Mathematical Geoscience

The course is divided roughly into three sections, on Climate, Rivers, and Glaciers.

This is primarily a course in mathematical modelling, with application to real world problems. It will use a variety of techniques for developing and solving models based on ordinary and partial differential equations. A certain amount of physics and chemistry will be introduced and translated into the language of differential equations, so an interest in the applications of mathematics to wider branches of science is helpful.

1 Climate

1.1 Energy balance models

We begin with a simple climate model to describe the temperature of the Earth's atmosphere.

Most of the mass in the atmosphere is contained within the first 10 km (the troposphere), so we treat it simplistically as a layer of depth $d = 10$ km, average density ρ and temperature T (in fact, the density and temperature both decrease with height in the troposphere, as we discuss more later).

The primary components of the global energy balance are radiative fluxes: we receive shortwave radiation (UV and visible light) from the sun, and emit longwave radiation (infra-red) to space. The balance between these fluxes is the primary factor determining the temperature of the planet. We discuss the theory of radiation in more detail later; for the moment we require only some basic results.

The shortwave radiation received from the sun is $Q \approx 1370$ W m^{-2}. Part of this radiation is absorbed at the Earth's surface, while part is reflected back into space, either from the surface or from clouds in the atmosphere. The fraction reflected is called the albedo, a, and depends on properties of the surface (light surfaces, such as snow, have a high albedo, $a \approx 0.9$; darker surfaces, such as the ocean, have a smaller albedo, $a \approx 0.1$.) The global average albedo is $a \approx 0.3$.

The net shortwave energy flux received from the sun is therefore

$$\pi R^2 Q(1-a), \tag{1.1}$$

where R is the Earth's radius, Q is the solar radiation, and a is the planetary albedo.

A 'black body' with temperature T_e (units K, where 0 C $\approx$ 273 K) emits radiation Q_e (energy per unit time emitted per unit surface area, units W m^{-2}) according to the law,

$$Q_e = \sigma T_e^4, \tag{1.2}$$

where $\sigma \approx 5.67 \times 10^{-8}$ W m^{-2} K^{-4} is the Stefan-Boltzmann constant. (A surface emissivity ε is often included in this law, but we ignore it since it is approximately 1.) The Earth's surface emits radiation according to this law, but some of this longwave radiation is absorbed by the atmosphere and emitted back again. This is the greenhouse effect, which we will discuss further below. It results in the surface temperature T being larger than the *effective emiting temperature* T_e, and we write

$$T_e = \gamma^{1/4} T, \tag{1.3}$$

where $\gamma < 1$ is a greenhouse factor, which depends on the optical thickness of the atmosphere (a function of greenhouse gasses, water vapour, etc.).

The net longwave energy flux radiated from the Earth is therefore

$$4\pi R^2 \sigma \gamma T^4. \tag{1.4}$$

Combining these incoming and outgoing components, the net received radiation over the planetary surface is

$$\pi R^2 Q(1-a) - 4\pi R^2 \sigma \gamma T^4, \tag{1.5}$$

and this must be equated to the rate of change of the planetary heat content, $4\pi R^2 d\rho c_p T$, where d is the thickness of the atmosphere, ρ is the average density, and c_p is the specific heat capacity of the air. Thus we have

$$c\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{1}{4}Q(1-a) - \sigma\gamma T^4, \tag{1.6}$$

where $c = \rho c_p d$ is the heat capacity of the atmosphere.

This equation has a unique steady state,

$$T = \left(\frac{Q(1-a)}{4\sigma\gamma}\right)^{1/4}. \tag{1.7}$$

The timescale for evolution to the steady state is (balancing terms in the equation),

$$[t] = \frac{d\rho c_p T}{Q(1-a)} \approx 35 \text{ d}, \tag{1.8}$$

using $d \approx 10$ km, $\rho \approx 1$ kg m^{-3}, $c_p \approx 10^3$ J kg^{-1} K^{-1}, $T \approx 288$ K, $Q \approx 1370$ W m^{-2}, and $a \approx 0.3$. This relatively rapid timescale means that the atmosphere responds rapidly to changes in forcing (eg. an increase in CO$_2$ causing a decrease in γ).

If we take $\gamma = 1$, the equilibrium temperature for the Earth is predicted to be $T \approx 255$ K, compared to the actual average temperature of around 288 K. We see that the greenhouse effect is important in keeping the Earth warm enough for us to live on; the value of γ inferred from (1.3) is $\gamma \approx 0.61$.

The same simple model can be used to estimate the equilibrium temperature of other planets. The solar radiation falls off with the inverse square of distance from the sun, so if planetary albedos were the same, the temperatures would fall off as the 1/8th power of distance from the sun. However the albedo depends on surface and atmosphere properties and varies significantly between planets, so the relationship is not so straightforward. In addition, the greenhouse factor γ is different for each planet.

Taking $\gamma = 1$ for Venus, with $Q \approx 2640$ W m^{-2} and $a \approx 0.77$, would give $T \approx 230$ K, whereas the actual surface temperature averages around 740 K. We infer that the greenhouse factor for Venus is $\gamma \approx 0.01$, so the greenhouse effect is much stronger than on Earth.

1.2 Radiation and the greenhouse factor

Here we describe some basic theory of radiative energy transfer, with the goal to provide a description of the greenhouse effect.

1.2.1 Radiative energy transfer

Radiation is the transfer of energy by electromagnetic waves. At each point in space the wave field can be broken down into waves of different frequencies travelling in different directions. We define the intensity

$$I_\nu(\mathbf{x}, \hat{\mathbf{s}}), \tag{1.9}$$

as the energy flux per unit surface area of waves with frequency ν travelling in direction $\hat{\mathbf{s}}$, at position $\mathbf{x}$. Frequency is related to wavelength by $\lambda = c/\nu$, where c is the speed of light. The total radiative energy flux may be written as

$$\mathbf{q}(\mathbf{x}) = \int_\circ \int_0^\infty I_\nu(\mathbf{x}, \hat{\mathbf{s}})\hat{\mathbf{s}}\ \mathrm{d}\nu\ \mathrm{d}\omega, \tag{1.10}$$

where the first integral is taken over all frequencies ν and the second is taken over all directions, where $\mathrm{d}\omega = \mathrm{d}\omega(\hat{\mathbf{s}})$ is the element of solid angle associated with direction $\hat{\mathbf{s}}$. Solid angle is the three-dimensional generalisation of a normal angle, and can be thought of as the projected area of a beam onto a unit sphere. In terms of the two polar angles, $\hat{\mathbf{s}} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$, and $\mathrm{d}\omega = \sin\theta\ \mathrm{d}\theta\ \mathrm{d}\phi$.

