

KINETIC THEORY OF GASES

ANDERS DAHLKILD

1. INTRODUCTION

The present text is based on a set of lectures given as part of a post graduate course in fluid mechanics at the Department of Mechanics, KTH School of Engineering Sciences. The topic of kinetic gas theory was chosen as to broaden the students knowledge in the field of fluid mechanics in general. In particular the students should get a new perspective on the continuum theory approach applied in their every day research task. Also, the topic has bearing on the theory of two phase flow for dispersed systems, where the molecules of kinetic gas theory are replaced with macroscopic, discrete particles suspended in a continuous fluid. The formalism for expressing averaged kinetic transport of gas properties is also in very close analogy to the averaging of continuum properties in a turbulent flow field, a subject the students usually are more familiar with. In all, the subject is a quite central part of the field of mechanics, and provides a link between undergraduate courses in mechanics of particle systems, classical equilibrium thermodynamics and courses in continuum fluid mechanics.

The present lectures notes are complemented by each class with a set of project reports. Each group of two(or three) students performs a DSMC(Direct Simulation Monte-Carlo) simulation on a specific problem using an available designated code provided with the text book by Bird [1]. The results of these simulations are summarized by each group in a project report that is distributed to all participants as part of the course literature.

1.1. Macroscopic versus kinetic theory approach. In the macroscopic, or continuum approach for the description of local fluid properties in a flow field, it is assumed that the fluid matter occupies every point in space. The density of matter in a point is defined as the ratio of mass to volume of a small fluid element as its size, centered around the point in question, approaches zero. Likewise, the velocity component in a given direction, \mathbf{n} , at a given point is defined as the ratio of the volumetric flow rate to area that crosses a small surface element of unit normal \mathbf{n} as the surface area approaches zero. This is illustrated in figure 1. The true limiting process of a decreasing measuring volume for evaluation of the macroscopic point value of density in a physical experiment is illustrated qualitatively in figure 2. For large measuring volumes, variation of the evaluated mass density as the size decreases is associated with a non-homogeneous macroscopic spatial distribution of mass. As the measuring size is small enough to encompass a sufficiently homogeneous macroscopic amount of mass, the evaluated mass density levels out on a local value, virtually insensitive to small relative variations of the measuring size. This value is defined as the macroscopic density of mass at the given point around which the measuring volume is centered. However, should the measuring

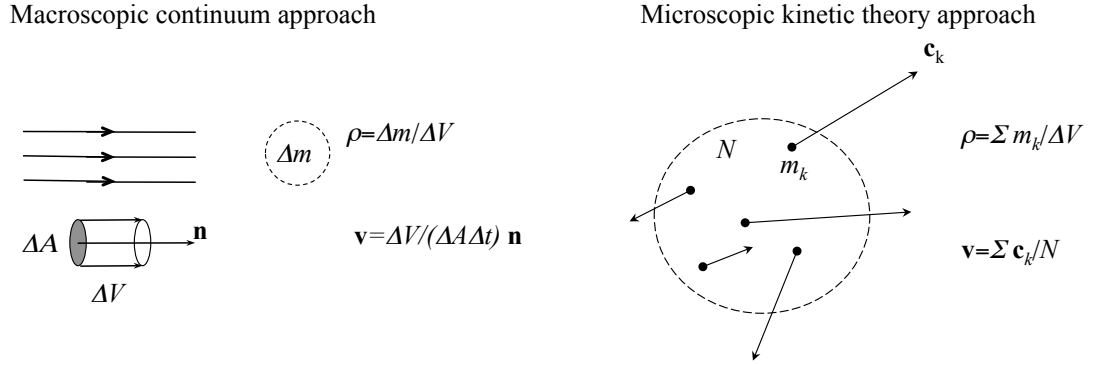


FIGURE 1. The macroscopic and microscopic approaches.

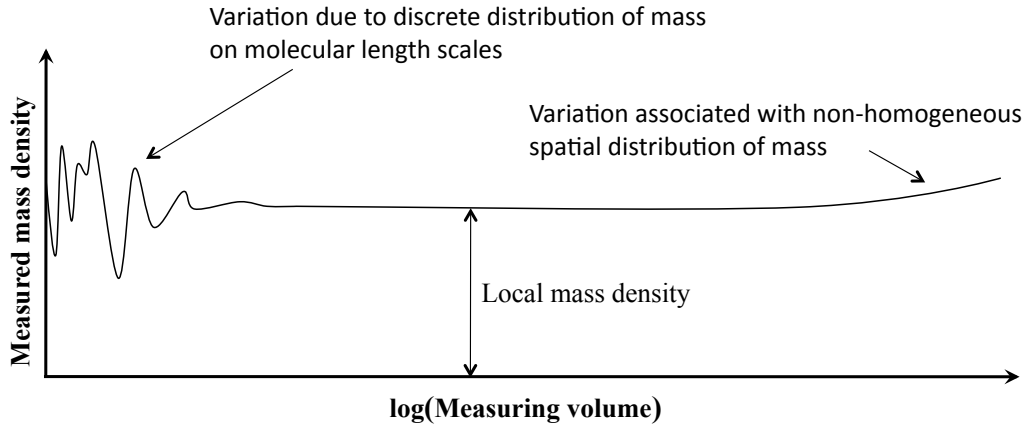


FIGURE 2. Effect of varying measuring volume for evaluation of mass density.

volume be too small, statistical fluctuations on molecular scales are affecting the evaluated mass density. Changing the measuring size for volumes containing only a few molecules, the measured number of molecules(mass) will not be proportional to the volume in each measurement due to the non-homogeneous distribution of matter on this small length scale. This pin points the difference in the macroscopic, continuum approach and the microscopic kinetic theory approach.

In kinetic theory, the local mass density is the mass to volume ratio of the discrete molecular masses within a given volume. A measurement of this density for a small volume of a macroscopically homogeneous gas at thermal equilibrium may give an average value over many samples equal to the macroscopic density of the gas. However, the statistical fluctuations in the series of individual samples will increase with decreasing measuring size. Thus, there is an obvious break down of the continuum theory approach as the number of molecules in the typical volume of a local fluid element is too small. The probability of finding a given number of particles, N , within a measuring volume

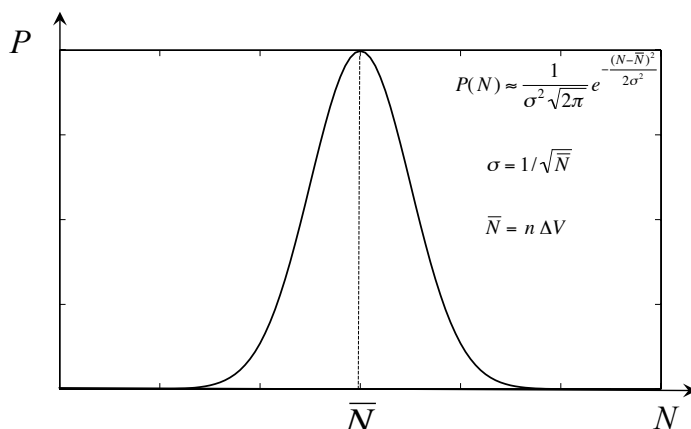


FIGURE 3. Probability density of finding N particles in a measuring volume, ΔV , in a macroscopically homogeneous gas with overall number density n .

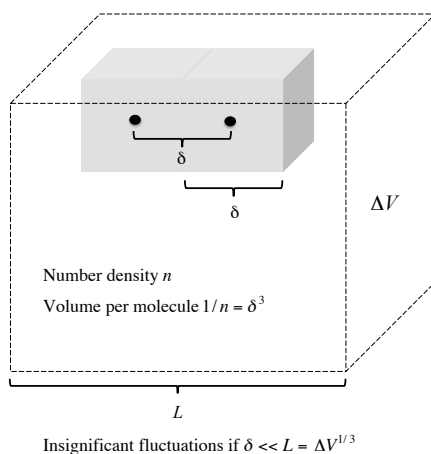


FIGURE 4. Relation between number density, n , and distance between molecules, δ in a cubical gitter structure.

