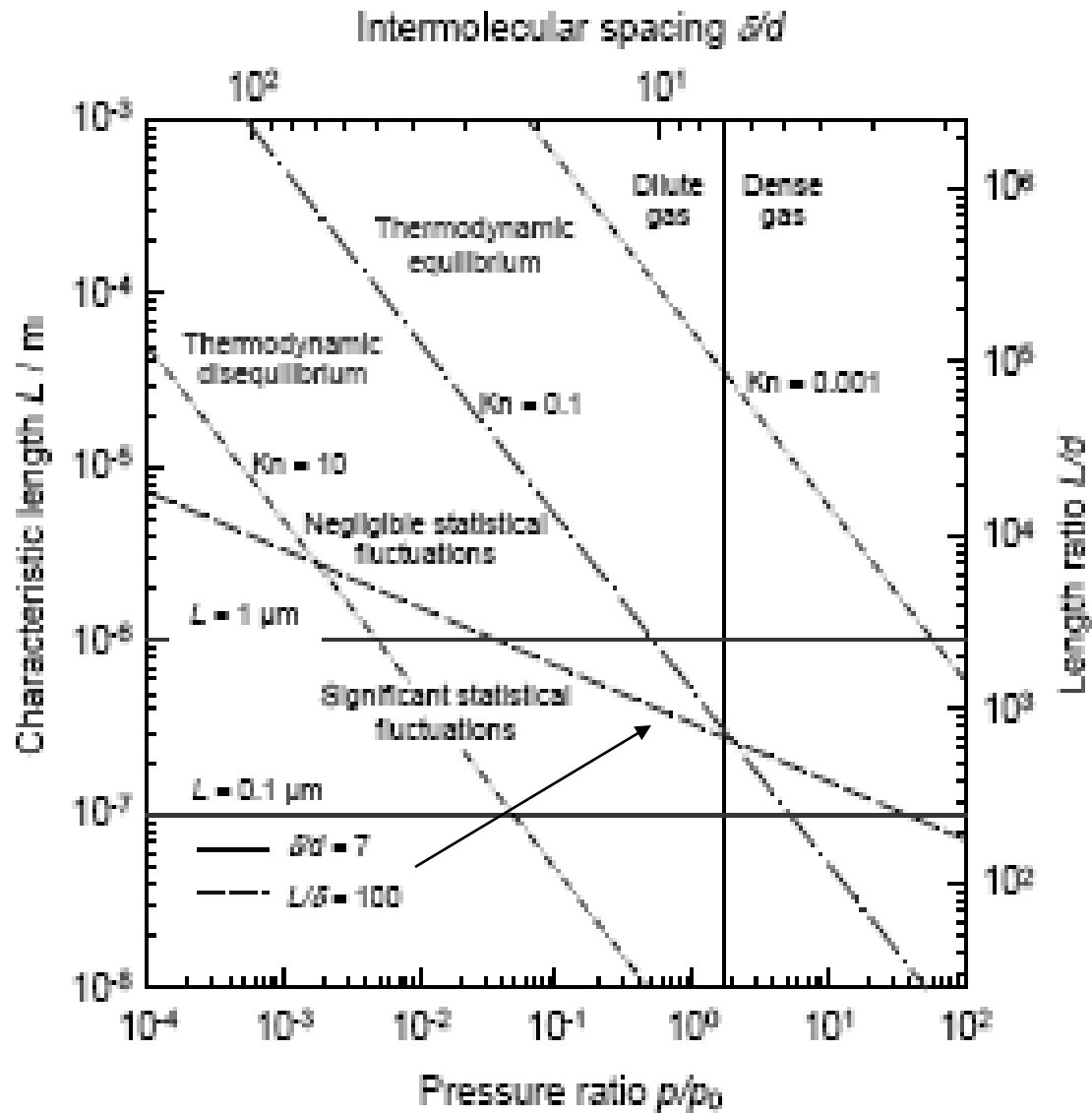
$\delta / d = 7, L / \delta = 100, Kn = \lambda / L = 10^{-1}$

The left-hand ordinate represents the characteristic length scale  $L$ , while the right-hand ordinate shows the length scale normalized with the molecular diameter,  $L/d$ .

