2. Kinetic Theory of Gases

Coverage of this section:

▶ Conventional Fluid Dynamic Descriptions

▶ Flow Regimes for a Monatomic Gas

▶ Statistical-Based Microscopic Description

▶ Density Functions

▶ Macroscopic Averages and Moments

▶ Maxwell-Boltzmann Distribution

▶ Boltzmann Equation

▶ Boltzmann Collision Integral

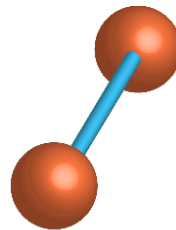▶ Maxwell's Equation of Change

▶ Boltzmann's H-Theorem

2. Kinetic Theory of Gases

monatomic   diatomic

Focus:

▶ **Single species monatomic gas**

▶ No internal modes or degrees of freedom (i.e., translational energy modes only)

▶ Monatomic gases: inert or noble gases, e.g., helium (He), neon (Ne), and argon (Ar)

▶ Diatomic and polyatomic molecules with additional internal energy modes associated with rotational and vibrational energy will be briefly discussed

2.1 Conventional Fluid Dynamic Descriptions

Before discussing the formalisms associated with kinetic theory, it is useful to first review conventional continuum-based, macroscopic, fluid dynamic mathematical models of gaseous behaviour. This continuum approximation is a mathematical idealization for modeling the response, or state, of a collection of gaseous particles or molecules. Although fluid dynamic descriptions can be derived directly from kinetic theory using the Chapman-Enskog technique (as will be shown), they can also be derived using the Reynolds transport theorem, also known as the Leibniz-Reynolds transport theorem, and control-volume analysis (as was originally done).

2.1 Conventional Fluid Dynamic Descriptions

2.1.1 Navier-Stokes Equations for a Compressible Gas

The basis for conventional fluid-dynamic descriptions of a gas is the so-called Navier-Stokes equations. This is a non-linear set of partial-differential equations (PDEs) governing the conservation of mass, momentum, and energy of the gaseous motion. They consist of two scalar equations and one vector equation for five unknowns (dependent variables) in terms of four independent variables, the three-component position vector, $\vec{x}$ or x_i, and the scalar time, t.

2.1 Conventional Fluid Dynamic Descriptions

2.1.2 Continuity Equation

The continuity equation represents the principle of conservation of mass for the gas and has the form

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{u}) = 0 \,,$$

where ρ and $\vec{u}$ are the gas density and flow velocity, respectively.

2.1.3 Momentum Equation

The momentum equation represents the application of Newton's 2nd Law of Motion for the gas and has the form

$$\frac{\partial}{\partial t}(\rho \vec{u}) + \vec{\nabla} \cdot \left(\rho \vec{u}\vec{u} + p\vec{\vec{I}} - \vec{\vec{\tau}} \right) = \rho \vec{f} \,,$$

where p and $\vec{\vec{\tau}}$ are the gas pressure and fluid stress dyad or tensor, respectively, and $\vec{f}$ represents the action of external body forces.

2.1 Conventional Fluid Dynamic Descriptions

2.1.4 Energy Equation

The energy equation represents the application of the 1st Law of Thermodynamics to the gaseous motion. It describes the time rate of change of the total energy of the gas (the sum of kinetic energy of bulk motion and internal kinetic or thermal energy) and has the form

$$\frac{\partial}{\partial t}(\rho E) + \vec{\nabla} \cdot \left[\rho \vec{u} \left(E + \frac{p}{\rho} \right) - \vec{\vec{\tau}} \cdot \vec{u} + \vec{q} \right] = \rho \vec{f} \cdot \vec{u} \,,$$

where E is the total specific energy of the gas given by $E = e + \vec{u} \cdot \vec{u}/2$ and $\vec{q}$ is the heat flux vector representing the flux of heat out of the gas.

2.1 Conventional Fluid Dynamic Descriptions

Summarizing, we have

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{u}) = 0 \,,$$

$$\frac{\partial}{\partial t}(\rho \vec{u}) + \vec{\nabla} \cdot \left(\rho \vec{u}\vec{u} + p\vec{\vec{I}} - \vec{\vec{\tau}} \right) = \rho \vec{f} \,,$$

$$\frac{\partial}{\partial t}(\rho E) + \vec{\nabla} \cdot \left[\rho \vec{u} \left(E + \frac{p}{\rho} \right) - \vec{\vec{\tau}} \cdot \vec{u} + \vec{q} \right] = \rho \vec{f} \cdot \vec{u} \,.$$

The Navier-Stokes equations as given above are incomplete (not closed). Additional information is required to relate various thermodynamic variables and specify the fluid stress tensor, τ_{ij}, and heat flux vector, q_i. The following must be specified:

- thermodynamic relationships;
- constitutive relations; and
- expressions for transport coefficients.

7

2.1 Conventional Fluid Dynamic Descriptions

2.1.5 Thermodynamic Relationships

It is often assumed that the gas satisfies the ideal gas equation of state, which relates ρ, p, and T, and is given by

$$p = \rho R T \,,$$

and behaves as a calorically perfect gas with

$$e = c_v T = \frac{p}{(\gamma - 1)\rho} \quad \text{and} \quad h = e + \frac{p}{\rho} = c_p T = \frac{\gamma p}{(\gamma - 1)\rho} \,,$$

where R is the gas constant, c_v and c_p are, respectively, the specific heats at constant volume and pressure (both are constants), and

$$\gamma = \frac{c_p}{c_v} = \frac{5}{3} \,,$$

for a monatomic gas.

8

2.1 Conventional Fluid Dynamic Descriptions

2.1.6 Constitutive Relationships

The Navier-Stokes relation, relates the fluid stress tensor to strain rate and is given by

$$\tau_{ij} = \mu \left[\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) - \frac{2}{3} \delta_{ij} \frac{\partial u_k}{\partial x_k} \right] \qquad (\tau_{ii} = 0, \text{ traceless}) ,$$

where μ is the dynamic viscosity. Fourier's Law relates the heat flux to the temperature gradient as follows:

$$q_i = -\kappa \frac{\partial T}{\partial x_i} \quad \text{or} \quad \vec{q} = -\kappa \vec{\nabla} T ,$$

where κ is the coefficient of thermal conductivity.

2.1 Conventional Fluid Dynamic Descriptions

2.1.7 Transport Coefficients

In general, the transport coefficients, μ and κ, are functions of both pressure and temperature:

$$\mu = \mu(p, T) \quad \text{and} \quad \kappa = \kappa(p, T) ,$$

and empirical-based expressions are often used.

One of the primary constributions of kinetic theory to date has been to provide expressions for the transport coefficients and mixing rules for fluid dynamic descriptions of single and multi-component gases.