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The radiative transfer equation describes the rate of change of intensity I_ν in direction $\hat{\mathbf{s}}$,

$$\frac{\partial I_\nu}{\partial s} = -\rho\kappa_\nu I_\nu + \rho\kappa_\nu B_\nu. \tag{1.11}$$

Here, $\partial/\partial s = \hat{\mathbf{s}} \cdot \nabla_{\mathbf{x}}$. The first term describes absorption by the atmosphere and the second term describes re-emission, where ρ is the density and κ_ν are absorption coefficients. Re-emssion is assumed to be independent of direction (i.e. independent of $\hat{\mathbf{s}}$) and is described by the Planck function

$$B_\nu = \frac{2h\nu^3}{c^2(e^{h\nu/kT} - 1)}, \tag{1.12}$$

which describes the emission of radiation for given local temperature T. Here $h \approx 6.6 \times 10^{-34}$ J s is Planck's constant, $c \approx 3.0 \times 10^8$ m s^{-1} is the speed of light, and $k \approx 1.38 \times 10^{-23}$ J K^{-1} is Boltzmann's constant.

In reality the atmosphere absorbs radiation of different frequencies at different rates (depending on its composition), so that κ_ν are strongly dependent on frequency, and the radiative transfer equation (1.11) must be solved separately for each frequency. To make analytical progress, however, we make the approximation that the atmosphere is 'grey', meaning that $\kappa_\nu = \kappa$ is independent of frequency.

We can then define the total radiation intensity and emission intensity as

$$I(\mathbf{x}, \mathbf{s}) = \int_0^\infty I_\nu \, \mathrm{d}\nu, \qquad B(\mathbf{x}) = \int_0^\infty B_\nu \, \mathrm{d}\nu, \tag{1.13}$$

and integrate the radiative transfer equation assuming $\kappa_\nu = \kappa$ to give

$$\frac{\partial I}{\partial s} = -\rho\kappa(I - B). \tag{1.14}$$

In fact, a truly grey atmosphere is not a good approximation. Some frequencies are much more strongly absorbed, but there are 'windows' in the absorption spectrum that allow more effective transmission of short wave radiation ($\lambda \approx 0.3 - 1$ μm, including visible light), and long wave radiation ($\lambda \approx 8 - 14$ μm). We are mostly interested in the latter window (the greenhouse effect depends on how much of the longwave radiation emitted from the Earth's surface is absorbed and emitted back again), and can effectively consider just the frequency/wavelength range corresponding to this window. By assuming the absorption coefficient is independent of frequency *within* that window, we may still make use of the grey approximation.

If we also make the assumption of *local radiative equilibrium*, which assumes that radiation is the only heat transfer mechanism, then B must be equal to the average of the radiation over all directions at each point,

$$B(\mathbf{x}) = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi I(\mathbf{x}, \hat{\mathbf{s}}) \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi. \tag{1.15}$$

This statement is due to energy conservation, because the energy absorbed and emitted by an infinitesimal parcel of the medium must be equal in the absence of other methods of energy transfer.

Note that (1.12) can be integrated (exercise) to give,

$$B = \frac{\sigma T^4}{\pi}, \tag{1.16}$$

where $\sigma = 2\pi^5 k^4 / 15 h^3 c^2$ is the Stefan-Boltzmann constant, so that B is also related to the local temperature at each point.

1.2.2 Two-stream approximation

We consider a one-dimensional atmosphere so $I = I(z,\theta)$, where θ is the angle of $\hat{\mathbf{s}}$ to the vertical. Then $\partial/\partial s = \cos\theta\partial/\partial z$, so the radiative transfer equation becomes

$$\cos\theta\frac{\partial I}{\partial z} = -\rho\kappa(I - B). \tag{1.17}$$

Since ρ may depend on z, it is helpful to define a new vertical coordinate, the optical depth τ, by

$$\tau = \int_z^\infty \rho\kappa \, \mathrm{d}z. \tag{1.18}$$

If we also write $\mu = \cos\theta$, then $I = I(\tau, \mu)$ satisfies

$$\mu\frac{\partial I}{\partial\tau} = I - B, \tag{1.19}$$

where the radiative equilibrium assumption is

$$B = \frac{1}{2\pi}\int_0^{2\pi}\int_0^{\pi} I\sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi = \int_{-1}^{1} I(\tau,\mu) \, \mathrm{d}\mu. \tag{1.20}$$

We next make an approximation (the Schuster-Schwarzschild approximation) to reduce all the different directions of radiation to just two averages, over upwards and downwards directions,

$$I_+ = \frac{1}{2\pi}\int_0^{2\pi}\int_0^{\pi/2} I\sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi = \int_0^1 I \, \mathrm{d}\mu, \tag{1.21}$$

$$I_- = \frac{1}{2\pi}\int_0^{2\pi}\int_{\pi/2}^{\pi} I\sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi = \int_{-1}^{0} I \, \mathrm{d}\mu. \tag{1.22}$$

The net upwards and downwards radiative fluxes (*i.e.* the vertical components $I(z,\theta)\cos\theta$) are given by

$$F_+ = \int_0^{2\pi}\int_0^{\pi/2} I\cos\theta\sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi = 2\pi\int_0^1 I\mu \, \mathrm{d}\mu \approx \pi I_+, \tag{1.23}$$

$$F_- = -\int_0^{2\pi}\int_{\pi/2}^{\pi} I\cos\theta\sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi = -2\pi\int_{-1}^{0} I\mu \, \mathrm{d}\mu \approx \pi I_-, \tag{1.24}$$

where the final approximations are based on the fact that $\int_0^1 \mu \, \mathrm{d}\mu = \frac{1}{2}$.

Using this same approximation, we can integrate (1.19) with respect to μ (from -1 to 0 and from 0 to 1) to give

$$\frac{1}{2}\frac{\mathrm{d}I_+}{\mathrm{d}\tau} = I_+ - B, \tag{1.25}$$

$$-\frac{1}{2}\frac{\mathrm{d}I_-}{\mathrm{d}\tau} = I_- - B. \tag{1.26}$$

With the local radiative equilibrium assumption, $B = \frac{1}{2}(I_+ + I_-)$, these become

$$\frac{\mathrm{d}I_+}{\mathrm{d}\tau} = \frac{\mathrm{d}I_-}{\mathrm{d}\tau} = I_+ - I_-. \tag{1.27}$$

Boundary conditions are $I_- = 0$ at $\tau = 0$, which expresses the fact that there is no incoming radiation at the top of the atmosphere, and $\pi I_+ = \sigma T_s^4$, which expresses the flux from the surface according to the Stefan-Boltzmann law, where T_s is the surface temperature.