The bottom abscissa represents the density normalized with a reference pressure  $p/p_0$ , which is equivalent to the normalized number density  $n/n_0$  or density ratio  $p/p_0$ .

The top axis represents the average distance between the molecules normalized with the molecular diameter  $\delta/d$ .

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 $\delta$  = average  
 distance  
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$$\delta / d = 7, L / \delta = 100, Kn = \lambda / L = 10^{-1}$$

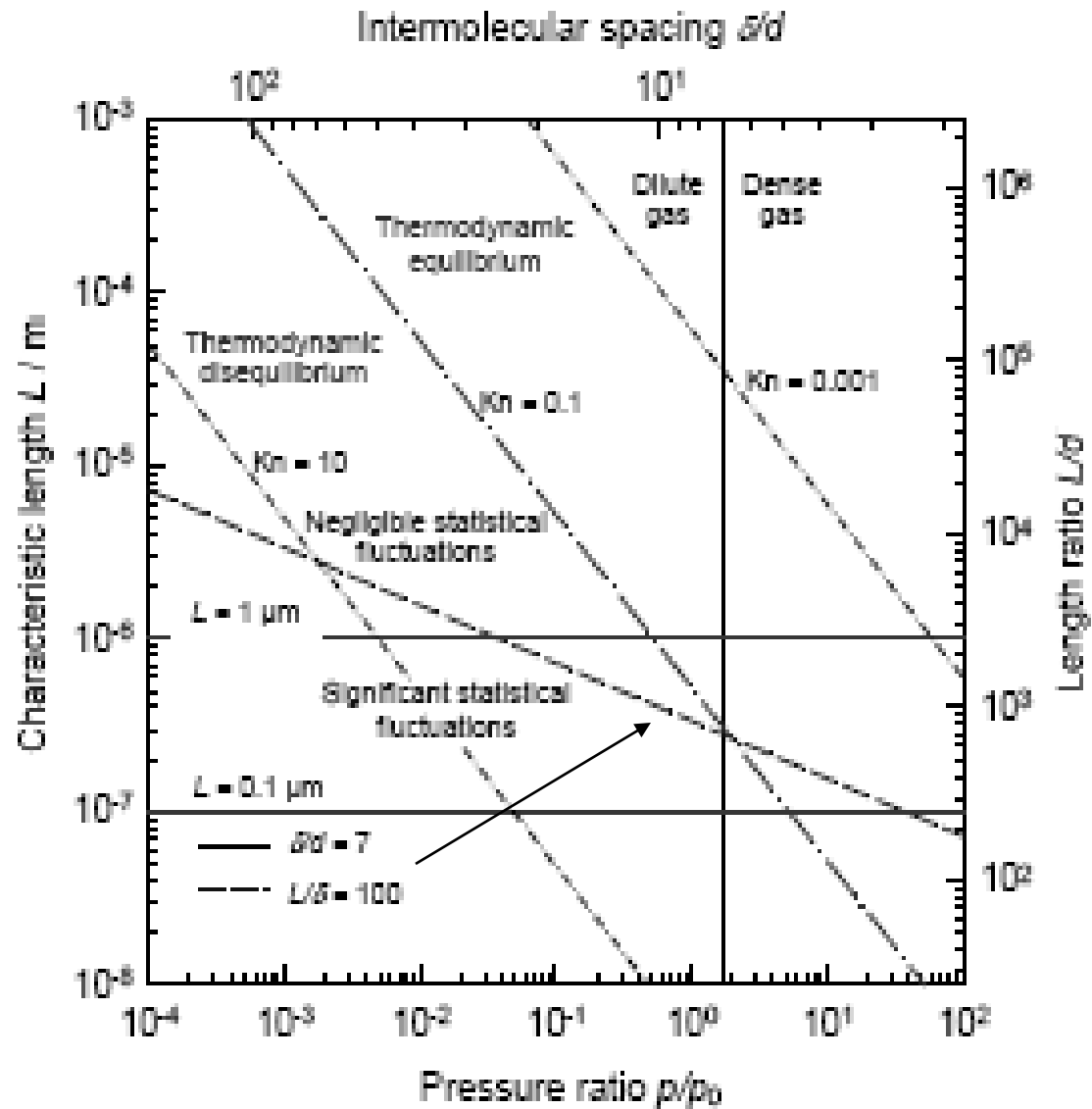
The figure shows the applicability limits of the Navier-Stokes equations given by  $\delta / d = 7$ ,  $L / \delta = 100$ , and  $\text{Kn} = \lambda / L = 10^{-1}$ .

