Transport equations : Mass and heat balances

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The transport equations for mass and heat are obtained from conservation laws of mass, on one hand, and energy, on the other hand. We consider a volume V fixed in space and bounded by a surface $\partial V = S$ and we write the balance between the change of mass or energy within V and the net fluxes of mass or energy crossing the bounding surface S.

Different types of fluxes need to be considered : *diffusive* fluxes resulting from thermally activated motion at the molecular scale, *convective* fluxes resulting from the macroscopic motion of a fluid, and for heat transport, *radiative* fluxes due to electromagnetic radiation.

The variation of mass of a given chemical species within the volume V can also be due to a chemical reaction. Likewise, heat can be produced by different mechanisms : chemical reactions, nuclear reactions, viscous dissipation, electrical resistance. These phenomena have to be included in the overall balance.

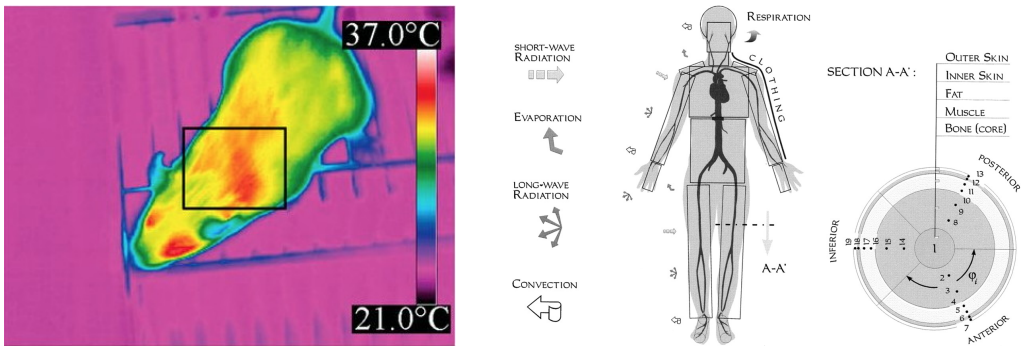

FIGURE 1 – Heat transfer in mammals. Left : heat is generated within the body of the mouse by its metabolism. This heat is exchanged with the surrounding air, first by transport within the body by diffusion and convection by the blood flow, then by transport through the air by diffusion, convection and radiation. The map of temperature on the body surface is obtained by analysis of the infrared radiation. Image reproduced from A. Warner et al., PNAS, 110,16241 (2013). Right : model for thermoregulation of the human body taking into account exchanges within different layers of the limbs and transport of heat in the surrounding air. Image reproduced from D. Fiala et al., J. Appl. Physiol. 87, 1957 (1999).

1 Transport of energy and heat

As said above, we consider a control volume V fixed in space and we examine the rate of change of total energy E (internal U + kinetic K + potential Φ) inside this volume. The change of energy per unit time results from the following mechanisms :

— production of heat within V by reactions, nuclear or chemical, by phase changes or dissipative processes such as the Joule effect

— net flux of kinetic energy through the bounding surface S due to the macroscopic flow

— net flux of heat through the bounding surface S due to the macroscopic flow
— net flux of heat through the bounding surface S due to molecular diffusion
— rate of work done by volume forces (e.g. gravity) on the material contained within V
— rate of work done by stresses (surface forces)

If the potential does not change with time and depends only on the spatial coordinates, since the volume V is fixed in space, there is no variation of potential energy.

When the fixed control volume contains only a solid material there is no macroscopic motion and we do not have to take into account the kinetic energy. For a fluid material however, it is possible to write an equation of change for the macroscopic kinetic energy K alone using Newtons' laws of motion. For an incompressible newtonian fluid,the Navier-Stokes equation leads to the following equation for dK/dt, using the decomposition of the stress tensor into a pressure term $-p\mathbf{I}$ and a viscous term $\mathbf{d} = \eta(\nabla\mathbf{u} + \nabla\mathbf{u}^T)$ where η is the dynamic viscosity [1] :

$$\frac{dK}{dt} = -\nabla.\left[\mathbf{u}\left(\frac{\rho u^2}{2} + p\right) - \mathbf{u}.\mathbf{d}\right] + \mathbf{u}.\mathbf{f} - \mathbf{d}.\nabla\mathbf{u} \tag{1}$$

The divergence term on the right hand side of the equation involves the transport of kinetic energy by the flow, the work done per unit time on the system by the pressure and the viscous stresses. The following term is the work done per unit time by volume forces $\mathbf{f}$ such as gravity. The last term involving the velocity gradient, i.e. the rate of deformation of material elements, is the energy dissipated per unit time by viscosity. This dissipated energy is converted into heat. For example, in a car tire made of a viscoelastic material, essentially vulcanized rubber loaded with small mineral particles, viscous dissipation contributes significantly to the rolling resistance and leads to an increase of the tire temperature.