2.2 Flow Regimes for a Monatomic Gas

2.2.1 Knudsen Number

The Knudsen number, Kn, is a measure of a gas' potential to maintain conditions of thermodynamic equilibrium. It is defined as the ratio of the mean free path (the average distance traveled by a gas particle between collisions, λ) to an appropriate reference length scale, ℓ, characterizing the flow:
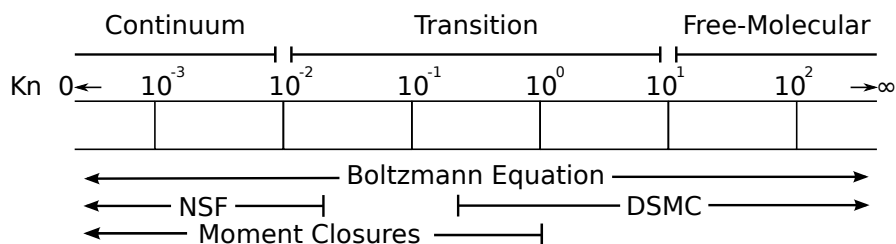
$$\text{Kn} = \frac{\lambda}{\ell} \, .$$

2.2 Flow Regimes for a Monatomic Gas
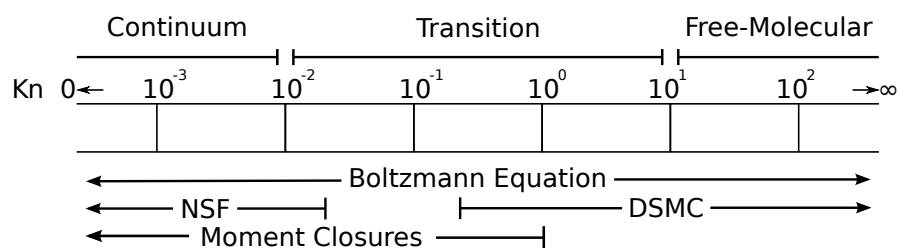
When the mean free path is small compared with the characteristic length scale (i.e., for Kn $\ll 1$), the gas will undergo a large number of collisions over the length scales of interest and assumptions of near thermal equilibrium apply. In this case, the continuum hypothesis applies and conventional fluid dynamic (macroscopic) descriptions (i.e., the Navier-Stokes equations) are appropriate (note that on average gas particles must undergo only about 3 to 4 binary collisions to equilibrate the translational energy modes).

2.2 Flow Regimes for a Monatomic Gas

When the mean free path is large compared to the characteristic length scale (i.e., for Kn $\approx$ 1 and Kn $>$ 1), thermal equilibrium cannot be maintained and the continuum hypothesis fails. Consequently, conventional fluid dynamic descriptions break down. For such flows, a microscopic description of fluid behaviour is required, such as that provided by gaskinetic theory. The latter is valid for the full range of Knudsen numbers.

2.2 Flow Regimes for a Monatomic Gas
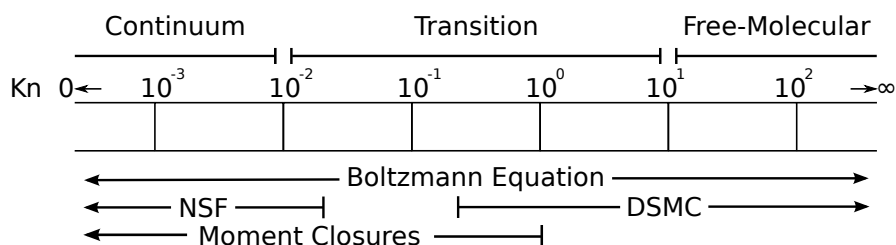
Four flow regimes may be identified:

▶ **Continuum Regime**
  – Kn $\leq$ 0.01
  – collision-dominated flow
  – conventional fluid-dynamic equations (i.e., the Navier-Stokes Equations) are valid

▶ **Slip-Flow Regime**
  – 0.01 $<$ Kn $\leq$ 0.1
  – fluid dynamic equations can be augmented with slip boundary conditions for the flow velocity and temperature
  – Knudsen layer analyses are generally used to formulate appropriate boundary conditions

2.2 Flow Regimes for a Monatomic Gas
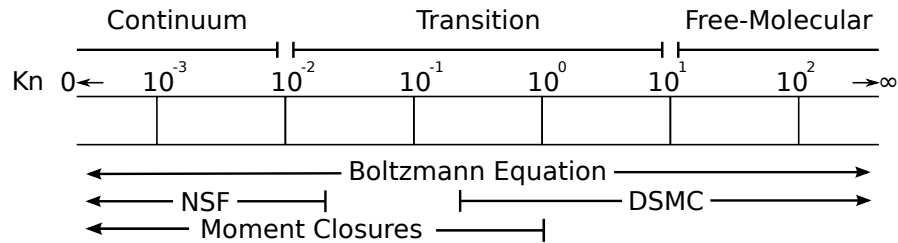
Transition Regime

- $0.1 < \text{Kn} \leq 10\text{–}100$
- collisions are less frequent but cannot be neglected
- very difficult regime to model

Free-Molecular Flow Regime

- $\text{Kn} > 10\text{–}100$
- collisionless flow
- inter-particle collisions negligible, must only consider particle interactions with flow field boundaries

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2.2 Flow Regimes for a Monatomic Gas

2.2.2 Flow Regimes in Terms of Mach and Reynolds Number

In general, the mean free path is related to the fluid viscosity, μ. For hard sphere collisions, the mean free path is given by

$$\lambda = \frac{16\mu}{5\rho} \frac{1}{\sqrt{2\pi RT}} \, ,$$

where ρ, T, and R are the density, temperature, and gas constant. This expression can be used to evaluate the flow Knudsen number given a characteristic length scale. ℓ.

Some simple analysis can be used to relate the Knudsen number, Kn, to the Reynolds number, $\text{Re} = \rho u \ell / \mu$, and Mach number, $\text{Ma} = u/a$, where $a = \sqrt{\gamma RT}$ is the sound speed for the gas and γ is the specific heat ratio.

2.2 Flow Regimes for a Monatomic Gas

2.2.2 Flow Regimes in Terms of Mach and Reynolds Number

For low Reynolds number flows in the range $0 < \mathrm{Re} < 100$ such that the <u>inertial terms are small compared to viscous forces</u>, can write

$$\mathrm{Ma} = \frac{u}{a} = \frac{u}{a}\frac{\mathrm{Re}\,\mu}{\rho u \ell} = \frac{\mu}{\rho a \ell}\mathrm{Re} \approx \frac{\rho a \lambda}{\rho a \ell}\mathrm{Re} = \mathrm{Kn}\,\mathrm{Re}\,,$$

or as originally derived by von Karman

$$\mathrm{Kn} = \frac{\mathrm{Ma}}{\mathrm{Re}}\,,$$

where, for this derivation, it has been assumed that $\mu \approx \rho a \lambda$ and the characteristic length ℓ is chosen to be some typical body length.

2.2 Flow Regimes for a Monatomic Gas

2.2.2 Flow Regimes in Terms of Mach and Reynolds Number

For intermediate Reynolds number flows in the range $100 < \mathrm{Re} < 10^5$, inertia effects become important and the flows are typically <u>laminar</u>. Basing the Knudsen number on the thickness of the laminar boundary layer, $\delta_l \approx 10\ell/\mathrm{Re}^{1/2}$ (valid for a developing flat plate laminar boundary layer), then

$$\mathrm{Ma} = \frac{u}{a} = \frac{u}{a}\frac{\mathrm{Re}^{1/2}}{\mathrm{Re}^{1/2}} \approx \frac{u}{a}\frac{10\ell}{\delta_l}\frac{1}{\mathrm{Re}^{1/2}} = 10\frac{\mu}{\rho a \delta_l}\frac{\rho u \ell}{\mu \mathrm{Re}^{1/2}}$$

$$\approx 10\frac{\rho a \lambda}{\rho a \delta_l}\mathrm{Re}^{1/2} = 10\mathrm{Kn}\,\mathrm{Re}^{1/2}\,,$$