Air at standard ambient conditions has a pressure of 101.315 kPa, a number density of  $2.68666 \times 10^{25} \text{ m}^{-3}$ , a density ratio of unity (by definition) and  $\delta / d = 8.5$ .

With these values, air can be assumed to be a dilute gas, but is close to the upper limit of the dilute gas assumption.

The  $L / \delta = 100$  line represents the limit of statistical fluctuations. The continuum approximation is only valid if there are sufficient molecules within a given volume to achieve a statistically stable estimate of the macroscopic flow properties.

$d$  = mol. dia.  
 $\delta$  = average  
 distance  
 between the  
 molecules



$$\delta / d = 7, L / \delta = 100, Kn = \lambda / L = 10^{-1}$$

Thermodynamic equilibrium       $\text{Kn} = \lambda/L = 10^{-1}$

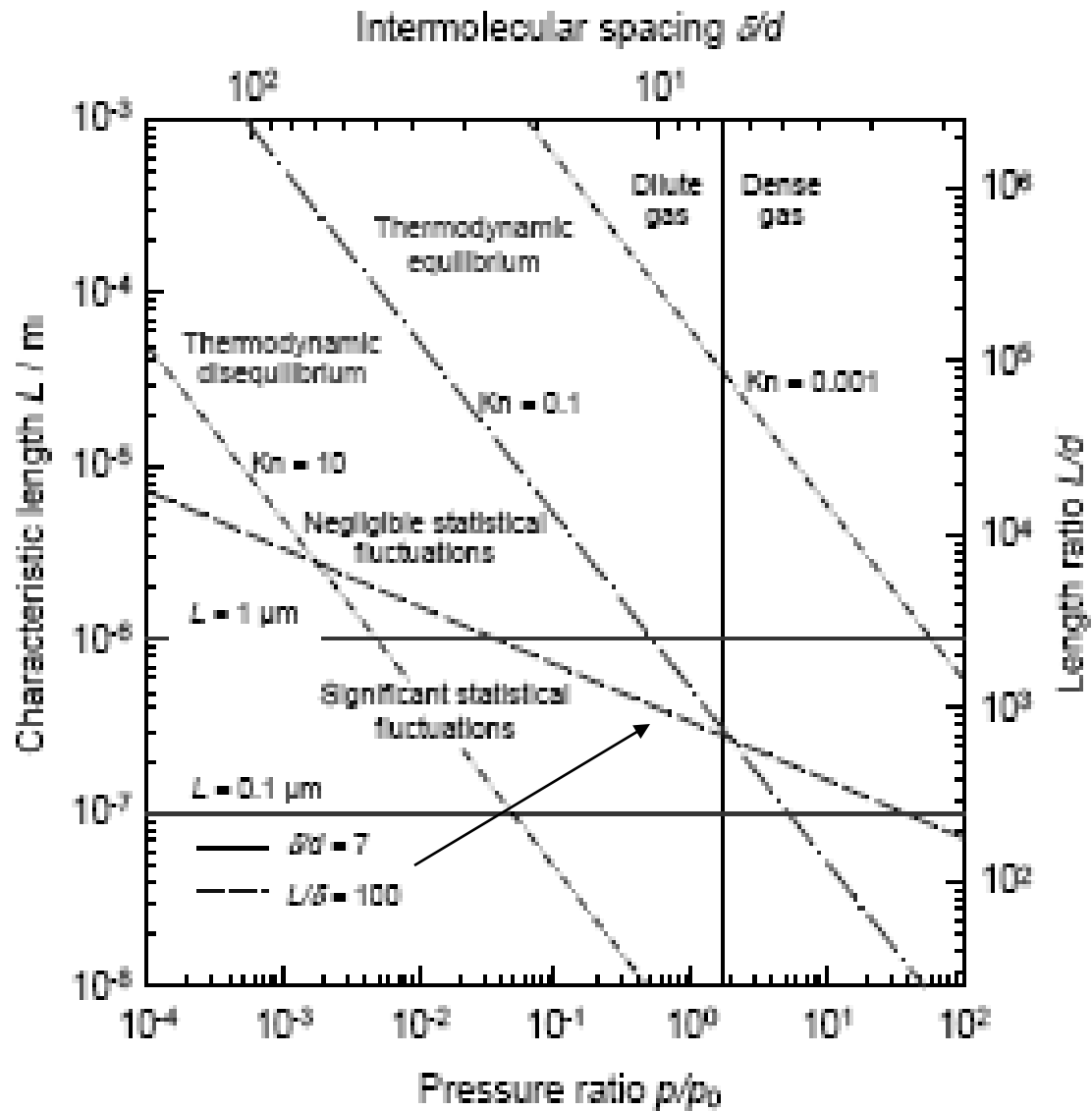
Continuum Approximation       $L/\delta = 100$

