

Transport Processes I: Heat and Mass Transfer
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Lecture - 18
Diffusion: Thermal diffusion coefficient

Welcome to this, this will be our final lecture on the molecular origins of diffusion. I had taken you through the previous three lectures on mass diffusion in gases, mass diffusion in liquids and momentum diffusion in gases. The fundamental principle is that diffusion takes place due to the molecular fluctuating velocity whenever there is a variation in the density of the quantity that is being transported; whether its mass density momentum density or energy density.

In the case of gases the picture can be made quite clear if you look at mass diffusion for example.

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Diffusion coefficients & constitutive relations:

Gases:

Net flux $J = BC \left| \frac{U_{rms}}{2\lambda} - BC \left| \frac{U_{rms}}{2\lambda} \right. \right.$

$$C \left| \frac{C}{2-\alpha} \right| \frac{C}{2\lambda} - A \lambda \frac{dc}{dz} + \frac{(A\lambda)^2}{2\lambda} \frac{d^2c}{dz^2} + \dots$$

$$C \left| \frac{C}{2+\alpha} \right| \frac{C}{2\lambda} + A \lambda \frac{dc}{dz} + \frac{(A\lambda)^2}{2\lambda} \frac{d^2c}{dz^2} + \dots$$

Net flux $= BU_{rms} [C]_{2-\alpha} - C]_{2+\alpha}]$

$$= -2AB \rho U_{rms} \left(\frac{dc}{dz} \right)_{z=0}$$

Number of red molecules coming downwards $= BC \left| \frac{U_{rms}}{2\lambda} \right.$

Area \times time

Number of red molecules going upwards $= BC \left| \frac{U_{rms}}{2\lambda} \right.$

Area \times time

In this case diffusion takes place because molecules which are transported across the surface are coming on average at distances above and below the surface. So, it is a concentration variation then the net number of molecules coming below will be different from the net molecules the number of molecules going above. Therefore, the diffusion flux is related to the variation in the number of molecules over a distance comparable to

the mean free path, because these molecules coming above and below or coming from distance is comparable to the mean free path.

Therefore, the variation over distance is comparable to the mean free path is what is causing molecular diffusion, and that variation is proportional to the mean free path times the derivative of the concentration the velocity or the temperature across that surface. So, there is a fundamental principle of diffusion.

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$$j = -2(AB)\lambda v_{rms} \frac{dc}{dx}$$

$$j = -D \frac{dc}{dx}$$

$$D = \frac{2(AB)\lambda v_{rms}}{3}$$

$$A \approx \frac{2}{3} \quad B \approx \frac{1}{4}$$

$$D = \frac{1}{3} \lambda v_{rms}$$

$$\frac{1}{2} m v_{rms}^2 = \frac{3}{2} kT \Rightarrow v_{rms} = \sqrt{\frac{3kT}{m}}$$

Hydrogen gas at STP
 Mass of 1 mole = 2gms = 2×10^{-3} kg
 $kT = (1.38 \times 10^{-23}) / k \times 300K = 4 \times 10^{-21} J$

Oxygen $m_2 = 16 \times m_1$
 $v_{rms 2} = \frac{1}{4} v_{rms 1} \approx 300 m/s$

And that is the reason that all diffusion coefficients in gases will scale approximately as the product of the mean free path and the molecular fluctuating velocity, times some constant. I had shown you in detail how this derivation is calculated is carried out. We had estimated in gases what is the root mean square fluctuating velocity, what is the mean free path.

The root mean square of the fluctuating velocity is comparable to the speed of sound in the gas. So, it is comparable to about 300 meters per second in gases like oxygen nitrogen and air in small molecule gases it is significantly higher because the diameter is lower. The mean free path varies approximately between about half a micron to 0.01 microns.

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Mean free path:

Hydrogen $d = 1.3 \text{ \AA} = 1.3 \times 10^{-10} \text{ m}$

$n = \frac{p}{kT} = \frac{1.01 \times 10^5 \text{ Pa}}{4 \times 10^{-21} \text{ J}}$

$n \approx 2.5 \times 10^{25} \text{ molecules/m}^3$

$\lambda = \frac{1}{\sqrt{2} n d^2} = \frac{1}{\sqrt{2} \pi (2.5 \times 10^{25}) (1.3 \times 10^{-10})^2}$

$= 5 \times 10^{-7} \text{ m} \approx 0.5 \mu\text{m}$

Oxygen, Nitrogen, Air:

$d_{O_2} \approx 3.3 \text{ \AA}$

$\lambda \approx 6 \times 10^{-8} \text{ m} = 0.06 \mu\text{m}$

Volume of cylinder swept out $= \pi d^2 L$

Number of second molecules $\approx n \pi d^2 L$

$n \pi d^2 \lambda \approx 1 \Rightarrow \lambda \approx \frac{1}{n \pi d^2}$

$\lambda = \frac{1}{\sqrt{2} \pi n d^2}$

$D \approx C v_{rms} \lambda \approx \sqrt{\frac{3kT}{m}} \frac{1}{\sqrt{2} \pi n d^2}$

$D_{O_2} \approx C (300 \text{ m/s}) (6 \times 10^{-8} \text{ m})$

$= C (1.8 \times 10^{-4} \text{ m}^2/\text{s})$

$D_{H_2} \approx C (1200 \text{ m/s}) (5 \times 10^{-7} \text{ m})$

$= C (6 \times 10^{-4} \text{ m}^2/\text{s})$

We had done that calculation a couple of lectures ago where we had estimated it on the basis of the volume travel swept by molecule as it travels in the gas I mean. And on that basis we had got the diffusion coefficients in gases after in the range of approximately 10 power minus 5 meters square per second.