ΔV is approximately given by a Gaussian distribution around the mean value \bar{N} with a standard deviation $\sigma = 1/\sqrt{\bar{N}}$, see figure 3 (Bird [1, page x]). The average number of molecules in the measuring volume is related to the number density, n , of the homogeneous gas as $\bar{N} = n\Delta V$. Thus, the standard deviation will be small if the linear size of the measurement volume, $\Delta L = \Delta V^{1/3}$, is large compared to $n^{-1/3}$. If, by approximation, the molecules are distributed in a cubical gitter with distance δ between the molecules, the number density is $n = 1/\delta^3$, see figure 4. The requirement of insignificant fluctuations in the measurement volume then gives $\delta = n^{-1/3} \ll \Delta L$, i.e. the size of

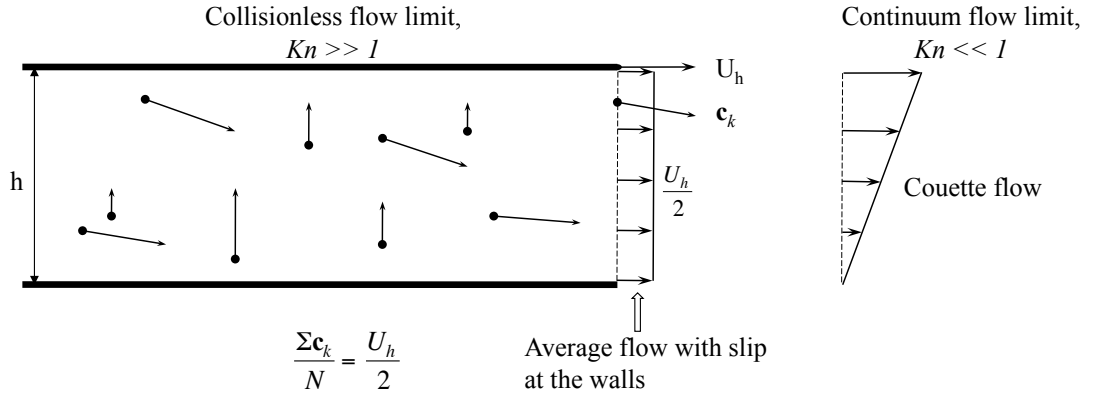


FIGURE 5. *Left:* Microscopic description of collisionless flow between two parallel plates illustrating the wall slip of the average motion at large Knudsen numbers. *Right:* Continuum flow limit with frequent interactions between molecules at small Knudsen numbers.

the volume is much larger than the distance between molecules. As a rule of thumb one may require $\Delta L/\delta \geq 100$, i.e. $\bar{N} \geq 10^6$ with $\sigma \leq 10^{-3}$. Air at standard temperature and pressure has a number density of about $n_0 = 3 \cdot 10^{25}/m^3$ giving $\delta_0 = 3 \cdot 10^{-9}m$. The measuring volume should then be $L_0 \geq 0.3\mu m$. Thus at normal conditions the breakdown of continuum theory, due to significant statistical fluctuations, appear on quite small lengthscales, which would apply rather to gas dynamical nano-technology. However, for applications in the low density part of the earths atmosphere this restriction may appear for much larger dimensions.

1.2. The Knudsen number. The obvious break down of continuum theory due to statistical fluctuations turns out not to be the most restrictive criteria regarding the density of the gas. The continuum description of a gas in motion, i.e. a gas which departs from thermal equilibrium, also requires frequent collisions between the molecules. These collisions transfer properties of the gas, like energy and momentum, between the molecules in addition to the trivial transport of the property carried by the individual molecules themselves even without collisions. Without molecular collisions, the macroscopic behaviour of the gas would not be that of the Newtonian fluid we are used to even if statistical fluctuations were insignificant. To see this, consider the planar Couette flow between two infinitely long plates at distance h apart. Let the lower plate be stationary and the upper plate move with constant speed U_h in the x-direction, parallel to the plates, see figure 5. In a gas without intermolecular collisions the molecules would collide with the planar plates only (provided they initially have at least some speed component perpendicular to the surface of the plates). Assume, for simplicity, that half the number of molecules are moving towards the upper plate and the other half are moving towards the lower plate, let's say uniformly distributed in space. The molecules moving towards the upper plate on the average have a zero velocity component parallel to the plates since their last collision was with the lower stationary plate, which transfers its

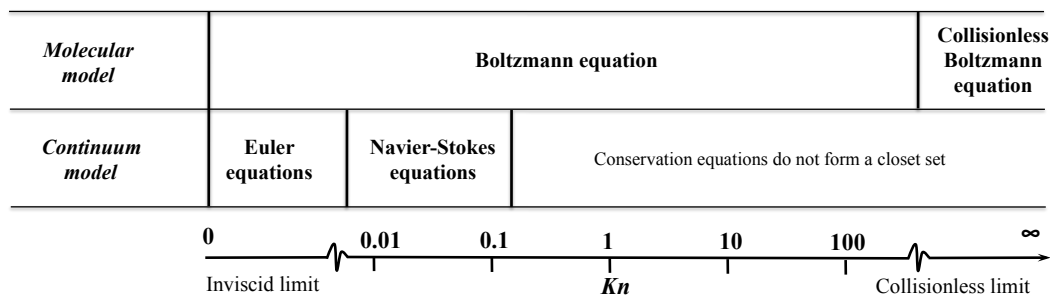


FIGURE 6. Validity of mathematical models versus Knudsen number.

zero momentum to the molecules. Molecules moving towards the lower plate have, on the average, the same velocity as the upper plate. Thus, by averaging over both classes of molecules the mean velocity of molecules in the direction of the plates is $U_h/2$. This average represents the macroscopic value of the velocity. Thus a gas without molecular collisions does not satisfy *no slip* conditions at the plates. Although scattered molecules from the plate attains a parallel component of velocity biased by the plate, the averaging over also the incoming molecules carrying a different parallel velocity component, results in a slip of the macroscopic average velocity at the plate.

A collisionless gas therefore has a macroscopic velocity profile which largely differs from the result of the continuum theory using the Navier-Stokes equation. The linear velocity profile in Couette flow of a Newtonian fluid may be interpreted as a result of the frequent interactions between the molecules themselves, where the macroscopic viscosity of the continuum model may be related to kinetic properties of the thermal molecular motion. The key parameter to differ between the two limiting cases discussed, i.e. a gas without collisions and a gas with frequent collisions, is the Knudsen number, $Kn = \lambda/L$, where λ is the average molecular mean free path between collisions in the gas and L is a typical length scale of the macroscopic flow field. The collisionless gas is characterized by $Kn \gg 1$ whereas the Newtonian continuum limit follows as $Kn \ll 1$. The limit $Kn = 0$ corresponds to the Euler equations of inviscid flow. Then the gas is assumed to be in local thermodynamic equilibrium in each point of the flow field. The limits of the Knudsen number for different models are summarized in figure 6 (Bird [1, page y]). What is there referred to as the Boltzmann equation is the model equation of statistical kinetic theory governing the distribution of molecular velocities in a gas that is dilute enough that molecular interactions can be treated as short instance collisions in the overall molecular motion.

The shear stress acting on the wall of the example studied above for the collisionless gas comes about from averaging the gain/loss of momentum experienced by the molecules colliding with the upper/lower plate. If the average speed of the molecules in the vertical direction is $\bar{c} = \sqrt{c_y^2}$, and half of the molecules belongs to each class, the

loss of momentum on the lower wall per unit time and area can be estimated to

$$(1) \quad \tau_w = \frac{mn\bar{c}}{2}U_h,$$

where m is the mass of one molecule and n is the number density. In fact, this expression is a momentum flux density that defines the shear stress on a plate-parallel surface element at any position in between the plates. (The sign of the stress, as usual, shifts with the direction of the unit normal in the vertical direction.) The corresponding relation for a Newtonian fluid in Couette flow is

$$(2) \quad \tau_w = \mu \frac{\partial u}{\partial y} = \mu \frac{U_h}{h}.$$

We may note that the limit $Kn \gg 1$ in (1) is independent of h , whereas the limit for small Kn in (2) does depend on h . As we shall see in more detail later the continuum approach can be interpreted from the result of a microscopic approach with $Kn \ll 1$ if one assumes that the molecules retain their momentum on distances of the order of the mean free path. Thus, the continuum gas can be considered *collisionless* on this very small length scale. The loss of momentum of molecules colliding with the lower wall is then proportional to the average speed in a fluid layer a distance λ above the plate, i.e. $\sim \lambda \frac{\partial u}{\partial y} = \frac{\lambda}{h}U_h$, rather than the velocity of the upper plate. Reforming the collisionless result (1) for a small mean free path we obtain in this case for $Kn \ll 1$

$$(3) \quad \tau_w \sim \frac{mn\bar{c}\lambda}{2} \frac{\partial u}{\partial y} = \frac{mn\bar{c}}{2} \frac{\lambda}{h} U_h,$$

which is a factor Kn smaller than the result in (1). In more general flow cases one may define a local Knudsen number of the form

$$(4) \quad Kn = \lambda \frac{1}{u} \frac{\partial u}{\partial y},$$

or use any other relevant macroscopic gradient in the flow. Next we shall see how to determine the mean free path in a gas.