Dilute gas       $\frac{\delta}{\sigma} > 7$

The line with  $\text{Kn} = \lambda/L = 10^{-1}$  gives the validity limit of the thermodynamic equilibrium assumption.

According to Figure, the thermodynamic equilibrium assumption first fails if the flow dimensions are reduced in size, followed by a failure in the continuum assumption for a dilute gas.

$d$  = mol. dia.  
 $\delta$  = average  
 distance  
 between the  
 molecules  
 $\lambda$  = mean free  
 path



$$\delta / d = 7, L / \delta = 100, Kn = \lambda / L = 10^{-1}$$



For a dense gas, the continuum assumption first fails, followed by a failure in the thermodynamic equilibrium assumption.

Hence, special care should be taken for the limiting conditions of the Navier-Stokes equations.

The usual flow classification system based solely on the magnitude of the local Knudsen number, is only one parameter to completely describe the system.

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## Statistical mechanics and mean free path

In a perfect gas, the molecules are regarded as hard spheres interacting only in very short encounters with other molecules or with the boundary (wall, surface, or other limiting elements).

At the molecular scale, the ratio of the mean molecular spacing  $\delta$  and the mean molecular diameter  $\sigma$  is an important parameter.

Gases with the condition  $\frac{\delta}{\sigma} > 7$

are referred to as **dilute gases**. If the condition is not satisfied the gas is considered a **dense gas**.

Air at standard conditions is regarded as a dilute gas, but pressurized air with 0.6 MPa is considered as a dense gas.

It can be assumed that the **probability of a molecule moving in a certain direction is equal for all three space coordinates.**

This can be expressed by the constant ratio of the derivative of the **probability distribution function (PDF)  $f(w)$**  to the function itself and the velocity component  $w$ .

$$\frac{f'(w)}{w f(w)} = \frac{d \ln f(w)}{w dw} = -2\gamma$$

$$\ln f(w) = c_i - \gamma w^2$$

For convenience, the integration constant is set to  $-2\gamma$  and determined with the kinetic energy of the molecules

$$\gamma = \frac{M_m}{2kT} = \frac{M}{2RT}$$

with the mass of a single molecule  $M_m = Mk/R$ , the Boltzmann constant  $k = 1.38 \times 10^{-23}$  J/K, and the universal gas constant  $R = 8.314$  J/kmol K.

The integration constant  $c_i$  is determined by normalizing the sum of the probability to unity.

The integration gives the probability distribution for one velocity component  $w$ , which stands for the other components  $u$  and  $v$  as well.