Subtracting (1.26) from (1.25) we see that the net upwards flux $F = F_+ - F_- = \pi(I_+ - I_-)$ is constant (independent of τ), and each of the equations can therefore be integrated to give

$$F_- = \pi I_- = F\tau, \qquad F_+ = \pi I_+ = F(1+\tau). \tag{1.28}$$

The surface boundary condition therefore gives

$$F = \frac{\sigma T_s^4}{1+\tau_s}, \tag{1.29}$$

where $\tau_s = \int_0^\infty \rho\kappa \, \mathrm{d}z$ is the optical thickness of the atmosphere.

Note that the net upwards flux F defines the effective emitting temperature T_e according to

$$F = \sigma T_e^4, \tag{1.30}$$

and therefore

$$T_s = (1+\tau_s)^{1/4} T_e. \tag{1.31}$$

This explains why the surface temperature is warmer than the effective emitting temperature, and we may read off how the greenhouse factor γ, defined earlier, is related to the optical thickness of the atmosphere,

$$\gamma = \frac{1}{1+\tau_s}. \tag{1.32}$$

Moreover, $B = F(\frac{1}{2} + \tau)/\pi$, so the atmospheric temperature T from (1.16) is related to T_e by

$$T = \left(\frac{\frac{1}{2}+\tau}{1+\tau_s}\right)^{1/4} T_e, \tag{1.33}$$

which suggests that the temperature decreases with height.

In reality, this expression does not well describe the temperature variation with height, because the assumption of local radiative equilibrium is not valid. Convection and moisture transport are also important mechanisms of heat transport within the atmosphere.

1.3 The runaway greenhouse effect

The optical thickness of the atmosphere depends on its composition. Water vapour, carbon dioxide, methane, and other gasses contribute to increasing the absorption coefficient κ, which in turn causes an increase in the optical thickness τ_s and a decrease in the greenhouse factor γ.

An interesting question is what determines this value, and why there appears to be a large difference in the greenhouse factor between Earth and Venus. We have seen that an increase in the greenhouse effect results in larger surface temperature, which we would expect to enhance evaporation and therefore increase the quantity of water vapour in the atmosphere. This provides a positive feedback, resulting in continued increase in temperature.

During the formation of the Earth's early atmosphere, the positive feedback was most likely limited by the formation of clouds. Clouds (liquid water droplets) form when the air becomes saturated with water vapour, resulting in condensation and eventually rain, which removes water from the atmosphere. A possible explanation for the high temperatures on Venus is that this limiting process did not apply, leading to a continued increase in temperature and vapour content (eventually, UV radiation causes dissociation of H_2O into H_2 and O_2, and the hydrogen escapes into space).

The amount of water vapour in the atmosphere can be described in terms of the partial vapour pressure p_v, or the water vapour density ρ_v (mass of water vapour molecules per unit volume). These are related by the ideal gas law

$$p_v = \frac{\rho_v R T}{M_v}, \tag{1.34}$$

where R is the gas constant, T the temperature and M_v the molecular weight. However, for a given temperature there is a maximum possible vapour pressure, the saturation vapour pressure $p_{sv}(T)$, which varies with temperature according to

$$\frac{\mathrm{d}p_{sv}}{\mathrm{d}T} = \frac{\rho_v L}{T}, \tag{1.35}$$

were L is the latent heat. If p_v reaches p_{sv} it cannot increase further without the atmosphere becoming supersaturated. Instead, the partial pressure becomes constrained to p_{sv}, and any further increase in water content results in condensation to produce clouds, which subsequently produce rain and remove the excess water from the atmosphere. The slope of this saturation curve may be combined with the ideal gas law (with $p_v = p_{sv}$) to obtain

$$\ln \frac{p_{sv}}{p_{sv0}} = \frac{M_v L}{R T_0}\left(1 - \frac{T_0}{T}\right), \tag{1.36}$$

were p_{sv0} is the reference value at temperature T_0.

As an illustration, suppose we approximate the dependence of the greenhouse factor on water vapour by $\gamma \approx 1/\tau_s \approx K/\rho_v$, where K is a constant. The equilibrium temperature from (1.7) is then

$$T = \left(\frac{Q(1-a)}{4\sigma K}\rho_v\right)^{1/4}, \tag{1.37}$$

or, using the ideal gas law,

$$T = \left(\frac{Q(1-a)M_v}{4\sigma K R} p_v \right)^{1/5}. \tag{1.38}$$

During the early stages of formation of the planetary atmosphere (there was initially no atmosphere or indeed ocean), we presume that water vapour and other dissolved gases were released by volcanism from the planet's interior. This resulted in a slow increase in the partial vapour pressure, and hence an increase in temperature described by (1.38). There is a corresponding increase in the saturation vapour pressure according to (1.36). Depending on the relative rates of increase of p_v and p_{sv}, there are two options: either the partial pressure reaches the saturation pressure and clouds form, preventing further increase in T; or the partial pressure remains below the saturation value (which itself increases with temperature), in which case the temperature continues to increase.

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Which of these possibilities occurs depends on whether the curves described by (1.36) and (1.38) intersect. If we approximate $1 - T_0/T \approx (T - T_0)/T_0$, based on $T \approx T_0$, write $T = T_0\theta$, $p_v = p_{sv0}e^{5\xi_v}$, and $p_{sv} = p_{sv0}e^{5\xi_{sv}}$, these curves can be written as

$$\theta = 1 + \alpha\xi_{sv}, \qquad \theta = \beta e^{\xi_v}, \tag{1.39}$$

where

$$\alpha = \frac{5RT_0}{M_v L}, \qquad \beta = \left(\frac{Q(1-a)M_v p_{sv0}}{4\sigma K R T_0^5} \right)^{1/5}. \tag{1.40}$$

These do not intersect if

$$\beta > \beta_c = \alpha \exp\left(\frac{1-\alpha}{\alpha} \right), \tag{1.41}$$

(the limiting case occurs when the curves meet tangentially). Non-intersection, leading to the runaway greenhouse effect, therefore occurs if the solar radiation Q is sufficiently large. This indicates the distinction between Earth and Venus, for which the value of Q is approximately twice as large (the critical flux depends on the value of the constant K, but the situation in reality is more complicated because the greenhouse factor does not only depend on water vapour).

1.4 Vertical structure of the atmosphere

Until now we have largely ignored the vertical density and temperature variations within the atmosphere (although we considered the temperature profile in a purely radiative atmosphere).