1.3. The molecular model. The force interaction between molecules is of electrostatic origin. The pair interaction may be described by an interaction potential ϕ which depends on the distance r between the centres of the molecules. The simplest model is the *hard sphere* model, which assumes the interaction force is zero except at contact at $r = d$, the diameter of the molecule. More advanced interaction potentials are sketched in figure 7. The *soft sphere* model accounts for the repulsive near field interaction, whereas the *Sutherland* model accounts for the attractive far field interaction and acts as a hard sphere in the near field. A model that accounts for both far and near fields is e.g. the Lennard-Jones (6-12) potential.

The *cross-section* for a molecular collision is loosely defined as the surface area a molecule must cross in order for the collision to appear. For the hard sphere model it is straight forward to see that this area is given by $\sigma_T = \pi d^2$, see figure 8. For the more advanced molecular models the cross-section will depend on the relative speed, c_r , between the colliding pair. For the Sutherland model, e.g., the cross-section will be larger than for the hard sphere model with the same diameter, since the attraction between molecules increases the probability for a collision. Fast molecules will see a

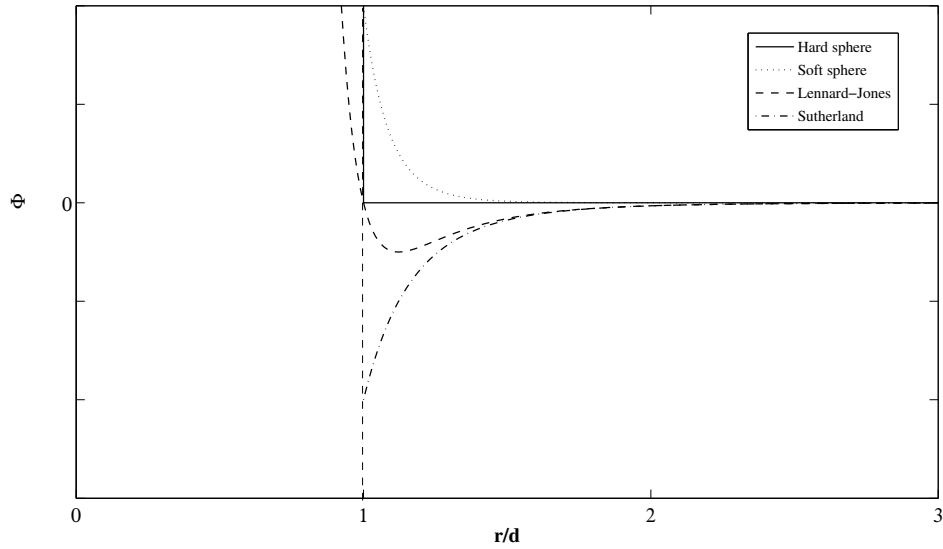


FIGURE 7. Pair interaction potentials of a simple molecule. *Soft sphere*: $\Phi = K/(r/d)^n$, *Lennard-Jones potential*: $\Phi = K[(d/r)^{12} - (d/r)^6]$, *Sutherland potential*: $\Phi = -K(d/r)^6$

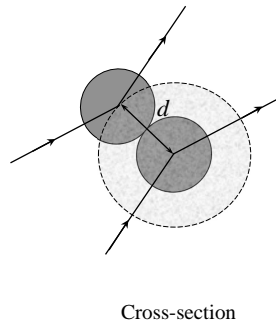


FIGURE 8. Definition of cross-section of a collision.

smaller cross-section than will slow molecules, since the time for interaction decreases with the relative speed. Often one uses a phenomenological model for the cross-section directly rather than derive the cross-section from the actual interaction potential. The *variable hard sphere* model, Bird [1, page y], uses an effective particle diameter

$$(5) \quad d = d_{ref} \left(\frac{c_{r,ref}}{c_r} \right)^\nu,$$

where the subscript *ref* refers to a known reference state and ν is a constant model parameter.

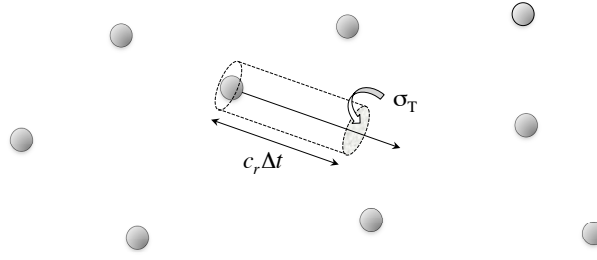


FIGURE 9. Volume swept out by cross-section of test molecule moving relative to the field molecules.

1.4. The dilute gas approximation and the mean free path. At standard temperature and pressure in air the equivalent molecular diameter is $\bar{d}_0 \approx 4 \cdot 10^{-10} m$. This is one order of magnitude smaller than the average distance between the molecules, $\delta_0 \approx 3 \cdot 10^{-9}$. The dilute gas approximation builds on the assumption that $d \ll \delta$. In such a gas binary collisions are the overwhelming dominant events, since the probability of three, or more, particles appearing in the same position in space is so much lower. To obtain the collision frequency of a *test* molecule with speed c_t with the other molecules in a gas, consider first the collision rate with *field* molecules in a specific velocity interval $([c_x, c_x + dc_x], [c_y, c_y + dc_y], [c_z, c_z + dc_z])$. Let the number density of this class of field molecules be denoted dn . The number of collisions within the time interval Δt is then proportional to the volume $\sigma_T c_r \Delta t$ swept out by the cross-section of test molecule in its motion, c_r , relative to the field molecules, see figure 9. The number of collisions of this class is then

$$(6) \quad dn \sigma_T c_r \Delta t.$$

Let $f(\mathbf{c})dc_xdc_ydc_z$ denote the fraction of molecules within the considered class such that $dn = n f(\mathbf{c})dc_xdc_ydc_z$. Then the total number of collisions of the test molecule per unit time is obtained by integrating over all classes of field molecules

$$(7) \quad \nu_{coll}(\mathbf{c}_t) = n \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \sigma_T |\mathbf{c}_t - \mathbf{c}| f(\mathbf{c}) dc_x dc_y dc_z.$$

Considering all classes of test molecules, the average number of collisions of a test molecule is

$$(8) \quad \bar{\nu}_{coll} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \nu_{coll}(\mathbf{c}_t) f(\mathbf{c}_t) dc_{tx} dc_{ty} dc_{tz} = n \bar{\sigma}_T \bar{c}_r,$$

where the bar denotes an *average* over all velocity classes of test and field molecules. For the hard sphere model it is simply

$$(9) \quad (\bar{\nu}_{coll})_{h.s.} = n \pi d^2 \bar{c}_r.$$

The total collision rate per unit volume of gas can then be expressed as

$$(10) \quad \frac{n}{2} \bar{\nu}_{coll} = \frac{n^2}{2} \bar{\sigma}_T \bar{c}_r,$$

where care is taken that each collision is counted only once. Also, we note that this is proportional to the square of the number density as this gives the probability of finding two molecules at the same position.