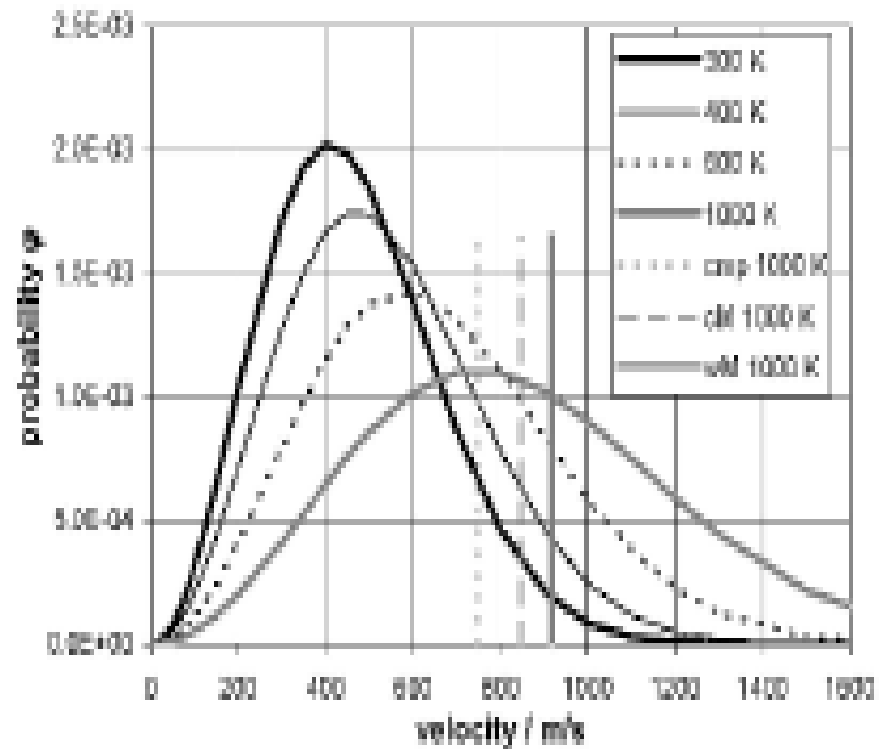
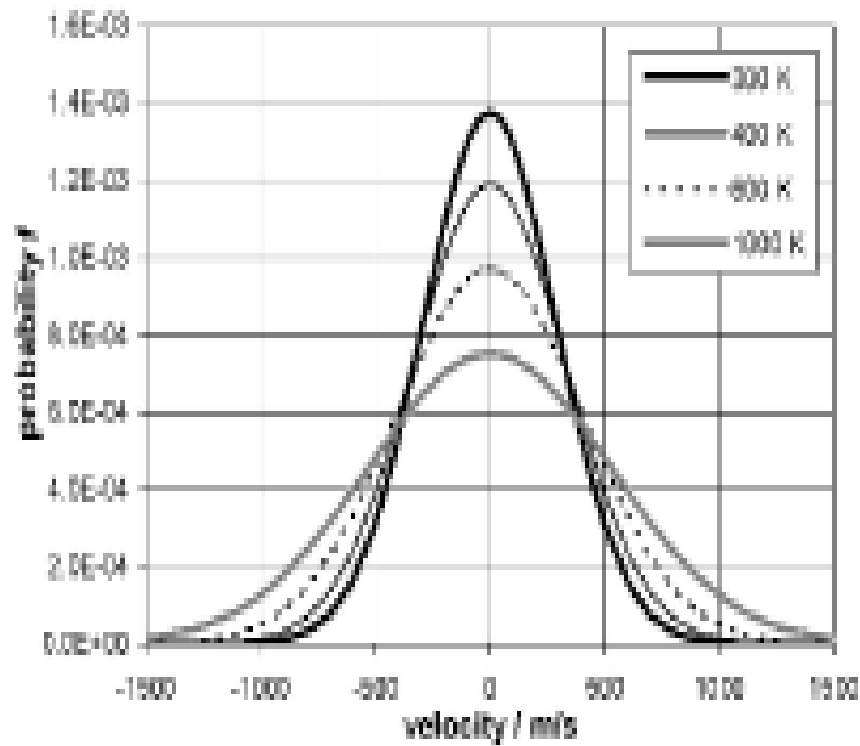
$$f(w) = \left( \frac{M}{2\pi R T} \right)^{1/2} \exp \left( -\frac{M}{2R T} w^2 \right)$$

This is the Maxwell velocity distribution of a perfect gas in thermodynamic equilibrium.