or

$$\mathrm{Kn} = \frac{1}{10}\frac{\mathrm{Ma}}{\mathrm{Re}^{1/2}}\,.$$

2.2 Flow Regimes for a Monatomic Gas

2.2.2 Flow Regimes in Terms of Mach and Reynolds Number

Finally, for $\text{Re} > 10^5$, flows are typically <u>turbulent</u>. Basing the Knudsen number on the thickness of the turbulent boundary layer, $\delta_t \approx \ell/3\text{Re}^{1/5}$ (valid for a developing flat plate turbulent boundary layer), then

$$\text{Ma} = \frac{u}{a} = \frac{u}{a}\frac{\text{Re}^{1/5}}{\text{Re}^{1/5}} \approx \frac{u}{a}\frac{\ell}{3\delta_t}\frac{1}{\text{Re}^{1/5}} = \frac{1}{3}\frac{\mu}{\rho a \delta_t}\frac{\rho u \ell}{\mu \text{Re}^{1/5}}$$

$$\approx \frac{1}{3}\frac{\rho a \lambda}{\rho a \delta_t}\text{Re}^{4/5} = \frac{1}{3}\text{Kn}\,\text{Re}^{4/5}\,,$$

or

$$\text{Kn} = 3\frac{\text{Ma}}{\text{Re}^{4/5}}\,.$$

2.2 Flow Regimes for a Monatomic Gas

2.2.2 Flow Regimes in Terms of Mach and Reynolds Number

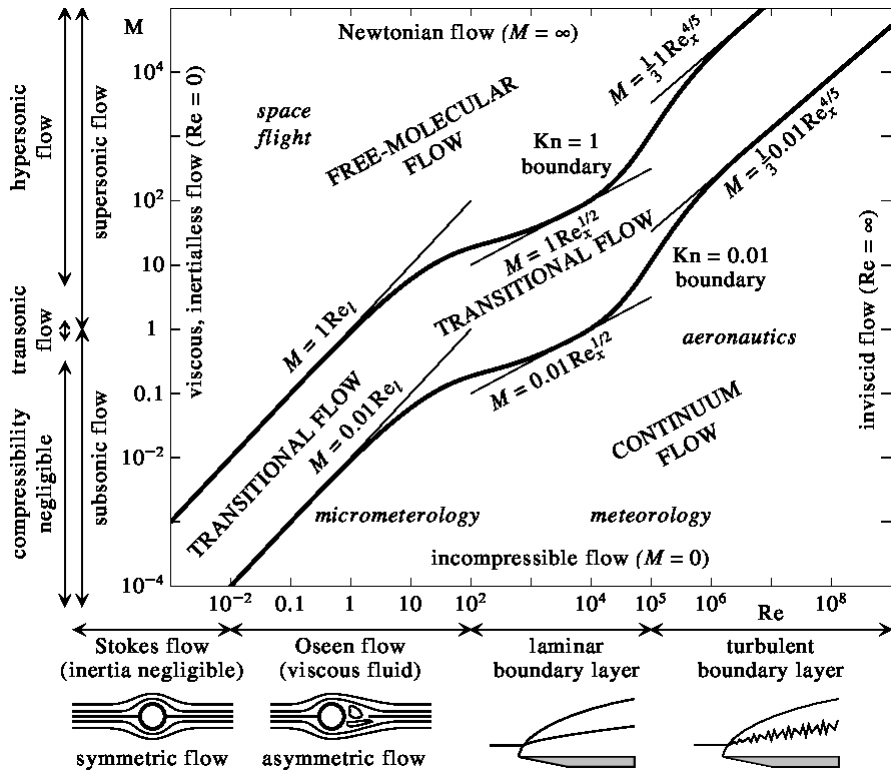Summarizing, the Knudsen number can be related to the Reynolds and Mach numbers as follows:

$$\text{Kn} = \begin{cases} \dfrac{\text{Ma}}{\text{Re}} & 0 < \text{Re} < 100\,, \\[2ex] \dfrac{1}{10}\dfrac{\text{Ma}}{\text{Re}^{1/2}} & 100 < \text{Re} < 10^5\,, \\[2ex] 3\dfrac{\text{Ma}}{\text{Re}^{4/5}} & \text{Re} > 10^5\,. \end{cases}$$

2.2 Flow Regimes for a Monatomic Gas

2.3 Statistical-Based Microscopic Description

▶ A fundamental assumption of gas kinetic theory is the molecular hypothesis which implies that: (i) a gas is a collection of very many discrete particles or molecules; (ii) all molecules of a given gas are structurally alike and have a molecular mass, m; and (iii) the molecules have a point-like structure, and, for a monatomic gas, have no internal degrees of freedom.

2.3 Statistical-Based Microscopic Description

- ▶ A statistical-based approach is then adopted for describing the state of this collection of gaseous particles.

- ▶ In the case of a single-species monatomic gas, the many microscopic states of the gas are represented in terms of a probability density function (PDF), f, with independent variables associated with the position coordinates, $\vec{x}$, of the atoms in physical space at time, t, as well as the random variable associated with the translational velocity of the atoms, $\vec{v}$.

- ▶ This statistical descriptions requires that a relatively large ensemble of particles within the infinitessimal volumes of six-dimensional phase space, $(\vec{x}, \vec{v})$.

2.4 Density Functions

2.4.1 Univariate Probability Density Function (PDF)

In the univariate case, the probability density function (PDF), $f(x)$, for a single continuous random variable, x, is a function whose value provides a measure of the probability for the occurrence of $x = x_*$. In particular, the probability of the random variable falling in the infinitessimal interval $[x, x + \mathrm{d}x]$, $P(x \leq x_* \leq x + \mathrm{d}x)$, is given by

$$P(x \leq x_* \leq x + \mathrm{d}x) = f(x)\,\mathrm{d}x \,,$$

or

$$P(x_* \in [a, b]) = \int_a^b f(x)\,\mathrm{d}x \,.$$

The PDF, $f(x)$, is non-negative everywhere and its integral over the entire space for the random varible is equal to 1 (i.e., the total probability must be equal to unity).

2.4.1 Univariate Probability Density Function (PDF)

For the random variable defined on a finite domain, i.e., $x \in [-1, 1]$, then

$$\int_{-1}^{1} f(x)\,\mathrm{d}x = 1\,.$$

In the case of a semi-infinite domain, i.e., the positive real line with $x \in [0, \infty)$, then

$$\int_{0}^{\infty} f(x)\,\mathrm{d}x = 1\,.$$

Finally, for a fully infinite domain, i.e., the real line with $x \in (-\infty, \infty)$, have

$$\int_{-\infty}^{\infty} f(x)\,\mathrm{d}x = 1\,.$$

For gaskinetic theory, the latter is of primary interest.

2.4.1 Univariate Probability Density Function (PDF)

For all of the cases above, the expected or mean value of the random variable, $\bar{x}$, can be evaluated by integrating x against $f(x)$ over the full range of x. In the case of the infinite domain, $\bar{x}$ is given by

$$\bar{x} = \int_{-\infty}^{\infty} xf(x)\,\mathrm{d}x = \int_{\infty} xf(x)\,\mathrm{d}x = \langle\, xf(x)\,\rangle\,,$$

where the operator $\langle\, \phi(x)\,\rangle$ denotes integration of the function, $\phi(x)$, over the real line.