From the collision rate we define the mean free path as the average distance travelled by the molecules in their *thermal* motion. The thermal motion, \mathbf{c}' , is the random motion of the molecules in addition to the average bulk motion, \mathbf{v} . Thus we can write

$$(11) \quad \mathbf{c} = \mathbf{v} + \mathbf{c}'.$$

The mean free path is then

$$(12) \quad \lambda \equiv \frac{\bar{c}}{\nu_{coll}} = \frac{\bar{c}}{n\bar{\sigma}_T\bar{c}_r},$$

where

$$(13) \quad \bar{c} = |\bar{\mathbf{c}}'|.$$

For hard spheres in a gas in equilibrium (12) reduces to

$$(14) \quad \lambda_{h.s.} = \frac{\bar{c}/\bar{c}_r}{n\pi d^2} = \frac{1}{\sqrt{2}n\pi d^2}.$$

We may now compare the mean free path with the average distance between the molecules with the estimate

$$(15) \quad \frac{\lambda}{\delta} \sim \frac{1}{\sqrt{2}n\pi d^2\delta} \sim \frac{\delta^2}{d^2} \gg 1.$$

Therefore, in a dilute gas we have the scale separation

$$(16) \quad d \ll \delta \ll \lambda.$$

The rule of thumb for applying the dilute gas approximation may be taken as $\delta/d \geq 7$. The limits for applying the different approximations discussed is summarized in figure 10.

1.5. Thermal equilibrium and non-equilibrium. The thermal equilibrium of a dilute gas enclosed in a box is characterised by a uniform macroscopic distribution of mass, momentum ($= 0$) and temperature. There is no preferred direction of molecular speed and there is no energy loss from collisions with the walls of the box. Although collisions take place all the time, the gas appear collision less in a statistical sence. Each time a molecule disappears from a velocity class because of a collision, there is another molecule scattered into that class with the same probability. Therefore, the distribution of molecules on the different classes of molecular velocities does not change with time for a gas in equilibrium. As soon as there is a small departure from equilibrium, e.g. by increasing the wall temperature of the box, the intermolecular collisions act as to retrieve equilibrium again. If the departure from equilibrium is small one often use the concept of *local thermodynamic equilibrium flow*. This is an approximation in that the macroscopic gradients in the flow are so small that the gas is assumed to rapidly adjust to equilibrium according to the local properties of the gas, just as if it was enclosed in a box moving with the local average speed. This is also refered to as isentropic flow and is governed by the macroscopic Euler equations as mentioned earlier, valid for $Kn = 0$, in which mass, momentum and energy is only advected with the macroscopic velocity.

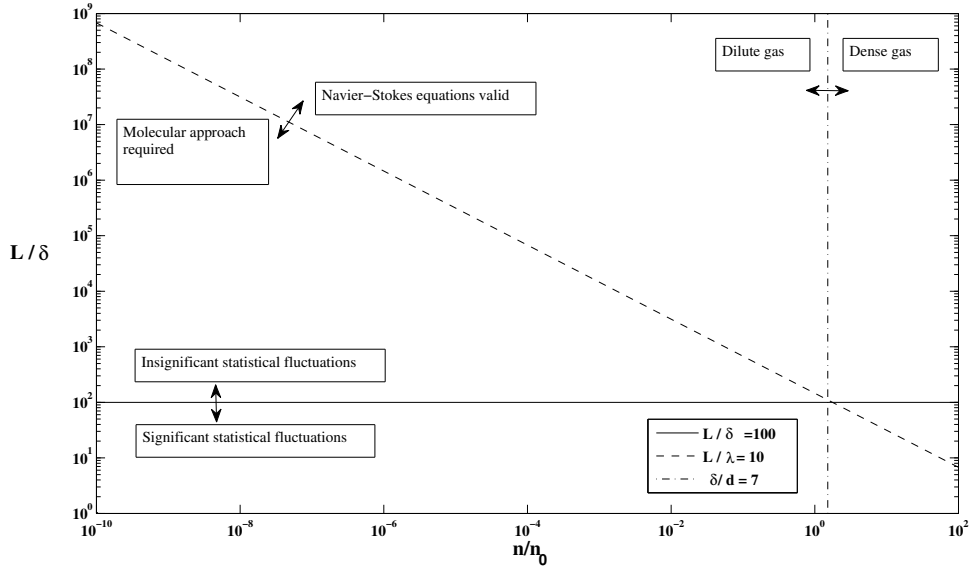


FIGURE 10. Limits for dilute gas approximation, Navier-Stokes equations and insignificant statistical fluctuations.

Sound waves are also part of this limit, where longitudinal transport of mass, momentum and energy occur through propagation of equilibrium pressure waves.

In the next level of approximation, small departures from equilibrium are accounted for. Then there is a small thermal/kinetic transport of both momentum and energy proportional to the corresponding macroscopic gradients. This *diffusion* is an essential part of the Navier-Stokes equations, valid for $Kn \ll 1$. The macroscopic model of diffusion includes the diffusivity D , and the time needed for diffusion of a property to reach a distance ΔL is

$$(17) \quad \Delta t_{diff} \sim \frac{\Delta L^2}{D}.$$

From a microscopic point of view the diffusion comes about by the irregular thermal motion of the molecules as a result of intermolecular collisions. Following a single particle in its thermal motion the average displacement in a chosen coordinate direction is zero when keeping track of positive and negative displacements. However, the average of its squared displacement, $\overline{\Delta x^2}$ is always non-zero, and in fact adding up the collisions $\overline{\Delta x^2} \sim \lambda^2 \nu_{coll} \Delta t_{diff}$. Identifying the root mean square displacement with the diffusion length of the macroscopic model we get

$$(18) \quad D \sim \lambda^2 \nu_{coll} = \lambda \bar{c}.$$

This result holds for the diffusivity of any property of a gas and shows the relation between the macroscopic diffusivity coefficient and the kinetic properties of the gas. It also demonstrates the quantitative importance of the mean free path in flows that

depart from equilibrium. The hand waving arguments leading to (18) will successively be replaced with more stringent theories in what follows.

As we have seen the continuum models break down if Kn is not small, or if the relaxation time to retain equilibrium, $\sim 1/\nu_{coll} = \lambda/\bar{c}$, is long compared to time scales of the flow $\sim 1/(\frac{\partial u}{\partial y})$. Thus, in terms of the mean free path we require for continuum flows also

$$(19) \quad \lambda \frac{\partial u / \partial y}{u} \frac{u}{\bar{c}} = KnM < 1,$$

which is a bit more restrictive in the Kn if $M > 1$. In general we require then $\max[Kn, KnM] \ll 1$ for continuum flow. A typical example from continuum fluid mechanics where the time scale of the flow is short may be found in a strong normal shock wave. Thus, the continuum model using the Navier-Stokes equations breaks down in the thin shock layer describing the rapid transition between the upstream and downstream conditions of the shock.

2. MACROSCOPIC VARIABLES - MICROSCOPIC VARIABLES

In this section we shall see how the macroscopic flow variables are expressed in terms of the kinetic variables. We will not follow each molecule individually in its path and change of velocity due to collisions. Rather we shall use a statistical approach where we classify the molecules in groups according to their velocity and position. Therefore, consider the molecules in a physical-space volume $d\mathbf{r} = dx dy dz$ centered around \mathbf{r} and with velocities in the velocity-space volume $d\mathbf{c} = dc_x dc_y dc_z$ centered around \mathbf{c} . The number of particles in this *phase-space* volume, $d\mathbf{r}d\mathbf{c}$, is expressed as

$$(20) \quad dN = \mathcal{F}(t, \mathbf{r}, \mathbf{c}) d\mathbf{r}d\mathbf{c},$$

where \mathcal{F} is the distribution function in *phase-space*. For the moment we consider \mathcal{F} to be a known function and we shall see how to obtain the macroscopic variables from that. The number density, $n(t, \mathbf{r})$, is obtained by integrating over all classes of velocities

$$(21) \quad n(t, \mathbf{r}) = \int_{-\infty}^{\infty} \mathcal{F}(t, \mathbf{r}, \mathbf{c}) d\mathbf{c}.$$