The pressure decreases with height due to the decreasing weight of the overlying air column. Vertical force balance gives

$$\frac{\mathrm{d}p}{\mathrm{d}z} = -\rho g, \tag{1.42}$$

and the ideal gas law relates pressure and density according to

$$p = \frac{\rho R T}{M_a}, \tag{1.43}$$

where R is the gas constant, T is the temperature and M_a is the molecular weight. Since the absolute temperature does not vary hugely over most of the atmosphere, a reasonable approximation of the density profile may be obtained by taking it as constant. Then the force balance becomes

$$-\frac{1}{\rho}\frac{\mathrm{d}\rho}{\mathrm{d}z} \approx \frac{M_a g}{RT}, \tag{1.44}$$

so ρ decreases approximately exponentially with height, over a length scale called the *scale height*,

$$H = \frac{RT}{M_a g} \approx 8 \text{ km}, \tag{1.45}$$

using values $T = 273$ K, $R = 8.3$ J K^{-1} mol^{-1}, $M_a = 28.8 \times 10^{-3}$ kg mol^{-1}, and $g = 9.8$ m s^{-2}. Similarly, the pressure also decreases approximately exponentially with height.

To go further and understand the temperature structure, we must also consider energy balance. The energy equation in a dry atmosphere (neglecting phase changes) is

$$\rho c_p \frac{\mathrm{D}T}{\mathrm{D}t} - \beta T \frac{\mathrm{D}p}{\mathrm{D}t} = \nabla \cdot (k \nabla T) - \nabla \cdot \mathbf{q}, \tag{1.46}$$

where the material derivatives, representing the rate of change following fluid parcels, are given in terms of velocity $\mathbf{u}$ by

$$\frac{\mathrm{D}f}{\mathrm{D}t} = \frac{\partial f}{\partial t} + \mathbf{u} \cdot \nabla f. \tag{1.47}$$

The terms on the left represent the advection of sensible heat and the work of thermal compression ($\beta = -\rho^{-1}\partial\rho/\partial T$ is the thermal expansion coefficient, equal to $1/T$ for an idea gas), and the terms on the right represent heat transfer by conduction and radiation. The latter was considered earlier, and is fundamentally important in determining energy transfer to and from the atmosphere. However, if we consider only the lower 10 km (the troposphere), the dominant energy transfer process *within* this region is convection, described by the terms on the left.

Convection occurs as a result of thermal expansion (warm air is lighter) and an unstable stratification. The temperature is usually higher nearer the ground and convective overturning is therefore widespread. (Temperature inversions, when colder air lies stably beneath warmer air, do sometimes occur, often at night under clear sky when the long wave radiative loss from he Earth is larger; the colder air can hold less water vapour and often results in low-lying clouds in valleys).

A one-dimensional steady state balance of the advective terms in (1.46), together with the ideal gas law, gives

$$\rho c_p \frac{\mathrm{d}T}{\mathrm{d}z} - \frac{\mathrm{d}p}{\mathrm{d}z} = 0, \tag{1.48}$$

and combing with the force balance (1.42) gives

$$\frac{\mathrm{d}T}{\mathrm{d}z} = -\frac{g}{c_p} \approx -10 \text{ K km}^{-1}. \tag{1.49}$$

This value is sometimes refered to as the dry adiabatic lapse rate. However, the average lapse rate of the Earth's atmosphere is closer to 6 K km^{-1}, due to the presence of water vapour and the heat associated with its condensation. The amount of water vapour can be expressed in terms of the mixing ratio

$$m = \frac{\rho_v}{\rho}, \tag{1.50}$$

where ρ_v is the water vapour density and ρ the total air density (typically $m \approx 0.02$, so the impact of water vapour on ρ is small). Alternatively we may express the amount of water vapour using the ideal gas law in terms of the partial vapour pressure,

$$p_v = \frac{\rho_v RT}{M_v}. \tag{1.51}$$

If the partial pressure reaches the saturation vapour pressure $p_{sv}(T)$, given by the Clausius-Clapeyron equation

$$\frac{\mathrm{d}p_{sv}}{\mathrm{d}T} = \frac{\rho_v L}{T}, \tag{1.52}$$

then condensation occurs so as to maintain $p_v = p_{sv}$. This condensation produces water droplets (clouds) which then grow and fall as rain. For unsaturated air, the ratio p_v/p_{sv} is the relative humidity, which measures how close the air is to saturation. Condensation acts as a heat source, so the energy equation (1.46) for a moist (saturated) atmosphere is modified to

$$\rho c_p \frac{\mathrm{D}T}{\mathrm{D}t} - \frac{\mathrm{D}p}{\mathrm{D}t} + \rho L \frac{\mathrm{D}m}{\mathrm{D}t} = 0, \tag{1.53}$$

(the conduction and radiation terms on the right are ignored). For a one-dimensional steady state dominated by convection, we have

$$\rho c_p \frac{\mathrm{d}T}{\mathrm{d}z} - \frac{\mathrm{d}p}{\mathrm{d}z} + \rho L \frac{\mathrm{d}m}{\mathrm{d}z} = 0, \tag{1.54}$$

and using the ideal gas laws combined with the saturation condition $p_v = p_{sv}$, we can find (exercise),

$$\frac{\mathrm{d}T}{\mathrm{d}z} = -\frac{g}{c_p}\left[\frac{1 + \frac{\rho_v L}{p}}{1 + \frac{\rho_v L}{p}\frac{M_v}{M_a}\frac{L}{c_p T}}\right] \approx 5.4 \text{ K km}^{-1}. \tag{1.55}$$

Here we have used values $M_v = 18 \times 10^{-3}$ kg mol^{-1}, $M_a = 29 \times 10^{-3}$ kg mol^{-1}, $L = 2.5 \times 10^6$ J kg^{-1}, $g = 9.8$ m s^{-2}, and $c_p = 10^3$ J kg^{-1} K^{-1}, and take $\rho_v \approx 0.01$ kg m^{-3}, $p \approx 10^6$ Pa, $T \approx 300$ K (ρ_v, p and T all vary with altitude, but the *variation* is relatively small, so the lapse rate is approximately constant).

The above discussion applies to the *troposphere*, the lower approximately 10 km of the atmosphere. The convection due to the unstable stratification, and on a larger planetary scale due to differential heating between equator and poles, gives rise to large scale motions of the atmosphere that we think of as the weather. The top of the troposphere is called the *tropopause*, and is distinguished by a temperature minimum of around 210 K, which occurs at around 10 km (it is higher nearer the equator). Commercial aeroplanes usually fly close to this altitude, where the air density is lower and therefore provides less drag.