The integration over a sphere in all three space coordinates gives the probability of the absolute velocity value  $c$ , independent from the direction

$$\varphi(c) dc = 4\pi c^2 F(c) dc$$

$$\Rightarrow \varphi(c) = 4\pi c^2 \left( \frac{M}{2\pi R T} \right)^{3/2} \exp \left( -\frac{c^2 M}{2R T} \right)$$



Both probability distributions are displayed for air ( $R_m = 287\text{J/kg K}$ ) with four different temperatures. For higher temperatures, the gas molecules move faster, and the distribution becomes wider.

The most probable velocity of a molecule is determined to be

$$\bar{c}_{mp} = \sqrt{\frac{2RT}{M}}$$

where the probability density distribution has its maximum  $[d\phi(c)/dc = 0]$ .  $\phi(c)$  is zero at  $c = 0$  and at  $c = 1$ . Thus a maximum is present in between. Value of  $c$  at this maximum is the most probable velocity.

The mean velocity (  $= \int_0^{\infty} w f(w) dw$  )

from the distribution is

$$\bar{c}_M = \sqrt{\frac{8RT}{\pi M}}$$

The mean velocity from the kinetic energy of a molecule is given by

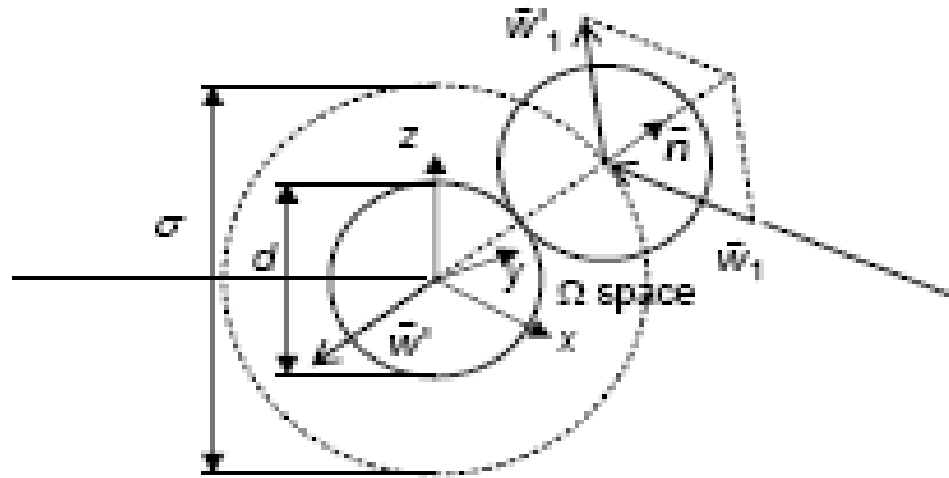
$$\bar{w}_M = \sqrt{\frac{3RT}{M}}$$



The model provides

- frequency at which the molecules collide
- distance traveled between collisions
- transport properties of gases

## Geometrical situation of a binary encounter



The molecules are treated as hard spheres with a diameter of  $d$  and a collision cross section  $\sigma = \pi d^2$ .

With the number of molecules in a unit volume  $N_A$ , the number of encounters between the molecules and the mean time between these encounters can be determined.

Multiplied with the mean velocity, an estimation of **the mean free path of a molecule**, the average length between two collisions, can be derived:

$$\lambda = \frac{kT}{\sqrt{2} p \sigma}$$

The mean free path can also be expressed by

$$\lambda = \frac{1}{\sqrt{2} n \sigma}$$

the number of particles  $n$  in a control volume, which is also given by  $n = N/V = \delta^{-3}$

With the mean velocity of the particles between two collision  $c_m$ , the characteristic time between two collisions is calculated by

$$t_c = \frac{\lambda}{c_M} = \frac{k}{4 p \sigma} \sqrt{\frac{\pi T}{R}}$$

The collision time is proportional to the square root of the temperature and inverse proportional to the pressure.

## Flame distance and explosion limits

The typical dimension of microstructured equipment is just below the extinction length or “quench distance” of many fast reactions and oxidations, which is approx. 1 mm. The measurement of the extinction length or distance is standardized. It is combined with the maximum experimental safety gap MESG, where a flame is stopped to proceed further on.

Concept important in reactions with strong exo, or endothermic behavior and high-energy transfer, like explosive reactions, fuel cell applications etc.

These applications benefit from the high transfer rates in microchannels with precise temperature control.