Now, let $Q(\mathbf{c})$ denote any property of the gas that is carried and transported by the molecule. The total amount of Q per unit volume is then

$$(22) \quad \int_{-\infty}^{\infty} Q(\mathbf{c}) \mathcal{F}(t, \mathbf{r}, \mathbf{c}) d\mathbf{c} = n(t, \mathbf{r}) \bar{Q}(t, \mathbf{r}),$$

where \bar{Q} defines the average of the molecular property $Q(\mathbf{c})$ in the unit volume

$$(23) \quad \bar{Q}(t, \mathbf{r}) = \frac{1}{n(t, \mathbf{r})} \int_{-\infty}^{\infty} \mathcal{F}(t, \mathbf{r}, \mathbf{c}) Q(\mathbf{c}) d\mathbf{c} = \int_{-\infty}^{\infty} f(t, \mathbf{r}, \mathbf{c}) Q(\mathbf{c}) d\mathbf{c}.$$

Here, we have also defined the *velocity distribution function* $f(t, \mathbf{r}, \mathbf{c})$ such that $\mathcal{F}(t, \mathbf{r}, \mathbf{c}) = n(t, \mathbf{r}) f(t, \mathbf{r}, \mathbf{c})$, where by (21)

$$(24) \quad \int_{-\infty}^{\infty} f(t, \mathbf{r}, \mathbf{c}) d\mathbf{c} = 1.$$

Thus, $f(t, \mathbf{r}, \mathbf{c})d\mathbf{c}$ is the local fraction of molecules in the velocity-space volume $d\mathbf{c}$. If we take the property $Q = m$ we have

$$(25) \quad n(t, \mathbf{r})\overline{Q} = nm = \rho,$$

where ρ is the density of the gas. If $Q = \mathbf{c}$ then

$$(26) \quad \overline{Q} = \overline{\mathbf{c}} = \mathbf{v},$$

where \mathbf{v} is the macroscopic velocity. The flux density vector of any property $Q(\mathbf{c})$ is given by

$$(27) \quad \int_{-\infty}^{\infty} \mathcal{F}(t, \mathbf{r}, \mathbf{c})Q(\mathbf{c})d\mathbf{c} = n(t, \mathbf{r})\overline{Q\mathbf{c}}.$$

Introducing the thermal speed $\mathbf{c}' = \mathbf{c} - \mathbf{v}$ in (27) the flux vector may be split in two parts according to

$$(28) \quad n(t, \mathbf{r})\overline{Q\mathbf{c}} = \underbrace{n\overline{Q\mathbf{v}}}_{\text{bulk transport}} + \underbrace{n\overline{Q\mathbf{c}'}}_{\text{kinetic/thermal transport}}.$$

If, e.g., we take $Q = m$ in (28) then

$$(29) \quad n(t, \mathbf{r})\overline{Q\mathbf{c}} = nm\overline{\mathbf{c}} = \rho\mathbf{v},$$

which is the bulk mass flux density vector.

2.1. Transport of momentum. If we take momentum as the *property*, then $Q = m\mathbf{c}$ and we get

$$(30) \quad n(t, \mathbf{r})\overline{Q\mathbf{c}} = \underbrace{\rho\mathbf{v}\mathbf{v}}_{\substack{\text{bulk transport} \\ \text{of momentum}}} + \underbrace{\rho\overline{\mathbf{c}'\mathbf{c}'}}_{\substack{\text{kinetic/thermal transport} \\ \text{of momentum}}}.$$

Equation (30) is a tensor relation since it expresses the average flux density in different directions of the momentum vector $m\mathbf{c}$. The flux density of momentum across a surface with unit normal \mathbf{n} is then the vector

$$(31) \quad n(t, \mathbf{r})\overline{Q\mathbf{c}} \cdot \mathbf{n} = \underbrace{\rho\mathbf{v}\mathbf{v} \cdot \mathbf{n}}_{\substack{\text{bulk transport} \\ \text{of momentum}}} + \underbrace{\rho\overline{\mathbf{c}'\mathbf{c}' \cdot \mathbf{n}}}_{\substack{\text{kinetic/thermal transport} \\ \text{of momentum}}}.$$

Now, consider the rate of change of the property Q in a fixed control volume V due to the net flux of the property out through the control surface S . Considering particles of all classes we have

$$(32) \quad \frac{d}{dt} \int_V n\overline{Q}dV = - \oint_S n\overline{Q\mathbf{c}} \cdot \mathbf{n}dS.$$

As we take $Q = m$ we obtain

$$(33) \quad \frac{d}{dt} \int_V \rho dV = - \oint_S \rho\mathbf{v} \cdot \mathbf{n}dS,$$

which is the equation for conservation of mass in the continuum approach. If there is no external force field acting on the particles (32) should hold also for the momentum vector $Q = m\mathbf{c} = m\mathbf{v} + m\mathbf{c}'$, such that

$$(34) \quad \frac{d}{dt} \int_V \rho \mathbf{v} dV + \oint_S \rho \mathbf{v} (\mathbf{v} \cdot \mathbf{n}) dS = \underbrace{- \oint_S \rho \overline{\mathbf{c}' \mathbf{c}'} \cdot \mathbf{n} dS}_{\text{macroscopic surface force}} .$$

Having transferred the thermal transport of momentum to the right hand side we may interpret it as a force in the average continuum approach, acting on the surface of the control volume. The integrand may be referred to as the *stress tensor*

$$(35) \quad \tilde{\boldsymbol{\sigma}} = -\rho \overline{\mathbf{c}' \mathbf{c}'} = -\rho \begin{pmatrix} \overline{c_x'^2} & \overline{c_x' c_y'} & \overline{c_x' c_z'} \\ \overline{c_y' c_x'} & \overline{c_y'^2} & \overline{c_y' c_z'} \\ \overline{c_z' c_x'} & \overline{c_z' c_y'} & \overline{c_z'^2} \end{pmatrix} .$$

As such it just represents the average flux density of momentum across an element of the control surface given a certain population of particles in the different classes of molecular velocities. Each element in (35) represents the flux in one given coordinate direction of a momentum component in an other independent coordinate direction. If the gas is in equilibrium the population is independent of the direction of the velocity and different velocity components are uncorrelated so that the stress tensor is isotropic

$$(36) \quad \tilde{\boldsymbol{\sigma}}_{eq} = -\rho \begin{pmatrix} \overline{c_x'^2} & 0 & 0 \\ 0 & \overline{c_y'^2} & 0 \\ 0 & 0 & \overline{c_z'^2} \end{pmatrix} ,$$

where $\overline{c_x'^2} = \overline{c_y'^2} = \overline{c_z'^2}$. By defining the *scalar pressure* $p = \rho(\overline{c_x'^2} + \overline{c_y'^2} + \overline{c_z'^2})/3$ from the magnitude of the trace of the general stress tensor we can write for the equilibrium state

$$(37) \quad \tilde{\boldsymbol{\sigma}}_{eq} = -p \tilde{\mathbf{I}} ,$$

where $\tilde{\mathbf{I}}$ is the unit tensor. If the gas is not in equilibrium the deviator defines the viscous stress tensor according to

$$(38) \quad \tilde{\boldsymbol{\tau}} = -(\rho \overline{\mathbf{c}' \mathbf{c}'} - p \tilde{\mathbf{I}}) .$$

Thus, the stress tensor may be expressed

$$(39) \quad \tilde{\boldsymbol{\sigma}} = -p \tilde{\mathbf{I}} + \tilde{\boldsymbol{\tau}} ,$$

and appears in the integral on the right hand side of (34). The viscous stress tensor at equilibrium is $\tilde{\boldsymbol{\tau}}_{eq} = 0$.