Above the tropopause lies the *stratosphere*, in which the temperature increases again with height to reach another maximum of around 270 K at the *stratopause*, around 50 km up. The stratosphere is therefore stably stratified and lacks the convective motions of the troposphere.

The temperature increase is due to the absorption of short wave (UV) solar radiation by ozone, which provides a significant internal heat source (the second term on the right of (1.46)).

Above the stratosphere is the *mesosphere* in which temperature again decreases with height, and then above about 80 km is the *thermosphere*, in which temperature increases again.

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1.5 Ice-albedo feedback

The planetary albedo depends on the relative proportion of ocean, snow, forest, deserts, etc over the Earth's surface. The amount of sea ice and land ice, which has a high albedo, can have a very pronounced effect on the climate, and provide a positive feedback that helps to explain the occurrence of ice ages.

Ice ages have occurred periodically for the last 2 million years, as evidenced by Antarctic ice cores and ocean-floor sediment cores. During the ice ages, ice sheets covered much of northern Europe (the Fenno-scandian ice sheet) and North America (the Laurentide ice sheet). The ice locked up in these ice sheets caused the sea level to be around 130 metres lower than it is today (for comparison, the current-day ice sheets of Greenland and Antarctica contain ice equivalent to around 65 metres of average sea level). The last glacial period ended quite abruptly around 10 thousand years ago, and we are currently in an *interglacial* period.

The timing of the ice ages is believed to relate to changes in solar forcing ($\approx 5\%$) that are due to slight variations in the Earth's orbit. The theory that these orbital variations are responsible for climate cycles is due to Milanković. There are three primary components to the orbital variations: the precision of the Earth's axis (which occur on a roughly 21 ky cycle), changes in the tilt of the axis (41 ky), and changes in the eccentricity of the elliptical orbit (100 ky).

On their own, the variations are not thought to be sufficient to explain the large temperature change between and glacial and interglacial periods (≈ 10 K), or their timing. However, the ice-albedo feedback can help to accentuate the change.

We can write the atmospheric energy balance (1.6) as

$$c\frac{\mathrm{d}T}{\mathrm{d}t} = R_i - R_o, \qquad R_i = \frac{1}{4}Q(1-a), \qquad R_o = \sigma\gamma T^4, \tag{1.56}$$

but now take the planetary albedo a to be a monotonically decreasing function of temperature, since we associate lower temperatures with greater ice cover. For example,

$$a(T) = a_+ - (a_+ - a_-)\frac{1}{2}\left[1 + \tanh\left(\frac{T - T_m}{\Delta T}\right)\right]. \tag{1.57}$$

We could also take γ to depend on temperature (due to varying amounts of atmospheric water vapour), but for simplicity we here keep it as constant.

Plotting the incoming and outgoing fluxes, $R_i(T)$ and $R_o(T)$, we see that there is the potential for multiple steady states, providing the dependence of a on T is strong enough, and provided Q is within a certain range.

Moreover, plotting $\mathrm{d}T/\mathrm{d}t$ as a function of T, we see that if there are multiple steady states, the lower and upper ones are stable and the middle one is unstable (as is typical for this type of system).

The stability can also be confirmed using a linear stability analysis, writing $T = T_0 + \theta$, where T_0 is the steady state and $\theta \ll T_0$, so that

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} \approx \big(R_i'(T_0) - R_o'(T_0)\big)\theta, \tag{1.58}$$

indicating that the steady state is stable (the perturbation θ decays) provided $R_o'(T_0) > R_i'(T_0)$.

Varying Q can cause multiple steady states to come and go. If Q is too small, only a low temperature solution exists (an ice age), and if Q is too large, only a high temperature solution exists (an interglacial). Orbital variations of Q between these values can cause jumps from the warm to the cold branches, which correspond to the inception and termination of an ice age.

The simple model in (1.56) does not correctly describe the timescale of climate change associated with ice ages, because we assumed a steady state relationship between the albedo and temperature, whereas in reality the timescale for adjustment of the albedo (due to the growth of ice sheets) is quite long. In fact this is by far the rate-limiting process, and the energy balance (1.56) can effectively be taken to be in a steady state. Such behaviour, when the time derivative is negligible on the longer timescales of interest, is referred to as *quasi-steady*, and the approximation to neglect the time derivative completely is referred to as a quasi-steady approximation.

To account for the longer timescale, a simple phenomenological model is

$$c\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{1}{4}Q(1-a) - \sigma\gamma T^4, \tag{1.59}$$

$$t_i\frac{\mathrm{d}a}{\mathrm{d}t} = a_0(T) - a, \tag{1.60}$$

where $a_0(T)$ is the equilibrium albedo for a given temperature, given by (1.57) for instance, and where $t_i \approx 10$ ky is the timescale associated with changes in ice cover.

If this equation is non-dimensionalised, by writing

$$Q \sim [Q]\hat{Q}, \qquad T \sim [T]\hat{T}, \qquad t \sim [t]\hat{t}, \tag{1.61}$$

and choosing $[t] = t_i$ and $[T] = ([Q]/4\sigma\gamma)^{1/4}$, we obtain

$$\varepsilon\frac{\mathrm{d}\hat{T}}{\mathrm{d}\hat{t}} = \hat{Q}(1-a) - \hat{T}^4, \qquad \frac{\mathrm{d}a}{\mathrm{d}t} = a_*(\hat{T}) - a, \tag{1.62}$$

where $\varepsilon = 4c[T]/t_i[Q] \ll 1$ is the ratio of timescales for temperature and albedo adjustment (and $a_*(\hat{T}) = a_0(T)$ is the equilibrium albedo expressed as a function of dimensionless temperature).

The quasi-steady approximation is to take $\varepsilon \to 0$, so that $\hat{T} = \hat{T}(a) = [Q(1-a)]^{1/4}$, and then

$$\frac{\mathrm{d}a}{\mathrm{d}t} = a_*(\hat{T}(a)) - a. \tag{1.63}$$

The steady states and stability of this differential equation can be analysed as for (1.56), with the same conclusions.

1.6 Carbon

In this section we extend the simple climate models above to include atmospheric and ocean carbon dioxide. We are partly interested in understanding the changes that are likely to occur due to human carbon emissions, and partly interested in whether feedbacks exist that can help to explain aspects of the ice-age cycles.

1.6.1 Carbon cycle

Carbon dioxide is released into the atmosphere by volcanism, plant and animal respiration, and by fossil fuel burning. It is taken out of the atmosphere by photosynthesis, by dissolution into the ocean, and by weathering (dissolution into rain-drops which then react with silicate rocks on the continents). We will largely ignore the contributions to this cycle from the terrestrial biosphere (respiration and photosynthesis), and concentrate on the effects of weathering, fossil fuel emissions, and the interaction with the oceans. (The neglected components are in fact quite large, but we must restrict our scope).

