Kinetic gas theory for gas in gravitational field

We approach the problem using kinetic gas theory. For simplicity all molecules are assumed to be identical of mass *m.* We assume that the temperature gradient is such that the system is statically stable, i.e. the decrease of the temperature with increasing altitude is slower than the adiabatic lapse rate or in in other words the potential temperature is not decreasing with altitude. It's also assumed that the system is homogenous in horizontal direction and that there are no large scale horizontal motions (winds).

In the spirit of kinetic gas theory it's assumed that the velocity distribution of the molecules is isotropic at all altitudes, but the horizontal degrees of freedom enter the calculation only indirectly.

Let us consider the density function *n(z, w, t)* where *z* is the altitude, *w* vertical velocity and *t* time. We do not consider explicitly the coordinates *x* and *y* or horizontal components of the velocity. The assumptions made at the beginning imply that there is no dependence on horizontal position, while the density function is taken to represent the integral over all values of horizontal velocities.

The number of particles with an altitude in the range (*z, z+dz*) and vertical velocity in the range (*w, w+dw*) at the moment *t* is

$$n(z, w, t)\ dz\ dw$$

At a differentially earlier time *t - dt* the same particles were at the vertical coordinate *z - w dt* and their vertical velocity was *w +* g *dt* where g is the gravitational acceleration. The influence of the change of velocity to the vertical coordinate is second order in time differential and can be neglected. The time differential is also taken to be so small that collisions can be left out of the consideration (role of collisions is discussed below). Thus we have

$$n(z, w, t) = \ n(z - w\ dt, w + \mathrm{g}\ dt, t - dt), \qquad (1)$$

In a stationary situation there is no explicit time dependence, and we have

$$n(z - w\ dt, w + \mathrm{g}\ dt, t - dt) = n(z, w, t) - w\ \frac{\partial n}{\partial z}\ dt + \mathrm{g}\ \frac{\partial n}{\partial w}\ dt, \qquad (2)$$

Combining the two above equations we have

$$\frac{\partial n}{\partial z} = \frac{\mathrm{g}}{w}\ \frac{\partial n}{\partial w}\ , \qquad (3)$$

as the condition required to have a stationary state, when molecules are moving in accordance with thermal motion in the atmosphere.

According to the kinetic gas theory every component of the velocity is distributed in accordance to the Maxwell-Boltzmann distribution. Combining that with altitude dependent density profile *ρ*(*z*) and temperature *T*(z) we can write

$$n(z,w) = \rho(z)\sqrt{\frac{m}{2\pi \mathrm{k}T(z)}}\exp\left(-\frac{mw^2}{2\mathrm{k}T(z)}\right), \qquad (4)$$

From this we have

$$\frac{\mathrm{g}}{w}\frac{\partial n}{\partial w} = -\frac{\mathrm{g}m}{\mathrm{k}T}n, \qquad (5)$$

and

$$\frac{\partial n}{\partial z} = \left(\frac{1}{\rho}\frac{d\rho}{dz} - \frac{1}{2}\left(1 + \frac{mw^2}{\mathrm{k}T}\right)\frac{1}{T}\frac{dT}{dz}\right)n, \qquad (6)$$

and finally from (3), (5), and (6)

$$\frac{1}{\rho}\frac{d\rho}{dz} - \frac{1}{2}\left(1 + \frac{mw^2}{\mathrm{k}T}\right)\frac{1}{T}\frac{dT}{dz} = -\frac{\mathrm{g}m}{\mathrm{k}T}, \qquad (7)$$

One solution of equation (7) is the isothermal case T = constant, where the second term of the left hand side is zero and the standard barometric formula is obtained

$$\rho(z) = \rho_0 \exp\left(-\frac{\mathrm{g}mz}{\mathrm{k}T}\right), \qquad (8)$$

While the above derivation doesn't prove that other solutions do not exist, it does prove that the isothermal solution is compatible with taking gravitation into account in the kinetic gas theory.

Expressed in other words, the above derivation shows how it's possible that the Maxwell-Boltzmann distribution of the same temperature can be valid at all altitudes in spite of the fact that the vertical motion of the molecules is affected by the gravitation. The result is dependent on the mathematical form of the Maxwell-Boltzmann distribution through the equation (5), whose simple form is true specifically for the Maxwell-Boltzmann velocity distribution of the vertical velocity. In this specific case the gravitational acceleration, the density profile and the influence of the initial vertical velocities of the molecules combine to maintain the stationary density and temperature profiles.

The equations (1), (2) and (3) represent the stationarity requirement that particles located in certain volume with certain velocities will at a later moment be replaced by an equal number of other particles which have the same velocities when the influence of gravity on velocity is taken into account. It's shown that the isothermal atmosphere with Maxwell-Boltzmann velocity distribution and barometric vertical density profile satisfies this requirement.

The role of molecular collisions

In the above discussion the collisions have been neglected and only the free movement between collisions considered. The collisions are, however, an essential part of kinetic gas theory as they are the mechanisms that maintains the local thermal equilibrium and the related isotropic Maxwell-Boltzmann velocity distribution. In kinetic gas theory the collisions are assumed to be momentary. Thus the particles are always in free motion, but the velocity can change discontinuously in collisions. If the velocity distribution differs from the equilibrium distribution, which is the Maxwell-Boltzmann distribution, then the collisions will bring the distribution towards the equilibrium distribution, but if the distribution is already the equilibrium distribution, then it remains unchanged.

The solution presented above tells that free molecular motion in gravitational field maintains the isothermal equilibrium, when it has been reached. Here we have seen that the collisions do also maintain the isothermal equilibrium. Thus it's indeed stationary both between collisions and in collisions. Furthermore the collisions provide a mechanism that brings a nonequilibrium state to local thermal equilibrium. Similarly temperature gradients will be removed by the random motion of molecules following the differential equation of heat conduction through a horizontal area A

$$\frac{dQ}{dt} = -\kappa A \frac{\partial T}{\partial z}, \qquad (9)$$

which is equally valid for gas in gravitational field as it's in other material. The conductivity is proportional to the mean free path between collisions λ and the average speed of the molecules $\bar{u}$

$$\kappa = \frac{1}{3} C_V \bar{u} \lambda, \qquad (10)$$