To see explicitly how the pressure tensor is related to, e.g., the normal force acting on a wall in a gas in equilibrium one can make the following considerations. The force per unit area of the wall will be equal to the rate of change of momentum of molecules colliding with the wall per unit area. The rate of molecules in a velocity class colliding with the wall per unit area will be $n f(\mathbf{c}') d\mathbf{c}' c'_x$ for all classes with a velocity c'_x in the opposite unit wall-normal direction (see figure 11). The change of momentum for each

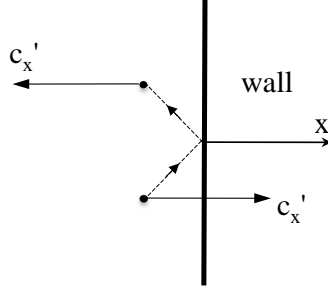


FIGURE 11. Sketch of molecule colliding with a wall indicating the change in direction of the x-momentum.

particle during a collision is $-2mc'_x$ such that the reaction force on the wall integrated over molecules in all classes per unit area is

$$(40) \quad \int_{c'_x > 0} n f(\mathbf{c}') c'_x 2mc'_x d\mathbf{c} = \int_{c'_x > 0} n f(\mathbf{c}') mc_x'^2 d\mathbf{c} + \int_{c'_x < 0} n f(\mathbf{c}') mc_x'^2 d\mathbf{c} = \\ = n \int_{-\infty}^{\infty} f(\mathbf{c}) mc_x'^2 d\mathbf{c} = \rho \overline{c_x'^2} = -\sigma_{xx}.$$

2.2. Transport of energy. We now turn to another property of the molecule, namely the energy. Apart from the kinetic energy molecules with several atoms also have internal modes of energy like rotational and vibrational energy. Thus we can write

$$(41) \quad Q = E = \frac{mc^2}{2} + \epsilon_{int}.$$

For the rotational energy of a spherically symmetric molecule, e.g., we have $\epsilon_{int,rot} = \frac{I\omega^2}{2}$, where I is the moment of inertia and ω the angular frequency. The amount of energy in a unit space volume is then

$$(42) \quad n\overline{Q} = \frac{\rho \overline{c^2}}{2} + n\overline{\epsilon_{int}} = \frac{\rho(\mathbf{v} + \mathbf{c}') \cdot (\mathbf{v} + \mathbf{c}')}{2} + n\overline{\epsilon_{int}} = \underbrace{\frac{\rho v^2}{2}}_{\text{bulk kinetic energy}} + \underbrace{\frac{\rho \overline{c'^2}}{2} + n\overline{\epsilon_{int}}}_{\text{thermal energy}}.$$

The thermal energy per unit mass is

$$(43) \quad e = \underbrace{\frac{\overline{c'^2}}{2}}_{e_{trans}} + \underbrace{\frac{\epsilon_{int}}{m}}_{e_{int}}.$$

From the definition of the scalar pressure, $p = \rho \overline{c'^2}/3$, we see that

$$(44) \quad \frac{p}{\rho} = \frac{2}{3} e_{trans}.$$

Thus, only the translational part of the thermal energy contributes to the pressure. From classical thermodynamics we have the familiar perfect gas law for a gas in equilibrium

$$(45) \quad \frac{p}{\rho} = RT = \frac{kT}{m}.$$

The thermodynamic temperature T is a property defined only for a system in thermodynamic equilibrium, whereas (44) is more generally valid. For non-equilibrium systems we can then generalize the definition and speak about *kinetic* temperatures, characterising the energy contained in a specific mode of molecular thermal energy. Thus the kinetic *translational* temperature is defined by

$$(46) \quad \frac{3}{2}RT_{trans} \equiv e_{trans} = \frac{\overline{c'^2}}{2} = \frac{\overline{c'_x{}^2} + \overline{c'_y{}^2} + \overline{c'_z{}^2}}{2}.$$

One may even define the kinetic translational temperature for motion in the x-direction separately according to

$$(47) \quad \frac{1}{2}RT_{trans, x} \equiv e_{trans, x} = \frac{\overline{c'_x{}^2}}{2}.$$

In equilibrium each translational degree of freedom contributes with the same amount of energy per unit mass $RT/2$. For thermal energy from the internal energy modes we can define a kinetic temperature T_{int} according to

$$(48) \quad \zeta RT_{int} \equiv e_{int} = \frac{I}{m} \frac{(\overline{\omega_x^2} + \overline{\omega_y^2} + \overline{\omega_z^2})}{2},$$

where ζ is the thermal degrees of freedom of the energy mode considered. Only at *equilibrium* we have that $T_{trans} = T_{int} = T$.

The energy flux density vector is obtained by taking $Q = E$ in (28). Thus

$$(49) \quad \begin{aligned} n(t, \mathbf{r})\overline{E\mathbf{c}} &= \underbrace{n\overline{E\mathbf{v}}}_{\text{bulk transport}} + \underbrace{n\overline{E\mathbf{c}'}}_{\text{kinetic/thermal transport}} = \\ &= \left(\frac{\rho\overline{c^2}}{2} + n\overline{\epsilon_{int}} \right) \mathbf{v} + \rho \frac{\overline{c^2\mathbf{c}'}}{2} + n\overline{\epsilon_{int}\mathbf{c}'} = \\ &= \overbrace{\left(\frac{\rho v^2}{2} + \frac{\rho\overline{c'^2}}{2} + n\overline{\epsilon_{int}} \right)}^{\text{bulk transport of energy}} \mathbf{v} + \underbrace{\rho \overline{\mathbf{v} \cdot \mathbf{c}'\mathbf{c}'}}_{\substack{\text{kinetic transport of} \\ \text{mixed term} \\ \mathbf{v} \cdot \mathcal{P} \\ \text{—work by pressure} \\ \text{and viscous forces}}} + \underbrace{\rho \frac{\overline{c'^2\mathbf{c}'}}{2} + n\overline{\epsilon_{int}\mathbf{c}'}}_{\substack{\text{kinetic transport of} \\ \text{thermal energy} \\ \mathbf{q} \\ \text{heat flux density vector}}}. \end{aligned}$$

Below the last line of equation (49) are given the continuum approach interpretations of each of the terms of the energy flux density vector. The first bracket is the bulk transport of bulk kinetic energy and thermal energy. The second, mixed term is the translational work rate performed per unit area by components of the pressure tensor on the surface of any control volume. The last term is the transport of heat by diffusion/heat conduction.

The rate of change of $Q = E$ in the control volume is then given by (32) and (49) as

$$(50) \quad \frac{d}{dt} \int_V \left(\frac{\rho v^2}{2} + \rho e \right) dV + \oint_S \rho \left(\frac{v^2}{2} + e + \frac{p}{\rho} \right) \mathbf{v} \cdot \mathbf{n} dS = \oint_S \mathbf{v} \cdot (\tilde{\boldsymbol{\tau}} \cdot \mathbf{n}) dS - \oint_S \mathbf{q} \cdot \mathbf{n} dS.$$

Here, the stress tensor has been split in the isotropic part, $-p \tilde{\mathbf{I}}$, where the scalar pressure appears on the left hand side as part of the heat function, $h = e + \frac{p}{\rho}$, and the viscous part, $\tilde{\boldsymbol{\tau}}$, appearing in the translational work rate integral over the surface of the control volume. This is the usual form of the energy equation used in the continuum approach, but here all quantities are properly defined from the microscopic kinetic theory approach. Together with (33) and (34) they form the conservation equations for mass, momentum and energy.

In general the velocity distribution function $f(t, \mathbf{r}, \mathbf{c}')$ is unknown and (34), (33) and (50) do not form a closed set of equations for the averaged motion. In reality, if the mean free path is small compared to the size of the control volume, the momentum and energy of the particles entering/leaving the control volume will be transferred by collisions to other particles in the very neighbourhood of the control surface. Macroscopically the flux of momentum is then experienced as a *surface force* acting on the control volume, which magnitude can be related to the *local* gradients of the bulk velocity via the Newtonian viscosity concept, c.f. (2). Similarly, the thermal transport of heat, \mathbf{q} , can be related to the *local* gradient of the temperature. This closed set of equations for small Kn are the Navier-Stokes equations. We shall see later that the Navier-Stokes equations are equivalent to a small but well defined departure from an equilibrium distribution function. For larger Knudsen numbers the thermal transports of momentum and energy across the control surface are no longer *local* phenomena, as the distances travelled by the molecules since their last collisions on the average are *not* small compared to the typical length scale of the problem. The gas is then far from an equilibrium state and the distribution function can no longer be related to the local gradients of the flow.