DIAGRAM

Ignoring the ocean for the moment, conservation of atmospheric CO_2 can be expressed as

$$\frac{\mathrm{d}m_{\mathrm{CO}_2}}{\mathrm{d}t} = v - W, \tag{1.64}$$

where m_{CO_2} is the total mass of CO_2 in the atmosphere, v represents emissions from volcanoes and from fossil fuel burning, W is the global weathering rate. It is convenient to express m_{CO_2} in terms of the atmospheric partial pressure p_{CO_2}, which we do using Dalton's law of partial pressures,

$$\frac{p_{\mathrm{CO}_2}}{p_a} = \frac{m_{\mathrm{CO}_2}}{m_a}\frac{M_a}{M_{\mathrm{CO}_2}}, \tag{1.65}$$

(here $M_a = 29 \times 10^{-3}$ kg mol^{-1} and $M_{\mathrm{CO}_2} = 44 \times 10^{-3}$ kg mol^{-1} are the molecular weights), and the fact that the atmospheric pressure is given by the hydrostatic balance $p_a A_E = m_a g$, where $A_E \approx 5.1 \times 10^{14}$ m^2 is the Earth's surface area. Thus

$$m_{\mathrm{CO}_2} = \frac{A_E M_{\mathrm{CO}_2}}{g M_a} p_{\mathrm{CO}_2}. \tag{1.66}$$

The other common way of quantifying atmospheric CO_2 is as a concentration in parts per million (ppm). This is equivalent to the ratio $10^6(p_{\mathrm{CO}_2}/p_a)$, and since $p_a \approx 10^5$ Pa, the concentration in ppm is approximately 10 times the partial pressure in Pa.

Volcanism provides an average flux of CO_2 to the atmosphere of around 0.3 Gt y^{-1} (1 Gt = 10^{12} kg). Current day CO_2 emissions from fossil fuels are around 30 Gt y^{-1} (although some of these emissions are offset by a corresponding increased dissolution in the oceans and photosynthesis). Note that we work in terms of CO_2 rather than C. Care is required with the units because emissions are often quoted in gigatons of carbon Gt(C), which can be converted to gigatons of CO_2 using the factor 44/12 (the ratio of molecular weights).

Weathering provides an important drawdown of CO_2 from the atmosphere. The CO_2 dissolves in rainwater and then reacts with calcium and magnesium silicates that are present in the Earth's crust. A principle reaction is

$$\mathrm{CaSiO_3} + 2\mathrm{CO_2} + \mathrm{H_2O} \rightarrow \mathrm{SiO_2} + \mathrm{Ca^{2+}} + 2\mathrm{HCO_3^-}, \tag{1.67}$$

which converts calcium silicate and carbon dioxide to silica, calcium ions and bicarbonate ions. The calcium and bicarbonate ions then undergo a further reaction to produce calcium carbonate,

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O, \tag{1.68}$$

which is incorporated in the shells of marine organisms, and ultimately deposited as sediments on the sea floor or dissolved back into the deep ocean. The net effect of these reactions is therefore to remove atmospheric CO_2 according to

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2. \tag{1.69}$$

The rate of weathering therefore depends on temperature (which controls the pace of the weathering reactions), precipitation (which itself can be taken to depend on temperature, due to the approximate balance with evaporation), and the atmospheric concentration of carbon dioxide. Thus we may take the weathering rate $W = W(T, p_{CO_2})$, where the partial pressure p_{CO_2} is used as a measure of the atmospheric concentration of CO_2. An empirical relation is

$$W = W_0 \left(\frac{p_{CO_2}}{p_0}\right)^{\mu} \exp\left[\frac{T - T_0}{\Delta T_c}\right], \tag{1.70}$$

where $\mu = 0.3$, $\Delta T_c = 13$ K, and $T_0 = 288$ K, $p_0 = 36$ Pa, and $W_0 = 3 \times 10^{11}$ kg y^{-1} are estimated current-day values.

1.6.2 An energy and carbon balance model

Combining the ingredients above with the earlier energy balance model, and the description of ice-sheet albedo feedback, we have the following model

$$c\frac{dT}{dt} = \frac{1}{4}Q(1 - a) - \sigma\gamma(p_{CO_2})T^4, \tag{1.71}$$

$$t_i\frac{da}{dt} = a_0(T) - a, \tag{1.72}$$

$$\frac{A_E M_{CO_2}}{gM_a}\frac{dp_{CO_2}}{dt} = v - W(T, p_{CO_2}), \tag{1.73}$$

where $a_0(T)$ is given by (1.57), $W(T, p_{CO_2})$ is given by (1.70), and we have included a dependence of the greenhouse factor γ on p_{CO_2} so that we may investigate CO_2 driven feedbacks. For simplicity, this may be taken as a linear function

$$\gamma = \gamma_0 - \gamma_1 p_{CO_2}, \tag{1.74}$$

with $\gamma_0 = 0.64$, $\gamma_1 = 0.8 \times 10^{-3}$ Pa^{-1}.

The principle ingredient missing from this model is the transfer of CO_2 between atmosphere and ocean, which we will include below. However it is worth exploring the behaviour of this model before adding greater complexity.

We have a nonlinear dynamical system in the three variables T, a and p_{CO_2}. In fact, the timescale associated with (1.71) is very rapid, so we may treat the temperature as quasi-steady and reduce the system to a two-dimensional system, which can be analysed in the phase plane. In particular, we are interested in whether steady states exist, whether they are stable, and whether there are stable periodic orbits, which would perhaps correspond to the ice-age cycle.