2.4.1 Univariate Probability Density Function (PDF)

A well-known univariate PDF is the normal distribution given by

$$f(x; \mu, \sigma) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2},$$

where μ and σ are the mean and standard deviation, respectively, and for which the first two non-central moments are

$$\bar{x} = \int_\infty x f(x)\,\mathrm{d}x = \langle\, x f(x)\,\rangle = \mu,$$

$$\int_\infty x^2 f(x)\,\mathrm{d}x = \langle\, x^2 f(x)\,\rangle = \mu^2 + \sigma^2,$$

and the central moments are

$$\int_\infty (x - \mu)\, f(x)\,\mathrm{d}x = \langle\, (x - \mu)\, f(x)\,\rangle = 0,$$

$$\int_\infty (x - \mu)^2\, f(x)\,\mathrm{d}x = \left\langle\, (x - \mu)^2\, f(x)\,\right\rangle = \sigma^2.$$

2.4 Density Functions

2.4.2 Multivariate Probability Density Function (PDF)

In the multivariate case, the PDF or so-called joint probability density function, $f(x_1, \ldots, x_n)$, can be defined in terms of n continuous random variables, $x_1, \ldots, x_n$, with

$$P(x_1, \ldots, x_n \in D) = \int \ldots \int_D f(x_1, \ldots, x_n)\,\mathrm{d}x_1 \ldots \mathrm{d}x_n$$

$$= \int \ldots \int_D f(x_1, \ldots, x_n)\,\mathrm{d}^n x,$$

and, for $x_i \in (-\infty, \infty)$,

$$\int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} f(x_1, \ldots, x_n)\,\mathrm{d}x_1 \ldots \mathrm{d}x_n = \int \ldots \int_\infty f(x_1, \ldots, x_n)\,\mathrm{d}^n x$$

$$= \langle\, f(x_1, \ldots, x_n)\,\rangle = 1.$$

2.4.2 Multivariate Probability Density Function (PDF)

In the multivariate case, the marginal density function, $f_{X_i}(x_i)$ for $i = 1, 2, \ldots, n$, can also be defined as

$$f_{X_i}(x_i) = \int \ldots \int_{\infty} f(x_1, \ldots, x_n)\, \mathrm{d}x_1 \ldots \mathrm{d}x_{i-1} \ldots \mathrm{d}x_{i+1} \ldots \mathrm{d}x_n\,,$$

and the conditional probability density function,
$f_{(X_1, X_{i-1}, X_{i+1}, X_n)|X_i}(\{x_1, x_{i-1}, x_{i+1}, x_n\}|x_i)$, for $\{x_1, x_{i-1}, x_{i+1}, x_n\}$ given x_i then follow as

$$f_{\{X_1, X_{i-1}, X_{i+1}, X_n\}|X_i}(\{x_1, x_{i-1}, x_{i+1}, x_n\}|x_i) = \frac{f(x_1, \ldots, x_n)}{f_{X_i}(x_i)}\,,$$

or

$$f(x_1, \ldots, x_n) = f_{\{X_1, X_{i-1}, X_{i+1}, X_n\}|X_i}(\{x_1, x_{i-1}, x_{i+1}, x_n\}|x_i) f_{X_i}(x_i)\,.$$

2.4.2 Multivariate Probability Density Function (PDF)

For two random variables, x, y, the joint PDF is

$$f = f(x, y)\,,$$

and can write

$$f_X(x) = \int_{\infty} f(x, y)\, \mathrm{d}y\,, \quad f_Y(y) = \int_{\infty} f(x, y)\, \mathrm{d}x\,,$$

with

$$f_{Y|X}(y|x) = \frac{f(x, y)}{f_X(x)}\,, \quad f_{X|Y}(x|y) = \frac{f(x, y)}{f_Y(y)}\,,$$

and finally that

$$f(x, y) = f_{Y|X}(y|x) f_X(x) = f_{X|Y}(x|y) f_Y(y)\,.$$

2.4.2 Multivariate Probability Density Function (PDF)

In the case that the n random variables are all independent of each other (i.e., random variables are all independent variables, as is the case in gaskinetic theory), the joint PDF, $f(x_1, \ldots, x_n)$, can be written as a product of n factors, $f_i(x_i)$,

$$f(x_1, x_2, \ldots, x_n) = f_1(x_1)f_2(x_2)\ldots f_n(x_n),$$

where $f_i(x_i)$ are univariate functions. In this case, the marginal distribution function is given by

$$f_{X_i}(x_i) = \int \ldots \int_\infty f_1(x_1)\ldots f_n(x_n)\,dx_1 \ldots dx_{i-1} \ldots dx_{i+1} \ldots dx_n$$

$$= f_i(x_i) \int \ldots \int_\infty f_1(x_1)\ldots f_{i-1}(x_{i-1})f_{i+1}(x_{i+1})\ldots f_n(x_n)\,dx_1 \ldots dx_{i-1} \ldots dx_{i+1} \ldots dx_n$$

$$= \frac{f_i(x_i)}{\displaystyle\int_\infty f_i(x_i)\,dx_i}.$$

2.4 Density Functions

2.4.3 Probability Density Function (PDF)

In gas kinetic theory, the PDF for a monatomic gas is taken to have the form

$$f = f(\vec{x}, \vec{v}, t),$$

where $\vec{x}$ is the position vector for the particles (molecules) in physical space, $\vec{v}$ is the total velocity vector for the particles (random variables defining velocity space), and t is the time. In this description, f is the dependent variable and a key assumption in the description offered by kinetic theory is that $\vec{x}$, $\vec{v}$, and t are all fully independent variables. This assumption will be discussed further in what follows later in the course.

2.4.3 Probability Density Function (PDF)

The PDF can evolve with time within phase space (the space represented by the union of the physical and velocity space) and satisfies the condition for the total probability in the random variable space:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(\vec{x}, \vec{v}, t)\, \mathrm{d}v_1 \mathrm{d}v_2 \mathrm{d}v_3 = \iiint_{\infty} f(\vec{x}, \vec{v}, t)\, \mathrm{d}^3 v$$

$$= \langle\, f(\vec{x}, \vec{v}, t)\, \rangle = 1\,.$$

The PDF is related to the probability of finding a gaseous particle at location $\vec{x}$ and time t having velocity $\vec{v}$.

2.4 Density Functions

2.4.4 Number Density Function (NDF)

It is also convenient to define a number density function (NDF), $\mathcal{F}$,

$$\mathcal{F} = \mathcal{F}(\vec{x}, \vec{v}, t) = n(\vec{x}, t)f(\vec{x}, \vec{v}, t)\,,$$

where n is the number of particles (molecules) per unit volume of physical space such that

$$\langle\, \mathcal{F}(\vec{x}, \vec{v}, t)\, \rangle = \langle\, n(\vec{x}, t)f(\vec{x}, \vec{v}, t)\, \rangle = \langle\, nf\, \rangle = n\langle\, f\, \rangle = n\,.$$

The NDF is related to the number of gaseous particle that may be found at location $\vec{x}$ and time t having velocity $\vec{v}$.

2.4.4 Number Density Function (NDF)

Accordingly, for a given volume in physical space, $\mathcal{V}$, the total number of gaseous particles within the volume, N, can be evaluated as

$$\iiint_{\mathcal{V}} \iiint_{\infty} \mathcal{F}(\vec{x}, \vec{v}, t)\, \mathrm{d}^3 v \mathrm{d}\mathcal{V} = \iiint_{\mathcal{V}} \langle\, \mathcal{F}(\vec{x}, \vec{v}, t)\, \rangle\, \mathrm{d}\mathcal{V}$$

$$= \iiint_{\mathcal{V}} n\, \mathrm{d}\mathcal{V}$$

$$= N \,.$$

Having, defined the PDF and NDF for the gas, we are now in a position to define various macroscopic properties of the gas which may be of interest.