3. THE MAXWELL-BOLTZMANN VELOCITY DISTRIBUTION FUNCTION.

We shall introduce here the velocity distribution function, $f(c_1, c_2, c_3)$, that prevails in thermodynamic equilibrium. The ideas in this section was first worked out by Maxwell 1859 and later derived also by Boltzmann using statistical mechanics. In forthcoming chapters we shall give another derivation of the equilibrium distribution function, based on the dilute gas approximation and the so called *H-theorem* (see chapter ??). As such, the velocity distribution function gives the probability density in velocity space of finding a molecule with a given velocity $\mathbf{c} = (c_1, c_2, c_3)$. Consider a frame of reference in which the gas is macroscopically at rest, i.e. in which the averages of the velocity components are zero. At equilibrium it turns out that the velocity components are uncorrelated, or independent, stochastic variables so that we must have

$$(51) \quad f(c_1, c_2, c_3) = f_1(c_1)f_2(c_2)f_3(c_3).$$

The equilibrium velocity distribution function is also isotropic, i.e., the value of f depends only on $|\mathbf{c}|$. Thus if we vary the velocity components in such way that

$$(52) \quad c^2 = c_1^2 + c_2^2 + c_3^2 \equiv g(c_1, c_2, c_3)$$

is kept constant the differential $df = 0$. Equivalently $d(\ln(f)) = df/f = 0$ for changes of the velocity components under the constraint $g(c_1, c_2, c_3) = \text{const.}$. We may formulate this according to the method of Lagrange multipliers: Find $\min\{\ln[f(c_1, c_2, c_3)]\}$ under the constraint $g(c_1, c_2, c_3) = \text{const.}$ Thus we require

$$(53) \quad \frac{\partial(\ln f)}{\partial c_i} = \lambda \frac{\partial g}{\partial c_i},$$

where λ is the Lagrange multiplier and i can be any one of the coordinate directions. With (51) and (52) we get from (53) that

$$(54) \quad \frac{d(\ln f_i)}{dc_i} = \lambda 2c_i.$$

Since this must hold for any direction i , λ must be a (single) constant, independent of the velocity components. By integration we find

$$(55) \quad \ln(f_i) = \lambda c_i^2 + \ln(\alpha),$$

and

$$(56) \quad f_i(c_i) = \alpha e^{\lambda c_i^2},$$

where α is an integration constant that is determined from the normalization condition $\int_{-\infty}^{\infty} f_i(c_i) dc_i = 1$. Thus, as f_i must be finite for large velocities, λ must be a negative constant, say, $\lambda = -\beta^2$. The normalization condition then gives $\alpha = \beta/\sqrt{\pi}$ and

$$(57) \quad f_i(c_i) = \frac{\beta}{\sqrt{\pi}} e^{-\beta^2 c_i^2}.$$

Apparently, f_1 , f_2 and f_3 are identical functions of c_1 , c_2 and c_3 respectively. The complete velocity distribution function at equilibrium is then

$$(58) \quad f(c_1, c_2, c_3) = \frac{\beta^3}{\pi^{3/2}} e^{-\beta^2(c_1^2 + c_2^2 + c_3^2)}.$$

The non-dimensional, one-component Maxwell-Boltzmann velocity distribution function f_i/β versus $c_i\beta$ is shown in figure 12. The parameter β is related to the mean square speed of the molecules

$$(59) \quad \overline{c^2} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} c^2 f dc_1 dc_2 dc_3 = \int_0^{\infty} c^2 \frac{\beta^3}{\pi^{3/2}} e^{-\beta^2 c^2} 4\pi c^2 dc = \frac{3}{2\beta^2}.$$

(In the second integral of (59) we have introduced spherical coordinates in velocity space for convenience). The last integral can be found evaluated in standard mathematical tables of integrals. Also, we have previously related the mean square speed to the macroscopic temperature at equilibrium via the perfect gas law

$$(60) \quad \frac{\overline{c^2}}{3} \equiv \frac{p}{\rho} = \frac{kT}{m}.$$

Thus, by (59) and (60) we have

$$(61) \quad \frac{1}{\beta^2} = \frac{2\overline{c^2}}{3} = 2 \frac{kT}{m}.$$

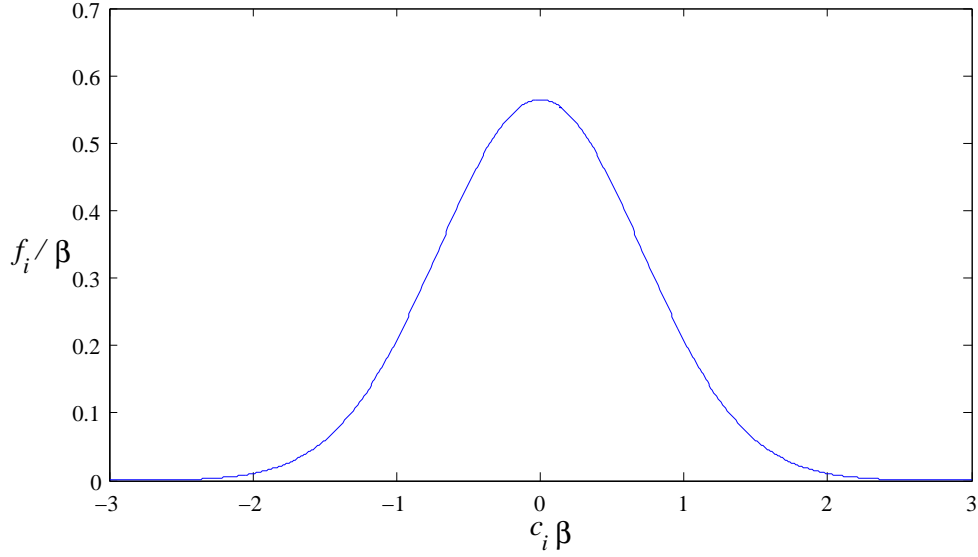


FIGURE 12. The one-component Maxwell-Boltzmann velocity distribution function.

In terms of the macroscopic temperature the Maxwell-Boltzmann distribution is then given by

$$(62) \quad f(c_1, c_3, c_3) = \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m}{2}(c_1^2 + c_2^2 + c_3^2)/(kT)}.$$

As the distribution is independent of the direction of the velocity, it is convenient to introduce spherical coordinates in velocity space, just as in (59). The distribution function is then expressed only in terms of the magnitude of the velocity, $c = \sqrt{c_1^2 + c_2^2 + c_3^2}$. The probability of finding a molecule with speed in the interval $[c, c + dc]$ with any direction is then $f(c)4\pi c^2 dc$. The probability density for the speed c is then

$$(63) \quad f_c(c) = f(c)4\pi c^2 = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{3/2} c^2 e^{-\frac{mc^2}{2}/(kT)}.$$

This function is plotted in figure 13 for some different temperatures in air. At higher temperatures the distribution is shifted towards higher molecular speeds and is spread over a wider range of velocities.

4. THE MACROSCOPIC DESCRIPTION OF KINETIC TRANSPORT PHENOMENA.

We have previously adressed the importance of the limit of small Knudsen numbers, $Kn \ll 1$, leading to the well known Navier-Stokes equations where the kinetic transport terms can be modelled as local phenomena. In this section we shall see how to relate the macroscopic concepts of viscosity, heat conduction and scalar diffusion to the kinetic variables of the gas. The approach will follow the *mean free path method* which emphasizes on the physical mechanisms of the kinetic transport. A more rigorous approach, the *Chapman-Enskog method*, will be discussed later in section ??.