We non-dimensionalise, writing

$$T = T_0 + \Delta T_c\hat{\theta}, \qquad p_{\mathrm{CO}_2} = p_0\hat{p}, \qquad t = t_i\hat{t}, \tag{1.75}$$

and defining dimensionless parameters

$$\varepsilon = \frac{c\Delta T_c}{t_i\sigma\gamma_0 T_0^4}, \quad \nu = \frac{4\Delta T_c}{T_0}, \quad q = \frac{Q}{4\sigma\gamma_0 T_0^4}, \quad \lambda = \frac{\gamma_1 p_0}{\gamma_0\nu}, \quad \alpha = \frac{vgM_a t_i}{A_E p_0 M_{\mathrm{CO}_2}}, \quad w = \frac{W_0}{v}. \tag{1.76}$$

The model is then (dropping the hats),

$$\varepsilon\frac{\mathrm{d}\theta}{\mathrm{d}t} = q(1-a) - (1-\nu\lambda p)(1+\tfrac{1}{4}\nu\theta)^4, \tag{1.77}$$

$$\frac{\mathrm{d}a}{\mathrm{d}t} = B(\theta) - a, \tag{1.78}$$

$$\frac{\mathrm{d}p}{\mathrm{d}t} = \alpha(1 - wp^\mu e^\theta), \tag{1.79}$$

where $B(\theta)$ is the dimensionless version of the equilibrium albedo function. Using values given above, along with $c = 10^7$ J K^{-1} m^{-2}, $g = 9.8$ m s^{-2}, $t_i = 10^4$ y, $v = 3\times 10^{11}$ kg y^{-1}, we find

$$\varepsilon \approx 1.6\times 10^{-6} \quad \nu \approx 0.18 \quad q \approx 1.4, \quad \lambda \approx 0.25, \quad \alpha \approx 1.1, \quad w \approx 1. \tag{1.80}$$

The fact that $\alpha = O(1)$ indicates that the CO$_2$ partial pressure in this model varies on a similar (long) timescale to the albedo. Since $\varepsilon \ll 1$, the temperature rapidly approaches the quasi-steady state, which we expand to first order in ν,

$$\theta \approx \Theta(a,p) = \frac{q(1-a)-1}{\nu} + \lambda p. \tag{1.81}$$

We are left with a phase plane governed by

$$\dot{a} = f(a,p) = B(\Theta) - a, \tag{1.82}$$

$$\dot{p} = g(a,p) = \alpha(1 - wp^\mu e^\Theta). \tag{1.83}$$

Steady states occur at the intersection of the null clines of this system. The p nullcline is always an increasing function $a = G(p)$, whereas the a nullcline is either a decreasing function $a = F(p)$, or is a multivalued function of p, depending on the magnitude of the gradient of $B(\theta)$. In either case, there must be at least one possible steady state.

The stability of a steady state depends on the relative slopes of the nullclines at the intorsection point. If we perturb around a fixed point (p_0, a_0) by writing $(p,a) = (p_0,a_0) + (P,A)$ where P and A are small, then linearising gives

$$\dot{\begin{pmatrix} A \\ P \end{pmatrix}} = \begin{pmatrix} f_a & f_p \\ g_a & g_p \end{pmatrix}\begin{pmatrix} A \\ P \end{pmatrix}, \tag{1.84}$$

with the partial derivatives evaluated at the fixed point. There are exponential solutions,

$$\begin{pmatrix} A \\ P \end{pmatrix} \propto e^{\lambda t}, \tag{1.85}$$

where λ is are the eigenvalues of the matrix of partial derivatives. The steady state is stable if both eigenvalues have negative real parts, which happens if

$$T = f_a + g_p < 0, \qquad D = f_a g_p - f_p g_a > 0. \tag{1.86}$$

(T and D are the trace and determinant of the matrix). Moreover the approach to the fixed point is oscillatory (a spiral) if $D > \frac{1}{4}T^2$.

It can be shown (exercise) that if the steady state occurs on a section of the a nullcline where a is *increasing* with p, and if α is small enough, then the steady state is an unstable spiral. In this case there is instead a limit cycle, in which the trajectory orbits around the fixed point. If $\alpha \ll 1$, the limit cycle takes the form of a relaxation oscillator, moving rapidly onto the a nullcline ($\alpha \ll 1$ corresponds to the ice adjusting must faster than the CO_2).

1.6.3 Ocean carbon

We now turn attention to the role of carbon in the ocean. The ocean contains much more carbon than the atmosphere, and exchange between the atmosphere and ocean provides an important buffering to changes in atmospheric CO_2. To understand this requires considering more than just dissolved CO_2, however, because there is rapid exchange between different forms of carbon in the ocean.

We focus only on the inorganic carbon (*i.e.* that not contained in plants and animals and their remains), of which there are three main species: dissolved carbon dioxide CO_2, carbonate ions CO_3^{2-}, and bicarbonate ions HCO_3^-. We write the sum of these species as the total *dissolved inorganic carbon* (DIC),

$$C = [CO_2] + [CO_3^{2-}] + [HCO_3^-]. \tag{1.87}$$

Here the square brackets denote molar concentration, expressed as mol kg^{-1}.

We will shortly right down a conservation equation for this total carbon content, which includes the exchange with the atmosphere. However, we first discuss the partitioning between the different species. This partitioning is important because atmospheric CO_2 will evolve towards equilibrium with its dissolved concentration in the ocean, $[CO_2]$, so we need to know how that relates to the total carbon content. The majority ($\approx 90\%$) is currently held as bicarbonate ions, with less than 1% as CO_2.

The partitioning between the carbon species is described by the reactions

$$CO_2 + (H_2O) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HCO_3^- + H^+, \tag{1.88}$$

$$HCO_3^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CO_3^{2-} + H^+. \tag{1.89}$$

The brackets on H_2O are to indicate that water molecules are so abundant that we can ignore their influence on the reaction rate. From these we can write down reaction rates using the law of mass action,

$$R_1 = k_1[CO_2] - k_{-1}[HCO_3^-][H^+], \tag{1.90}$$
$$R_2 = k_2[HCO_3^-] - k_{-2}[CO_3^{2-}][H^+]. \tag{1.91}$$

These reactions are relatively rapid, so can be considered in equilibrium, *i.e.* $R_1 \approx 0$, $R_2 \approx 0$ (the reactions themselves equilibrate in a few minutes, but the rate-limiting process here is really associated with mixing in the ocean; we treat the ocean as a single well-mixed compartment, which is evidently a simplification). Thus

$$[\mathrm{HCO_3^-}][\mathrm{H^+}] = K_1[\mathrm{CO_2}], \tag{1.92}$$

$$[\mathrm{CO_3^{2-}}][\mathrm{H^+}] = K_2[\mathrm{HCO_3^-}], \tag{1.93}$$

where $K_1 = k_1/k_{-1} \approx 1.3 \times 10^{-6}$ mol kg^{-1}, and $K_2 = k_2/k_{-2} \approx 9.1 \times 10^{-10}$ mol kg^{-1} are the equilibrium constants (in general functions of temperature, though we will treat them as constants).