2.5 Macroscopic Averages and Moments

Knowledge of the PDF (or NDF) provides a full and complete description of the gas, including the full prescription of all macroscopic quantities. In general, the conventional macroscopic quantities that are of practical and/or engineering interest can be evaluated as either appropriately selected expected values (or averages), $\mathcal{E}$, in terms of the PDF or so-called "moments", M, of the NDF.

2.5.1 Expected Values of PDF

An expected value, $\mathcal{E}_Q(\vec{x}, t)$, of any quantity, Q, associated with the gas particles can be evaluated as

$$\mathcal{E}_Q(\vec{x}, t) = \iiint_{\infty} Q(\vec{v}) f(\vec{x}, \vec{v}, t)\, \mathrm{d}^3 v = \langle\, Qf\, \rangle \,,$$

where $Q = Q(\vec{v})$ is a velocity-dependent quantity which in general is a polynomial (usually just a monomial) in $\vec{v}$.

2.5 Macroscopic Averages and Moments

2.5.2 Moments of NDF

In a similar fashion, the macroscopic quantities or moments, $M(\vec{x}, t)$, for weights, V, can be found using

$$M(\vec{x}, t) = \iiint_{\infty} V(\vec{v}) \mathcal{F}(\vec{x}, \vec{v}, t)\, \mathrm{d}^3 v = \langle\, V(\vec{v})\mathcal{F}\, \rangle \,,$$

where, in this case, $V(\vec{v})$ is a velocity-dependent weight which in general is a polynomial (usually just a monomial) in $\vec{v}$.

2.5 Macroscopic Averages and Moments

Some examples of expected values include $Q = 1$:

$$\mathcal{E}_1 = \langle\, f\, \rangle = 1\,,$$

which is the total probability; $Q = \vec{v}$:

$$\mathcal{E}_{\vec{v}} = \langle\, \vec{v}f\, \rangle = \vec{u}\,,$$

where here, by definition, $\vec{u}$ is the mean or expected velocity of the gaseous molecules; and, finally, $Q = mv^2/2$:

$$\mathcal{E}_{mv^2/2} = \left\langle\, \frac{m}{2}v^2 f\, \right\rangle = E_p = e_p + \frac{m}{2}u^2\,,$$

where E_p is the total kinetic energy of the gaseous particles and e_p is the kinetic energy associated with the random motion of the gaseous particles.

2.5 Macroscopic Averages and Moments

2.5.3 Total Velocity Moments

The so-called *total velocity moments* of increasing order are as follows:

Zeroth-Order Velocity Moments (mass):

$$V = 1 : \quad \langle \mathcal{F} \rangle = n \,,$$
$$V = m : \quad \langle m\mathcal{F} \rangle = m \langle \mathcal{F} \rangle = mn = \rho \,,$$

where $\rho = mn$ is again the gas density.

First-Order Velocity Moments (momentum or mass flux):

$$\vec{V} = \vec{v} : \quad \langle \vec{v}\mathcal{F} \rangle = n\vec{u} \,,$$
$$V_i = v_i : \quad \langle v_i\mathcal{F} \rangle = nu_i \,,$$
$$\vec{V} = m\vec{v} : \quad \langle m\vec{v}\mathcal{F} \rangle = m \langle \vec{v}\mathcal{F} \rangle = \rho\vec{u} \,,$$
$$V_i = mv_i : \quad \langle mv_i\mathcal{F} \rangle = m \langle v_i\mathcal{F} \rangle = \rho u_i \,.$$

2.5.3 Total Velocity Moments

Second-Order Velocity Moments (energy or momentum flux):

$$\vec{\vec{V}} = \vec{v}\vec{v} : \quad \langle \vec{v}\vec{v}\mathcal{F} \rangle = n\vec{u}\vec{u} + \frac{1}{m}\vec{\vec{P}} \,,$$
$$V_{ij} = v_i v_j : \quad \langle v_i v_j\mathcal{F} \rangle = nu_i u_j + \frac{P_{ij}}{m} \,,$$
$$\vec{\vec{V}} = m\vec{v}\vec{v} : \quad \langle m\vec{v}\vec{v}\mathcal{F} \rangle = m \langle \vec{v}\vec{v}\mathcal{F} \rangle = \rho\vec{u}\vec{u} + \vec{\vec{P}} \,,$$
$$V_{ij} = mv_i v_j : \quad \langle mv_i v_j\mathcal{F} \rangle = m \langle v_i v_j\mathcal{F} \rangle = \rho u_i u_j + P_{ij} \,,$$

where the pressure dyad, $\vec{\vec{P}}$, or pressure tensor, P_{ij}, is defined as

$$\vec{\vec{P}} = p\vec{\vec{I}} - \vec{\vec{\tau}} \,, \quad P_{ij} = p\delta_{ij} - \tau_{ij} \,,$$

and related to the the momentum flux of the particles produced by their random translation energy and is defined in terms of the usual hydrodynamic pressure, p, and fluid stresses, $\vec{\vec{\tau}}$ or τ_{ij}, such that

$$\frac{1}{3}P_{ii} = \frac{1}{3}\left(3p - \tau_{ii}\right) = \frac{1}{3}3p = p \,,$$

$$\tau_{ii} = 0 \,.$$

2.5.3 Total Velocity Moments

Second-Order Velocity Moments (energy or momentum flux):

So-called contracted second-order velocity moments are useful as given by

$$V = \frac{1}{2}v^2 : \quad \left\langle \frac{1}{2}v^2 \mathcal{F} \right\rangle = \frac{1}{2}\left\langle v^2 \mathcal{F} \right\rangle = nE = \frac{1}{2}nu^2 + ne$$

$$= \frac{1}{2}nu^2 + \frac{3}{2}\frac{p}{m} = \frac{1}{2}nu^2 + \frac{3}{2}\frac{nkT}{m},$$

$$V = \frac{m}{2}v^2 : \quad \left\langle \frac{m}{2}v^2 \mathcal{F} \right\rangle = \frac{m}{2}\left\langle v^2 \mathcal{F} \right\rangle = \rho E = \frac{1}{2}\rho u^2 + \rho e$$

$$= \frac{1}{2}\rho u^2 + \frac{3}{2}p = \frac{1}{2}\rho u^2 + \frac{3}{2}nkT,$$

where E is the total specific energy of the gas and the specific internal energy, e, which, for a monatomic gas, only includes the energy associated with random translation motion of the particles can be written as

$$e = \frac{3}{2}\frac{p}{\rho} = \frac{3}{2}RT = \frac{3}{2}\frac{k}{m}T = \frac{1}{\gamma - 1}RT = c_v T,$$

where the ideal gas equation of state, $p = \rho RT = nkT$, is again taken to apply, k is the Boltzmann constant, and $\gamma = 5/3$ for a monatomic gas.