If we set aside the evolution of kinetic energy, we get the following equation for the rate of change of internal energy U per unit volume, for an incompressible material :

$$\frac{dU}{dt} = R - \nabla.(\mathbf{J}_C + \mathbf{J_D} + \mathbf{J_R}) + \mathbf{d}.\nabla\mathbf{u} \tag{2}$$

where R is the amount of heat produced per unit time by reactions, $\mathbf{J}_C$, $\mathbf{J_D}$, and $\mathbf{J_R}$ are the fluxes of heat due to convection by the flow, diffusion and radiation respectively and the last term corresponds to heat generated by viscous dissipation.

1.1 Transport by diffusion

The diffusive flux of heat is given by Fourier's law :

$$\mathbf{J_D} = -\lambda\nabla T \tag{3}$$

where λ is the *thermal conductivity* of the material. λ is defined as a positive quantity and the minus sign is introduced in Fourier's law to satisfy the second principle of thermodynamics : heat flows down the temperature gradient, from the region of higher temperature towards the region of lower temperature. The heat flux varies linearly with the temperature gradient, because we are considering situations which are close to equilibrium and the microstructure of the material is not modified by the existence of the heat flux. In SI units, λ is expressed in $\mathrm{W.m^{-2}.K^{-1}}$.

1.2 Transport by convection

If the material is a fluid and if there is a macroscopic flow defined by a velocity field $\mathbf{u}$, the convective heat flux due this flow is :

$$\mathbf{J}_C = \rho C T\mathbf{u} \tag{4}$$

1. See Guyon, Hulin, Petit, Hydrodynamique Physique, § 5.3, or Batchelor, An introduction to Fluid Dynamics, § 3.4

where ρ is the density of the fluid and C is the specific heat per unit mass. $\rho\mathbf{u}$ is the mass of fluid crossing a unit surface per unit time and each unit mass of fluid at temperature T carries an amount of heat equal to CT.

1.3 The equation for heat transport

Using the equation of change for U (eqn. 2) and setting aside the radiative flux and heat generation by viscous dissipation, we get :

$$\int_V \frac{\partial U}{\partial t}\, dV = \int_V R\, dV + \int_S \lambda \nabla T.\mathbf{n}\, dS - \int_S \rho C T \mathbf{u}.\mathbf{n}\, dS \tag{5}$$

where $\mathbf{n}$ is the unit normal on S directed outwards.

For a system at constant volume, the change in internal energy is related to the change in temperature $dU = \rho C dT$ and the energy balance becomes :

$$\int_V \frac{\partial T}{\partial t}\, dV = \int_V \frac{R}{\rho C}\, dV + \frac{\lambda}{\rho C}\int_S \nabla T.\mathbf{n}\, dS - \int_S T\mathbf{u}.\mathbf{n}\, dS \tag{6}$$

Using the divergence theorem we get :

$$\int_V \left[\frac{dT}{dt} - \frac{\lambda}{\rho C}\Delta T + \nabla.(T\mathbf{u}) - \frac{R}{\rho C}\right]\, dV = 0 \tag{7}$$

The control volume V is chosen in an arbitrary manner and, if the fluid is incompressible ($\nabla.\mathbf{u} = 0$), we get finally :

$$\frac{\partial T}{\partial t} + \mathbf{u}.\nabla T = \kappa \Delta T + \frac{R}{\rho C} \tag{8}$$

where $\kappa = \lambda/\rho C$ is the *thermal diffusivity*, the diffusion coefficient of heat. In SI units, κ is expressed in $\mathrm{m}^2.\mathrm{s}^{-1}$.

To compare the relative importance of convective and diffusive transport, we define a dimensionless number, the *Peclet number* :

$$Pe = \frac{UL}{\kappa}$$

where U is an order of magnitude of the velocity and L is a length scale characteristic of the temperature gradient. The Peclet number is the analogous of the Reynolds number for momentum transport.