From this we see the important role also played by the hydrogen ions, which are directly related to the acidity of the ocean,

$$\mathrm{pH} = -\log_{10}[\mathrm{H^+}]. \tag{1.94}$$

The current pH of the ocean is around 8.2 (with $[\mathrm{H^+}] \approx 7 \times 10^{-9}$ mol kg^{-1}). If we assume the pH is known, the equilibrium conditions (1.92) and (1.93) provide two constraints on the concentrations of the three species $\mathrm{CO_2}$, $\mathrm{CO_3^{2-}}$, and $\mathrm{HCO_3^-}$. If we also suppose that we know the total carbon concentration (1.87), we can solve for the concentration of each. In particular

$$[\mathrm{CO_2}] = \frac{C}{1 + \frac{K_1}{[\mathrm{H^+}]} + \frac{K_1 K_2}{[\mathrm{H^+}]^2}}. \tag{1.95}$$

We will make use of this expression below. However there is no good reason to think that the pH should be fixed, and indeed it has been decreasing (a process referred to as ocean acidification). A better method to close the system is to consider the *alkalinity*. This is essentially a measure of charge balance, and it is (roughly) conserved. The total alkalinity includes contributions from many different compounds, but is dominated by the bicarbonate and carbonate ions. We thus define the alkalinity for our purpose as

$$A = 2[\mathrm{CO_3^{2-}}] + [\mathrm{HCO_3^-}], \tag{1.96}$$

and we suppose that this is fixed (the 2 is because there are two negative charges on the carbonate ion).

For a given total dissolved carbon content C and alkalinity A, we can use (1.87), (1.92), (1.93) and (1.96) to solve for all of $[\mathrm{CO_2}]$, $[\mathrm{CO_3^{2-}}]$, $[\mathrm{HCO_3^-}]$, and $[\mathrm{H^+}]$. Straightforward algebra leads to

$$[\mathrm{H^+}] = \frac{1}{2}(1-\gamma)K_1\left[\left(1 + \frac{(2\gamma-1)K_2}{(1-\gamma)^2 K_1}\right)^{1/2} - 1\right], \tag{1.97}$$

where $\gamma = C/A \approx 0.85$ under present-day conditions. Since $K_2 \ll K_!$, this can be well approximated by

$$[\mathrm{H^+}] \approx \left(\frac{2\gamma - 1}{1-\gamma}\right) K_2, \tag{1.98}$$

and hence

$$[\mathrm{HCO_3^-}] \approx 2C - A, \qquad [\mathrm{CO_3^{2-}}] \approx A - C, \qquad [\mathrm{CO_2}] \approx \frac{K_2}{K_1}\frac{(2C-A)^2}{A-C}, \tag{1.99}$$

More complicated models of the ocean chemistry take account of other ions, particularly calcium, and their effect on the alkalinity. In principle, one could attempt to model the concentrations of every species in the ocean, taking account of the sources and sinks (from weathering, precipitation, sedimentation etc.), but the model has to be closed at some stage in order to be manageable. Another common modification in more comprehensive models is to treat the surface and deep oceans as separate compartments.

Having established the partitioning between the different carbon species, we now return to the question of how the ocean carbon interacts with the atmosphere. For simplicity, we make use of (1.95) to relate the dissolved carbon dioxide to the total carbon content, effectively treating the pH as constant.

To describe the exchange with the atmosphere, we suppose that thermodynamic equilibrium holds at the ocean surface, and we parameterise the exchange of CO_2 between the surface and the mixed layer of the ocean below. Thermodynamic equilibrium is described by Henry's law which relates the surface concentration $[CO_2]_{surface}$ to the partial pressure in the atmosphere,

$$[\mathrm{CO_2}]_{surface} = K_H p_{\mathrm{CO_2}}, \tag{1.100}$$

where $K_H \approx 3.3 \times 10^{-7}$ mol kg^{-1} Pa^{-1} is the solubility (which decreases with increasing temperature). The exchange with the mixed layer is parameterised by

$$q = \tilde{h}\left([\mathrm{CO_2}]_{surface} - [\mathrm{CO_2}]\right), \tag{1.101}$$

where $\tilde{h}$ is an exchange coefficient, which is assumed constant (the exchange coefficient represents the effect of mixing in a narrow layer near the ocean surface, and in reality is likely to depend on factors such as wind speed). Putting these together, the CO_2 flux from atmosphere to ocean is given by

$$q = h\left(p_{\mathrm{CO_2}} - \frac{C}{K}\right), \tag{1.102}$$

where we write $h = \tilde{h}K_H$, and $K = K_H(1 + K_1/[\mathrm{H}^+] + K_1K_2/[\mathrm{H}^+]^2)$, making use of (1.95). The units of h are kg Pa^{-1} s^{-1} so that the flux is a mass flux.

In addition, the weathering flux of CO_2 transports carbon back into the ocean, so the sink term W in (1.64) should appear as a source term to the ocean.

Finally, we note that carbon is removed from the ocean by being incorporated into the shells of marine organisms, and then sedimenting to the ocean floor (a process referred to as the biological pump). We describe this using a simple exponential decay with rate constant b.

Thus, the overall ocean carbon budget is written as

$$\rho_O V_O \frac{\mathrm{d}C}{\mathrm{d}t} = \frac{h}{M_{\mathrm{CO_2}}}\left(p_{\mathrm{CO_2}} - \frac{C}{K}\right) + \frac{W}{M_{\mathrm{CO_2}}} - bC, \tag{1.103}$$

where ρ_O and V_O are the density and volume of the ocean, and $M_{\mathrm{CO_2}}$ is the molar mass, required as a conversion factor since C is the molar concentration.

1.6.4 An atmosphere and ocean carbon balance model

A simple model of the carbon cycle incorporating both atmosphere and ocean is now given by

$$\frac{A_E M_{\mathrm{CO}_2}}{g M_a}\frac{\mathrm{d}p_{\mathrm{CO}_2}}{\mathrm{d}t} = v - W - h\left(p_{\mathrm{CO}_2} - \frac{C}{K}\right), \tag{1.104}$$

$$\rho_O V_O \frac{\mathrm{d}C}{\mathrm{d}t} = \frac{h}{M_{\mathrm{CO}_2}}\left(p_{\mathrm{CO}_2} - \frac{C}{K}\right) + \frac{W}{M_{\mathrm{CO}_2}} - bC. \tag{1.105}$$

This can also be coupled with a model for the temperature and albedo, as in (1.71) and (1.72). For given emission v and weathering W, there is a steady state in which

$$C = \frac{v}{b}, \qquad p_{\mathrm{CO}_2} = \frac{C}{K} + \frac{v - W}{h}. \tag{1.106}$$

This state has a balance between emissions and sedimentation, and the atmospheric CO_2 is in equilibrium with the ocean. The timescale to achieve this equilibrium is large, of order $\rho_O V_O / b \sim 10^5$ y.