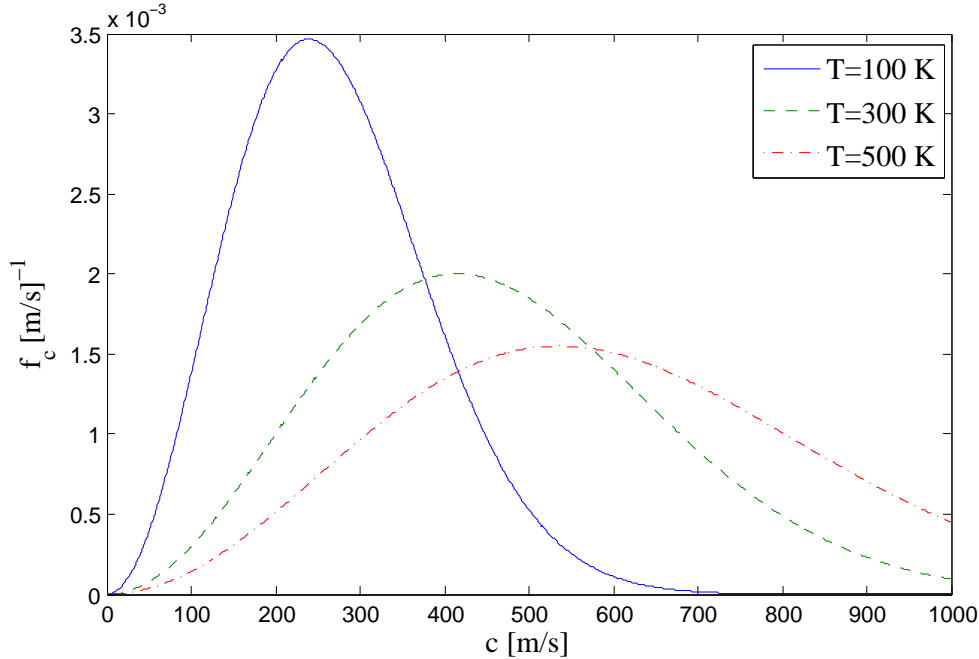


FIGURE 13. The Maxwell-Boltzmann distribution function of the molecular speed in air. $T = 100K, 300K, 500K$, $R = k/m = 287J/(kgK)$, corresponding to $c_{rms} = \sqrt{c^2} = \sqrt{3RT} = 293 m/s, 508 m/s, 656 m/s$.

| | | | |
|-----------------------------|---|--|---|
| non-uniform | flow velocity | temperature | composition |
| transported quantity | momentum | internal energy | mass of species |
| macroscopic model | viscosity | heat conduction | mass diffusivity |
| formula | $\tau_{xy} = \mu \frac{\partial u}{\partial y}$ | $q_y = -k \frac{\partial T}{\partial y}$ | $j_A = -D_{AB} \frac{\partial n_A}{\partial y}$ |

TABLE 1. Models of macroscopic transport phenomena.

In thermodynamic equilibrium all macroscopic variables of the gas are uniformly distributed in space, and there is no net transport of mass, neither of momentum nor energy. The *cause* of any transport is a non-uniform distribution of a macroscopic quantity. The resulting *action* of the non-equilibrium state is a transport of the property carried by molecules during their random movements. The relevant mathematical models are summarized in table 1. To see the basic mechanism behind thermal transport of a macroscopic quantity, consider the flux density vector (27) introduced in section 2. We are interested in the *thermal transport*, the second term of (27). Let's assume the quantity Q macroscopically is non-uniformly distributed in space according to $\bar{Q}(y)$. Thus, molecules at different positions of y on the average carry different values of Q which may be transferred to other positions in y due to the molecules random motion in the y -direction. A specific value of Q is carried by a molecule only until its next collision so that excess values of Q are transferred from one position to another position at an

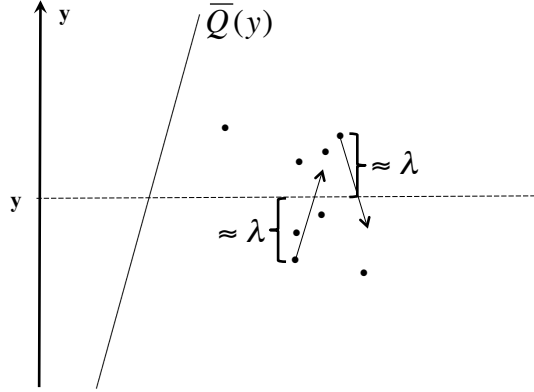


FIGURE 14. Schematic of molecular transport in y -direction of property Q .

average distance on order of the mean free path away. This is illustrated schematically in figure 14. The flux density of Q in the y -direction is given by $n(y)\overline{Qc'_y}$. To actually calculate this average we would need the expression for the velocity distribution function $f(t, \mathbf{r}, \mathbf{c})$. However, the previous discussion may be used to derive an estimate. First, let's divide the molecules in two classes according to the sign of c'_y . It is reasonable to believe that there are the same number of molecules in each of these classes at any y -position. The molecules in the class $c'_y > 0$ on the average come from a position $y - \lambda$ since their last collisions and carry a value $\overline{Q}(y - \lambda)$ of the transported quantity. The contribution to the flux density $n(y)\overline{Qc'_y}$ for this class can then be estimated to $\frac{1}{2}n(y)\overline{Q}(y - \lambda)|\overline{c'_y}|$, where the average magnitude of the speed in the y -direction can be estimated as $|\overline{c'_y}| \approx \sqrt{\overline{c_y^2}} \approx \overline{c'}$. For the other class, $c'_y < 0$, the corresponding estimate of the flux density is $\frac{1}{2}n(y)\overline{Q}(y + \lambda)(-\overline{c'_y})$. Adding the estimates to the contributions from the two classes we get

$$\begin{aligned}
 n(y)\overline{Qc'_y} &\approx \frac{1}{2}n(y)\overline{Q}(y - \lambda)\overline{c'} + \frac{1}{2}n(y)\overline{Q}(y + \lambda)(-\overline{c'}) = \\
 (64) \quad &= \frac{n(y)\overline{c'}}{2} \left(\frac{\overline{Q}(y - \lambda) - \overline{Q}(y + \lambda)}{2\lambda} \right) 2\lambda = -n(y)\overline{c'}\lambda \left(\frac{d\overline{Q}}{dy} + \frac{\lambda^2}{6} \frac{d^3\overline{Q}}{dy^3} + \dots \right).
 \end{aligned}$$

The last term of the expansion in (64) will be small compared to the first term if $\lambda^2\overline{Q}/L^3 \ll \overline{Q}/L$, i.e. if $\lambda^2/L^2 = Kn^2 \ll 1$. A more careful application of the *mean free path method* used here, based on the small departure from the Maxwell-Boltzmann velocity distribution, shows that the average distance travelled by a molecule in a given direction since its last collision is $2\lambda/3$ rather than λ , and that the number flux density of molecules in a given direction is $n\overline{c'}/4$ rather than $n\overline{c'}/2$. With these modifications we can write for small Knudsen numbers

$$(65) \quad n\overline{Qc'_y} \approx -\frac{n\overline{c'}\lambda}{3} \frac{d\overline{Q}}{dy}.$$

4.1. **Diffusion of momentum.** Now, let the transported quantity be the momentum in the x -direction, $Q = mc_x$. Then $\bar{Q} = m\bar{c}_x = mv_x$, and (65) gives

$$(66) \quad \overline{\rho c_x c_y'} = \overline{\rho c_x' c_y'} \equiv -\tau_{xy} = -\frac{\rho \bar{c}' \lambda}{3} \frac{dv_x}{dy}.$$

We may then identify the macroscopic Newtonian dynamic viscosity as

$$(67) \quad \mu = \frac{\rho \bar{c}' \lambda}{3},$$

and the kinematic viscosity

$$(68) \quad \nu = \frac{\bar{c}' \lambda}{3}.$$

Thus, it is clear that for a gas the viscosity, μ , and diffusivity of momentum, ν , increase with the magnitude of the thermal motion, \bar{c}' , and the mean free path, λ . Using the previous expression, (12), derived for the mean free path we get

$$(69) \quad \mu = \frac{m \bar{c}'^2}{3 \sigma_T \bar{c}_r}.$$

Using the simplifying assumption of hard spheres for the cross section, $\sigma_T = \pi d^2$, and since from the definition of scalar pressure and the perfect gas law $\frac{\bar{c}'^2}{3} = \frac{p}{\rho} = \frac{k}{m} T$, we find

$$(70) \quad \mu = \frac{kT}{\pi d^2 \bar{c}_r} \approx \frac{\sqrt{mkT}}{\pi d^2},$$

where we also use that the mean relative speed is proportional to the root mean square speed. Thus the viscosity in a gas of hard spheres increases with the square root of the temperature.

REFERENCES

- [1] Bird, G.A. (1994) *Molecular Gas Dynamics and the Direct Simulation of Gas Flows*. Oxford University Press.