When the Peclet number is much smaller than one, transport par convection can be ignored and the equation for heat transport reduces to a simple diffusion equation $\partial_t T = \kappa \Delta T$.

In steady state situations and without convection by a flow, we have only to solve Laplace's equation $\Delta T = 0$ with the appropriate boundary conditions (fixed temperature or fixed flux, i.e. fixed temperature gradient).

2 Mass transport

Similarly to heat transport, we can derive the equation for mass transport from a mass balance on a fixed control volume V. More specifically, we consider the variation in time of a given chemical species i within V : the rate of change of mass is equal to the net flux through $S = \partial V$ of species i with an additional source term if there is a chemical reaction producing i within V. The mass balance for i reads :

$$\int_V \frac{\partial \rho_i}{\partial t}\, dV = -\int_S \mathbf{n_i}.\mathbf{n_S}\, dS + \int_V r_i\, dV \tag{9}$$

where ρ_i is the mass of i per unit volume, $\mathbf{n_i}$ is the mass flux of i, $\mathbf{n_S}$ is the unit vector normal to surface S and r_i is the mass of i produced by unit volume and by unit time.

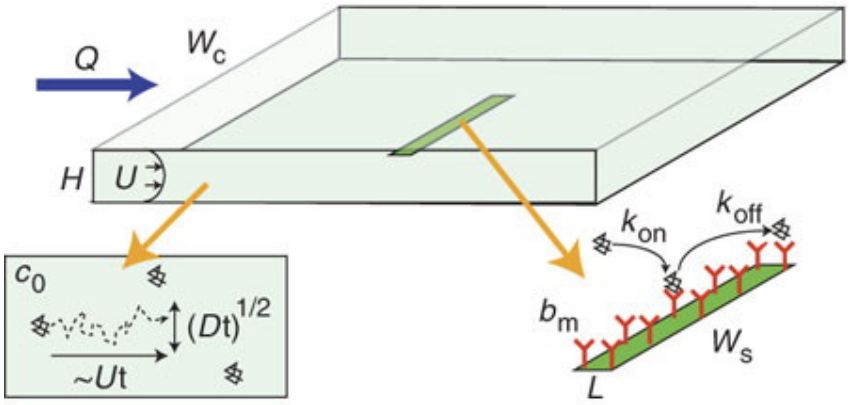

FIGURE 2 – An example of mass transfer in a biochemical sensor. A solution containing a biomolecule to be analyzed flows and diffuses within a channel. A strip on the channel floor is grafted with receptors on which the biomolecule binds and unbinds with rate constant k_{on} and k_{off}. Image reproduced from Squires et al., Nature Biotech. 26, 417 (2008).

This mass balance equation can be written with other variables than the concentration in mass, namely : the *molar concentration* $c_i = \rho_i/M_i$, the *mass fraction* $\omega_i = \rho_i/\rho$ or the *molar fraction* $x_i = c_i/c$ where M_i is the molar mass of i, ρ is the total mass per unit volume and c is the total molar concentration. Molar fractions are in particular useful to take into account the stoechiometric conditions in chemical reactions.

To write the convective and diffusive mass fluxes, it is important to define speeds of motion for each species and average speeds for the solution as a whole. Let us note $\mathbf{v_i}$ the global speed of species i,i.e. the speeds of molecules of i averaged over a length scale much lager than intermolecular distances. The mass flux of i *in a fixed reference frame* is $\mathbf{n_i} = \rho_i \mathbf{v_i}$ and the molar flux of i in the same reference frame is $\mathbf{N_i} = c_i \mathbf{v_i}$.

Now we define average speeds for the solution as a whole, a mass averaged speed :

$$\mathbf{v} = \frac{\sum_i \rho_i \mathbf{v_i}}{\sum_i \rho_i}$$

and equivalently an molar averaged speed :

$$\mathbf{v}* = \frac{\sum_i c_i \mathbf{v_i}}{\sum_i c_i}$$

So, we get, using the mass and molar fluxes :

$$\rho \mathbf{v} = \sum_i \mathbf{n_i} \text{ and } c\mathbf{v}* = \sum_i \mathbf{N_i}.$$