2.5.3 Total Velocity Moments

Third-Order Velocity Moments (energy flux and heat flux):

$$\overset{\leftrightarrow}{\vec{V}} = m\vec{v}\vec{v}\vec{v} : \quad m\left\langle \vec{v}\vec{v}\vec{v}\mathcal{F} \right\rangle = \rho\vec{u}\vec{u}\vec{u} + 3\vec{u}\overset{\leftrightarrow}{P} + \overset{\leftrightarrow}{\vec{Q}},$$

$$V_{ijk} = mv_iv_jv_k : \quad m\left\langle v_iv_jv_k\mathcal{F} \right\rangle = \rho u_iu_ju_k + u_iP_{jk} + u_jP_{ik} + u_kP_{ij} + Q_{ijk},$$

$$\vec{V} = \frac{m}{2}\vec{v}v^2 : \quad \frac{m}{2}\left\langle v_iv^2\mathcal{F} \right\rangle = \rho\vec{u}\left(\frac{1}{2}u^2 + \frac{5}{2}\frac{p}{\rho}\right) - \overset{\leftrightarrow}{\tau}\cdot\vec{u} + \vec{q},$$

$$V_i = \frac{m}{2}v_iv^2 : \quad \frac{m}{2}\left\langle v_iv^2\mathcal{F} \right\rangle = \rho u_i\left(\frac{1}{2}u^2 + \frac{5}{2}\frac{p}{\rho}\right) - \tau_{ij}u_j + q_i,$$

where here $\overset{\leftrightarrow}{\vec{Q}} = Q_{ijk}$ is the so-called third-order heat flux tensor and $\vec{q} = q_i$ is the usual heat flux vector appearing in the equations of fluid dynamics. The latter are related to the flux of energy by the random motion of the gaseous particles.

2.5 Macroscopic Averages and Moments

2.5.4 Random Velocity Moments

So-called random velocity moments can also be defined and are in fact the central moments of the density functions for the gas. Letting the random velocity of the gas, $\vec{c}$ or c_i, to be defined as

$$\vec{c} = \vec{v} - \vec{u}, \quad \text{or} \quad c_i = v_i - u_i,$$

the general form of the random velocity moments, $M_\circ(\vec{x}, t)$, for weights, V, is given by

$$M_\circ(\vec{x}, t) = \iiint_\infty V(\vec{c})\mathcal{F}(\vec{x}, \vec{c}, t)\, \mathrm{d}^3 c = \langle\, V(\vec{c})\mathcal{F}(\vec{x}, \vec{c}, t)\, \rangle,$$

where, in this case, the velocity-dependent weight, $V(\vec{c})$, is in general a polynomial (usually just a monomial) in $\vec{c}$.

2.5.4 Random Velocity Moments

The random velocity moment of increasing order are then as follows:

Zeroth-Order Velocity Moments (mass):

$$V = 1: \quad \langle\, \mathcal{F}\, \rangle = n,$$
$$V = m: \quad \langle\, m\mathcal{F}\, \rangle = m\langle\, \mathcal{F}\, \rangle = mn = \rho.$$

First-Order Velocity Moments (momentum or mass flux):

$$\vec{V} = m\vec{c}: \quad m\langle\, \vec{c}\mathcal{F}\, \rangle = 0,$$
$$V_i = mc_i: \quad m\langle\, c_i\mathcal{F}\, \rangle = 0,$$

where the first-order central moments are by definition zero.

2.5.4 Random Velocity Moments

Second-Order Velocity Moments (energy or momentum flux):

$$\vec{\vec{V}} = m\vec{c}\vec{c}: \quad m\langle \vec{c}\vec{c}\mathcal{F} \rangle = \vec{\vec{P}} = p\vec{\vec{I}} - \vec{\vec{\tau}},$$

$$V_{ij} = mc_i c_j: \quad m\langle c_i c_j \mathcal{F} \rangle = P_{ij} = p\delta_{ij} - \tau_{ij},$$

$$V = \frac{m}{2}c^2: \quad \frac{m}{2}\left\langle c^2 \mathcal{F} \right\rangle = \rho e = \frac{3}{2}p = \frac{3}{2}nkT.$$

Third-Order Velocity Moments (energy flux and heat flux):

$$\vec{\vec{\vec{V}}} = m\vec{c}\vec{c}\vec{c}: \quad m\langle \vec{c}\vec{c}\vec{c}\mathcal{F} \rangle = \vec{\vec{\vec{Q}}},$$

$$V_{ijk} = mc_i c_j c_k: \quad m\langle c_i c_j c_k \mathcal{F} \rangle = Q_{ijk},$$

$$\vec{V} = \frac{m}{2}\vec{c}c^2: \quad \frac{m}{2}\left\langle \vec{c}c^2 \mathcal{F} \right\rangle = \vec{q},$$

$$V_i = \frac{m}{2}c_i c^2: \quad \frac{m}{2}\left\langle c_i c^2 \mathcal{F} \right\rangle = q_i.$$

2.5.4 Random Velocity Moments

Fourth-Order Velocity Moments:

$$\vec{\vec{\vec{\vec{V}}}} = m\vec{c}\vec{c}\vec{c}\vec{c}: \quad m\langle \vec{c}\vec{c}\vec{c}\vec{c}\mathcal{F} \rangle = \vec{\vec{\vec{\vec{R}}}},$$

$$V_{ijkl} = mc_i c_j c_k c_l: \quad m\langle c_i c_j c_k c_l \mathcal{F} \rangle = R_{ijkl},$$

$$\vec{\vec{V}} = m\vec{c}\vec{c}c^2: \quad m\langle \vec{c}\vec{c}c^2 \mathcal{F} \rangle = \vec{\vec{r}},$$

$$V_{ijkk} = mc_i c_j c^2: \quad m\langle c_i c_j c^2 \mathcal{F} \rangle = R_{ijkk} = r_{ij},$$

$$V_{ijkk} = mc^4: \quad m\langle c^4 \mathcal{F} \rangle = R_{iijj} = r_{ii} = r,$$

and, while possibly not as physically relatable as the other lower-order moments, can be thought of as being related to the flux of the heat flux.

2.6 Maxwell-Boltzmann Distribution

In the important case of a gas in thermal equilibrium, the NDF is well established and are referred to as the Maxwell-Boltzmann distribution. James Clerk Maxwell originally derived this form for the NDF in 1859. In 1877, Ludwig Boltzmann later published a more rigorous derivation of the same distribution function. Hence, this equilibrium solution bears both of their names.

The equilibirum solution represented by the Maxwell-Boltzmann solution corresponds to situations in which there are a sufficiently high number of inter-particle collisions to ensure that the random (thermal) energy is equilibrated such that the thermal state of the gas can be described by a single temperature. While inter-particle collisions continue to occur, the equilibrium the distribution is independent of time.

2.6 Maxwell-Boltzmann Distribution

2.6.1 Maxwell-Boltzmann PDF and NDF

The forms of the Maxwell-Boltzmann PDF and NDF, f and $\mathcal{M}$, respectively, in terms of the random particle velocity, $\vec{c}$, are

$$f(\vec{c}) = \frac{1}{(2\pi p/\rho)^{3/2}} \exp\left(-\frac{1}{2}\frac{\rho c^2}{p}\right) = \frac{1}{(2\pi\theta)^{3/2}} \exp\left(-\frac{1}{2}\frac{c^2}{\theta}\right),$$

$$\mathcal{M}(\vec{c}) = \frac{\rho}{m\,(2\pi p/\rho)^{3/2}} \exp\left(-\frac{1}{2}\frac{\rho c^2}{p}\right) = \frac{\rho}{m\,(2\pi\theta)^{3/2}} \exp\left(-\frac{1}{2}\frac{c^2}{\theta}\right),$$

where $\mathcal{M} = nf$ and where m is again the particle mass, ρ is the gas density, p is the pressure, and $\theta = p/\rho$ has also been introduced.
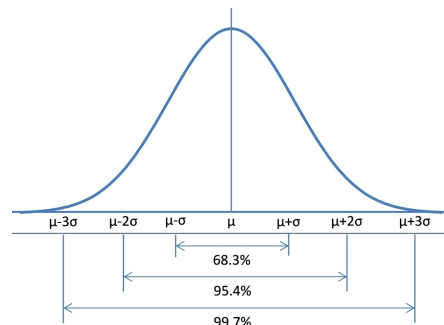
2.6.1 Maxwell-Boltzmann PDF and NDF

In terms of the total particle velocity, $\vec{v}$, the forms of the Maxwell-Boltzmann PDF and NDF, f and $\mathcal{M}$, respectively, are

$$f(\vec{v}) = \frac{1}{(2\pi\theta)^{3/2}} \exp\left(-\frac{1}{2}\frac{|\vec{v}-\vec{u}|^2}{\theta}\right),$$

$$\mathcal{M}(\vec{v}) = \frac{\rho}{m\,(2\pi\theta)^{3/2}} \exp\left(-\frac{1}{2}\frac{|\vec{v}-\vec{u}|^2}{\theta}\right),$$

where again $\theta = p/\rho$.

2.6.1 Maxwell-Boltzmann PDF and NDF

It is quite evident that the density functions correspond to normal distributions in each of the coordinate directions of the particle velocity, with a mean in each coordinate direction of $\mu_i = u_i$, and a standard deviation $\sigma = \sqrt{\theta} = \sqrt{p/\rho}$.

Additionally, the Maxwell-Boltzmann density functions are isotropic with respect to the mean velocity, with no preferred direction, and therefore also independent of the orientation of the coordinate system for the random velocities. It also follows that the values of $f(\vec{c})$ are constant on all $c^2 = $ constant surfaces in velocity space.
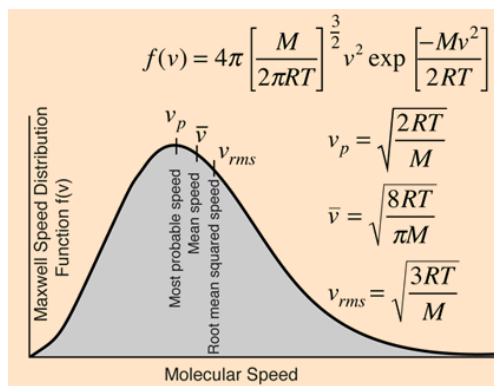
2.6 Maxwell-Boltzmann Distribution
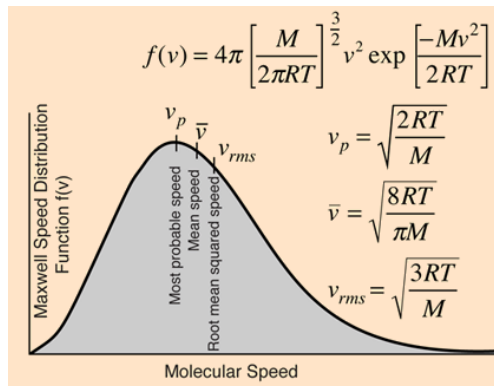
2.6.2 Distribution of Molecular Speeds

It can be shown that the well-known distribution of molecular speeds, $f^*(c = |\vec{c}|)$, corresponding to the equilibrium Maxwell-Boltzmann PDF is as follows:

$$f^*(c = |\vec{c}|) = 4\pi c^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{1}{2}\frac{m}{kT}c^2\right) ,$$

where $c = |\vec{c}|$ is now the speed of the gaseous particles.

2.6 Maxwell-Boltzmann Distribution

It can also be shown that the most probable, mean, and root mean square (RMS) particle speeds, $c_{\max}$, $\bar{c}$, and c_{rms}, respectively, are as follows:

$$c_{\max} = \sqrt{\frac{2kT}{m}} ,$$

$$\bar{c} = \int_0^\infty c f^*(c)\mathrm{d}c = \sqrt{\frac{8kT}{\pi m}} ,$$

$$c_{\mathrm{rms}} = \left[\int_0^\infty c^2 f^*(c)\mathrm{d}c\right]^{1/2} = \sqrt{\frac{3kT}{m}} .$$

2.6 Maxwell-Boltzmann Distribution

2.6.3 Random Velocity Moments

The random velocity moments of the Maxwell-Boltzmann NDF, $\mathcal{M}$, are as follows:

Zeroth-order velocity moment:

$$m \langle \mathcal{M} \rangle = \rho \,,$$

First-order velocity moments

$$m \langle c_i \mathcal{M} \rangle = 0 \,,$$

Second-order velocity moments:

$$m \langle c_i c_j \mathcal{M} \rangle = \delta_{ij} p \,,$$

$$m \langle c^2 \mathcal{M} \rangle = 3p \,,$$

2.6 Maxwell-Boltzmann Distribution

Third-order velocity moments:

$$m \langle c_i c_j c_k \mathcal{M} \rangle = 0 \,,$$

Fourth-order velocity moments:

$$m \langle c_i c_j c_k c_l \mathcal{M} \rangle = \frac{p^2}{\rho} [\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}] = \frac{p^2}{\rho} \{\delta_{ij}\delta_{kl}\}^{(3)}_{[ijkl]} \,,$$

$$m \langle c_i c_j c^2 \mathcal{M} \rangle = 5\frac{p^2}{\rho}\delta_{ij} \,,$$

$$m \langle c^4 \mathcal{M} \rangle = 15\frac{p^2}{\rho} \,,$$

Fifth-order velocity moments:

$$m \langle c_i c_j c_k c_l c_m \mathcal{M} \rangle = 0 \,,$$

2.6 Maxwell-Boltzmann Distribution

Sixth-order velocity moments:

$$m \langle c_i c_j c_k c_l c_m c_n \mathcal{M} \rangle = \frac{p^3}{\rho^2} \{\delta_{ij} \delta_{kl} \delta_{mn}\}^{(15)}_{[ijklmn]} \,,$$

$$m \langle c_i c_j c_k c_l c^2 \mathcal{M} \rangle = 7 \frac{p^3}{\rho^2} [\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}] = 7 \frac{p^3}{\rho^2} \{\delta_{ij} \delta_{kl}\}^{(3)}_{[ijkl]} \,,$$

$$m \langle c_i c_j c^4 \mathcal{M} \rangle = 35 \frac{p^3}{\rho^2} \delta_{ij} \,,$$

$$m \langle c^6 \mathcal{M} \rangle = 105 \frac{p^3}{\rho^2} \,.$$

Seventh-order velocity moments:

$$m \langle c_i c_j c_k c_l c_m c_n c_o \mathcal{M} \rangle = 0 \,,$$

Eighth-order velocity moments:

$$m \langle c_i c_j c_k c_l c_m c_n c_o c_p \mathcal{M} \rangle = \frac{p^4}{\rho^3} \{\delta_{ij} \delta_{kl} \delta_{mn} \delta_{op}\}^{(105)}_{[ijklmnop]} \,,$$

2.6 Maxwell-Boltzmann Distribution

Ninth-order velocity moments:

$$m \langle c_i c_j c_k c_l c_m c_n c_o c_p c_q \mathcal{M} \rangle = 0 \,,$$

where the notation $\{\}^{(N)}_{[ijk\ldots]}$ represents a symmetric tensor obtained by taking the sum of all independent permutations of the indices. The superscript N denotes the total number of terms in the summation.