Finally, we define fluxes *relative to the mean speed of the solution*, namely the relative mass flux :

$$\mathbf{j_i} = \rho_i(\mathbf{v_i} - \mathbf{v})$$

and the relative molar flux :

$$\mathbf{J_i}* = c_i(\mathbf{v_i} - \mathbf{v}*).$$

2.1 Transport by diffusion

Fick's law which is analogous to Fourier's law, gives an expression for these fluxes when we take into account the molecular diffusion processes :

$$\mathbf{j_i} = -D_i \nabla \rho_i = -D_i \rho \nabla \omega_i \qquad \text{and} \qquad \mathbf{J_i}* = -D_i \nabla c_i = -D_i c \nabla x_i \tag{10}$$

where D_i is the diffusion coefficient of species i within the solution. The linear relation between fluxes and concentration gradients comes from the fact that we consider small excursions from the thermodynamic equilibrium. The minus sign is consistent with the second law of thermodynamics, concentration gradients relax spontaneously towards an equilibrium situation without gradients.

2.2 Transport by convection

To get the total flux of species i, we have also to take into account the convective flux due to the macroscopic flow of the solution. The mass flux due to the average flow is $\rho_i \mathbf{v}$ and the molar flux is $c_i \mathbf{v}*$. When we add the contributions due to molecular diffusion and macroscopic flow, we get the total mass and molar fluxes $\mathbf{n_i}$ and $\mathbf{N_i}$:

$$\mathbf{n_i} = \rho_i \mathbf{v} - D_i \nabla \rho_i \qquad \text{and} \qquad \mathbf{N_i} = c_i \mathbf{v}* - D_i \nabla c_i \tag{11}$$

For the particular case of a binary solution A,B, the average speeds are such that : $\rho \mathbf{v} = \mathbf{n_A} + \mathbf{n_B}$ and $c\mathbf{v}* = \mathbf{N_A} + \mathbf{N_B}$ and the mass and molar fluxes of A are :

$$\mathbf{n_A} = \omega_A(\mathbf{n_A} + \mathbf{n_B}) - \rho D_A \nabla \omega_A \qquad \text{and} \qquad \mathbf{N_A} = x_A(\mathbf{N_A} + \mathbf{N_B}) - c D_A \nabla x_A \tag{12}$$

with similar expressions for the mass and molar fluxes of B.

2.3 The equation for mass transport

Using the expression for mass and molar fluxes in the mass balance (eqn. 9) together with the divergence theorem we get the transport equation for species i :

$$\frac{\partial \rho_i}{\partial t} = -\nabla.(\rho_i \mathbf{v}) + \nabla.(D_i \nabla \rho_i) + r_i \tag{13}$$

and ; similarly for the molar concentration :

$$\frac{\partial c_i}{\partial t} = -\nabla.(c_i \mathbf{v}*) + \nabla.(D_i \nabla c_i) + R_i \tag{14}$$

where $R_i = r_i / M_i$ is the number of moles of i produced per unit time and per unit volume.

These equations can be simplified if the fluid is *incompressible*, i.e. if $\rho = \sum_i \rho_i$ is constant and if the *diffusion coefficient D_i is constant*. This last hypothesis is valid in particular for dilute solutions. We get then :

$$\frac{\partial \rho_i}{\partial t} + \mathbf{v}.\nabla \rho_i = D_i \Delta \rho_i + r_i \tag{15}$$

and, for the molar concentration :

$$\frac{\partial c_i}{\partial t} + \mathbf{v}*.\nabla c_i = D_i \Delta c_i + R_i \tag{16}$$

These transport equations are exactly similar to the equation for heat transport. A Peclet number $Pe = UL/D_i$ can be defined to compare the transport by convection and the transport by diffusion. As before U is a characteristic speed of the flow and L is a characteristic length scale of the concentration gradient.

3 Vorticity, heat and mass transport : similar equations

The transport equations for mass (15) and heat (8) have exactly the same structure, if we ignore radiative transport for heat. These are *convection-diffusion* equations.

The Navier-Stokes equation for newtonian fluids can be written in terms of the vorticity $\omega = \nabla \wedge \mathbf{u}$:

$$\frac{\partial \omega}{\partial t} + \mathbf{u}.\nabla\omega - \nu\Delta\omega + \omega.\nabla\mathbf{u} = 0.$$

This equation has an advection term $\mathbf{u}.\nabla\omega$ and a diffusion term involving the kinematic viscosity of the fluid $\nu\Delta\omega$, but there is an additional term related to the vectorial nature of the vorticity. However, *in two dimensions*, ω and $\nabla\mathbf{u}$ are orthogonal and the equation for vorticity becomes :

$$\frac{\partial \omega}{\partial t} + \mathbf{u}.\nabla\omega = \nu\Delta\omega$$

The structure of the equation is exactly similar to the ones derived for heat and mass. It will then be interesting to transpose results obtain for one problem, say transport of momentum, to another one.

In particular, the concept of boundary layer for momentum transport, at large Reynolds number, can be readily extended to the transport of heat and mass when the Peclet number is much larger than unity. In fluid mechanics, we know that we cannot ignore completely viscosity at large Reynolds numbers, otherwise we get non physical values for drag forces (the paradox of Dalembert). Similarly, for transport phenomena, at large Peclet numbers, we will see that we cannot ignore completely the diffusive term, otherwise we would not be able to compute the flux of heat or mass towards a solid surface for example.

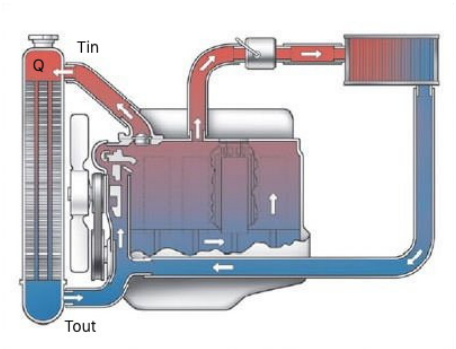

FIGURE 3 – A car combustion engine with a main radiator to regulate the temperature of the cold source of the thermal engine and a secondary radiator to heat the interior of the car.

4 Local equations vs global balances

In the preceding sections, starting from conservation laws for energy and mass, we have established convection-diffusion differential equations. Solving these equations with the appropriate boundary conditions, we can obtain analytical or numerical descriptions of the temperature and concentration fields. For example, in the biochemical sensor case described on fig. 2, the authors of the research article solved numerically the transport equation 15 and also found asymptotic analytical solutions for the concentration field.

But it is always possible to write also global balances. For the example of the biochemical sensor, the global balance of the biomolecule to be analyzed is simply : mass flow rate at the

entrance of the channel = mass flow rate at the exit of the channel + rate of adsorption on the strip grafted with receptors.

Another simple global balance, for heat transfer this time, can be written for a car radiator (fig. 3) : the total heat flux entering the radiator J_{in} is the mass flow rate of water ρQ (Q is the volumetric flow rate) multiplied by the inlet temperature T_{in} and the specific heat of water per unit mass C : $J_{in} = Q\rho CT_{in}$. It should be equal to the sum of the heat flux leaving the radiator due to the water flow : $J_{out} = Q\rho CT_{out}$ and the heat flux to the surrounding air due to the conduction through the metal fins and the boundary layer in air J_{cond}, that is : $QC(T_{in} - T_{out}) = J_{cond}$. This equation is obviously not sufficient to design the radiator, we need to model the heat diffusion through the fins, but if we measure the temperature at the inlet and outlet and the flow rate we know the value of J_{cond}.

5 Summary

Heat and mass transport are described by convection-diffusion equations having the following general form :

$$\begin{pmatrix} rate\ of\ change \\ of\ heat \\ or\ mass \end{pmatrix} = \begin{pmatrix} net\ diffusive\ flux \\ of\ heat \\ or\ mass \end{pmatrix} + \begin{pmatrix} net\ convective\ flux \\ of\ heat \\ or\ mass \end{pmatrix} + \begin{pmatrix} rate\ of\ production \\ of\ heat \\ or\ mass \\ by\ reactions \end{pmatrix} + \begin{pmatrix} net\ radiative\ flux \\ of\ heat \end{pmatrix} \tag{17}$$

More precisely, if H is the scalar quantity transported in a velocity field $\mathbf{v}$, with a diffusion coefficient D_H and a production term R_H :

$$\frac{\partial H}{\partial t} + \mathbf{v}.\nabla H = D_H \Delta H + R_H \tag{18}$$

The ratio of the convective flux to the diffusive flux is given by a dimensionless group, the Peclet number

$$Pe = \frac{UL}{D_H}. \tag{19}$$

When the Peclet number is much smaller than unity, the convective flux can be ignored and the transport occurs only through diffusion. Unfortunately, at large Peclet numbers, the diffusive flux cannot always be ignored.

For steady state situations ($\partial_t = 0$) and if convection is not present or negligible the transport equation reduces to Laplace's equation $\Delta H = 0$ or Poisson's equation $\Delta H = R_H$ if there is a source term.