Note that due to the symmetry of the Maxwell-Boltzmann distribution, all odd-order random velocity moments vanish and

$$P_{ij} = p \delta_{ij} \,, \quad \text{and} \quad \tau_{ij} = 0 \,,$$

$$Q_{ijk} = 0 \,, \quad \text{and} \quad q_i = 0 \,,$$

i.e., the fluid stress tensor, third-order heat flux tensor, and heat flux vector all vanish.

2.6 Maxwell-Boltzmann Distribution

2.6.4 Equipartition of Translational Energy

Note that, due to the symmetry of the equilibrium Maxwell-Boltzmann distribution, the kinetic energies associated with the translation motion in each of the coordinate directions are all equal:

$$\frac{m}{2} \left\langle c_x^2 \mathcal{M} \right\rangle = \frac{m}{2} \left\langle c_y^2 \mathcal{M} \right\rangle = \frac{m}{2} \left\langle c_z^2 \mathcal{M} \right\rangle = \frac{1}{2} p = \frac{1}{2} n k T \,,$$

and

$$\frac{m}{2} \left\langle \left(c_x^2 + c_y^2 + c_z^2 \right) \mathcal{M} \right\rangle = \frac{m}{2} \left\langle c^2 \mathcal{M} \right\rangle = \frac{3}{2} p = \frac{3}{2} n k T \,.$$

This result is in agreement with the equipartition of energy theorem from classical statistical mechanics which states that for a system in equilibrium, energy of the system can be defined by a single temperature and there is $kT/2$ of energy for each possible degree of freedom in the system.

2.7 Boltzmann Equation

2.7.1 Key Assumptions

The Boltzmann equations provides a description of the time evolution of the NDF in the case of general non-equilibrium flows. The following are key assumptions of gaskinetic theory:

▶ the mean free path is large compared to the effective range of the intermolecular forces governing collisional processes;

▶ most of the time the particles move freely through space acted on only by external forces;

▶ only binary collisions are considered (probability more than two particles colliding is considered to be very low) and the collisional processes are treated as point-like interactions; and

▶ the principle of molecular chaos is applied implying that the colliding particles are uncorrelated (i.e., particles which have already collided with each other will have many encounters with other molecules before they meet again).

2.7 Boltzmann Equation

As derived by Boltzmann (1872), the Boltzmann equation is an integro-differential equation of high-dimensionality that governs the time evolution of a single dependent variable, the NDF $\mathcal{F} = \mathcal{F}(\vec{x}, \vec{v}, t)$ in terms of 7 independent variables $(\vec{x}, \vec{v}, t)$. The Boltzmann can be expressed as

$$\frac{\partial \mathcal{F}}{\partial t} + \vec{v} \cdot \vec{\nabla}_x \mathcal{F} + \vec{a} \cdot \vec{\nabla}_v \mathcal{F} = \frac{\delta \mathcal{F}}{\delta t}$$

where here $\delta \mathcal{F} / \delta t$ represents the Boltzmann collision integral, which governs the impact of particle collisions on the NDF.

2.7 Boltzmann Equation

A change of coordinate frames can be introduced to re-express the the Boltzmann equation for the NDF in terms of the random component of the particle velocity, $\vec{c}$. Letting $\vec{c} = \vec{v} - \vec{u}(x, t)$, the Boltzmann equation describing the time evolution of $\mathcal{F} = \mathcal{F}(\vec{x}, \vec{c}, t)$ can be written as

$$\frac{\partial \mathcal{F}}{\partial t} + (u_i + c_i) \frac{\partial \mathcal{F}}{\partial x_i} - \left[\frac{\partial u_i}{\partial t} + (u_j + c_j) \frac{\partial u_i}{\partial x_j} - a_i \right] \frac{\partial \mathcal{F}}{\partial c_i} = \frac{\delta \mathcal{F}}{\delta t}$$

2.8 Boltzmann Collision Integral

The Boltzmann collision operator involves a 5-dimensional integral and can be written as

$$\frac{\delta \mathcal{F}}{\delta t} = \iiint_{\infty} \mathrm{d}^3 v_2 \int_0^{2\pi} \mathrm{d}\epsilon \int_0^{\pi} \mathrm{d}\chi \sin\chi S(g,\chi) g \left[\mathcal{F}' \mathcal{F}_2' - \mathcal{F} \mathcal{F}_2 \right] \, ,$$

where $g = |\vec{v}_2 - \vec{v}|$, S is the differential collision cross section (which is dependent on the interparticle potential for the binary collisions), and ϵ and χ are the azimuthal and deflection angles for the particle collision processes.

2.8 Boltzmann Collision Integral

2.8.1 BGK (Relaxation-Time) Approximation

In general, the emphasis here will not be on the collision operator and it can be convenient to adopt a so-called relaxation time or BGK model for the collision operator which can be written as

$$\frac{\delta \mathcal{F}}{\delta t} = -\frac{\mathcal{F} - \mathcal{M}}{\tau} \, ,$$

where τ is the characteristic time for the particle collsions and $\mathcal{M}$ is defined to a Maxwell-Boltzmann NDF sharing the collisional invariant moments with $\mathcal{F}$ associated with conservation of mass, momentum, and energy.

2.9 Maxwell's Equation of Change

For a given macroscopic moment of interest, M, given by

$$M(\vec{x}, t) = \langle\, V(\vec{v})\mathcal{F}\,\rangle\,,$$

Maxwell's equation of change (Maxwell, 1867) can be formulated by taking the appropriate moment of the Boltzmann equation to arrive at

$$\frac{\partial}{\partial t}\,(M) + \vec{\nabla}\cdot\langle\,\vec{v}V(\vec{v})\mathcal{F}\,\rangle = \left\langle\, V(\vec{v})\frac{\delta\mathcal{F}}{\delta t}\,\right\rangle\,,$$

where here it has been assumed that $\vec{a} = 0$. The preceding is a transport equation for the given moment of interest. It's solution however requires information about the moment flux given by

$$\langle\,\vec{v}V(\vec{v})\mathcal{F}\,\rangle\,.$$

This gives rise to the closure problem in moment methods.

2.10 Boltzmann's H-Theorem

It also follows from the Boltzmann H theorem of Boltzmann (1872) that

$$-k\left\langle\, \ln\mathcal{F}\frac{\delta\mathcal{F}}{\delta t}\,\right\rangle \geq 0\,,$$

is positive semi-definite (k here is again the Boltzmann constant). Thus, defining the physical entropy as

$$s(\mathcal{F}) = -\frac{k}{\rho}\,\langle\,\mathcal{F}\ln\mathcal{F}\,\rangle\,,$$

it is straightforward to show that this quantity satisfies the balance law

$$\frac{\partial}{\partial t}\,(\rho s) - k\frac{\partial}{\partial x_i}\,\langle v_i\mathcal{F}\ln\mathcal{F}\rangle = -k\left\langle\ln\mathcal{F}\frac{\delta\mathcal{F}}{\delta t}\right\rangle \geq 0\,,$$

showing that the physical entropy is a monotonically increasing function of time.

2.11 Polyatomic and Multi-Component Gases and Plasmas

▶ Polyatomic Gases:
Treatments are possible for molecules with internal degrees of freedom (i.e., kinetic energy of rotation and vibration and potential energy of vibration).

▶ Multi-Component Gases:
Separate density functions for each gaseous species s: f_s, $\mathcal{F}_s$.

▶ Plasmas:
Kinetic theory is also applicable to charged ions and electrons; however, care is required for the treatment of Coulomb interactions between charged particles.

These are all beyond the scope of this course.