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Mixture of two molecules A & B

$D_{AB} = \frac{3}{8} n d_{AB}^2 \left(\frac{kT(m_A + m_B)}{2\pi m_A m_B} \right)^{1/2}$

m_A & m_B = Molecular masses

$d_{AB} = \frac{d_A + d_B}{2}$

n = Total number density

Liquids:

Simplistically assume $D \approx v_{rms} d$

Ratio of diffusion coefficients $\frac{D_{gas}}{D_{liq}} \approx \left(\frac{d}{\lambda} \right) \frac{1}{100} \frac{1}{1000}$

$\lambda \sim 10^{-7}$ to 10^{-6} m

$d \sim 10^{-9}$ to 10^{-8} m

$D_{gas} \sim 10^{-5} \text{ m}^2/\text{s}$

$D_{liq} \sim 10^{-9}$ to $10^{-10} \text{ m}^2/\text{s}$

$\sim 10^{-4}$ to 10^{-5} or lower

Stokes-Einstein relation

$D = \frac{kT}{3\pi \eta d}$

η = liquid viscosity

d = diameter of cylinder particle

So, all gases the diffusion coefficient is approximately 10 power minus 5 meter square per second. If you use similar arguments you would estimate the diffusion coefficient in liquids to be about 10 to 100 times lower. That however is not true and the reason I had

said that was because the diffusion in liquids depends upon the physical transport of molecules in a liquid. And in a very densely packed cluster of molecules the transport of one molecule in any direction requires the cooperative motion of all other molecules around it. And therefore, the diffusion in liquids is a much slower process. And I have given you this relation for how to estimate the diffusion coefficient in liquids.

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We talked about momentum diffusion, instead of concentration you have the velocity in the x direction which is what is being transported the momentum in the x direction is what is being transported across the surface. And there is a variation of the momentum in the x direction only if there is a variation the mean velocity of the gas across that surface. So, note that x is the direction of the momentum itself or the velocity itself velocity is a vector, z is the direction in which that momentum is being transported; is being transported across a surface in the z direction because the perpendicular to that surface is in that z direction.

We had made slight distinction here the stress is defined as positive if the force is exerted on a volume whose outward unit normal is in the plus z direction. That corresponds to the volume below the surface because for this volume the outward unit normal is in the plus z direction. On that basis we had calculated the momentum flux across the surface and compare that with the expression for the Newton's law of viscosity and got an expression for the viscosity coefficient itself. Viscosity coefficient is equal to a number

density times the molecular mass, this is the mass density times the mean free path times the rms fluctuating velocity.

So, the kinematic viscosity is the ratio of the dynamic viscosity and the density and that just gives you the same expression as the mass diffusion coefficient, mean free path times the molecular fluctuating velocity times some constants. So, it is the mean free path times the molecular fluctuating velocity times some constants.

So therefore, the kinematic viscosity has the same dependence on the fluctuating velocity and the mean free path as the diffusion coefficient not surprising because both the transfer of mass and momentum takes place by the same physical mechanism, the transfer of physically the transfer of molecules across the surface.

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$$\mu = \frac{5}{16} \frac{\sqrt{m k T}}{\pi}$$

$$\mu = 2ABn m \bar{v}_{rms}$$

$$= 2AB \sqrt{\frac{m}{\pi}} \frac{1}{\sqrt{2\pi}} \sqrt{\frac{3kT}{m}}$$

$$\propto \frac{1}{\sqrt{2}} \sqrt{m k T}$$

$$Sc = \frac{\text{Momentum diffusion}}{\text{Mass diffusion}} = \text{Constant}$$

$$Sc = \frac{\nu}{D} \gg 1$$

Momentum diffusion in liquids:
 Water: $\mu = 10^{-3} \text{ kg/m s}$; $\rho = 10^3 \text{ kg/m}^3$
 $\nu \approx 10^{-6} \text{ m}^2/\text{s} \approx \nu_{mol}$
 $D \approx 10^{-9} - 10^{-8} \text{ m}^2/\text{s}$

Therefore the diffusion coefficients turn out to have the same dependence; and written down in a more exact expression for the diffusion coefficient here for you for the viscosity for a molecular gas. And therefore, the Schmidt number is equal to tends to a constant for a gas independent of any other parameters in a dilute gas.

Now, momentum diffusion in liquids; you take the simple case of water molecules. Water molecules have liquid water has a viscosity is about 10 power minus 3 kilogram per meter per second; and water molecules have a viscosity this is approximately 10 power minus 3 kilogram meter per second, and the density is approximately 1000

kilograms per meter cube if the density is approximately 1000 kilograms per meter cube. That means, that the kinematic viscosity is 10^{-6} meter square per second. It is just takes the dynamic viscosity divided by the density and I get about 10^{-6} meter square per second.

Recall that I had told you earlier that the mass diffusion in liquids is much slower, so of the order of 10^{-9} to 10^{-13} meter square per second. Therefore, in liquids the kinematic viscosity, the momentum diffusivity is much much larger than the mass diffusivity. And the reason for that is as follows: in a liquid all the molecules are densely packed and as I had explained in my discussion on mass diffusion the motion of any one molecule in any direction requires that other molecules nearby move cooperatively so that this molecule can move in any one direction. And for that reason mass diffusion is a very slow process in liquids.

Momentum diffusion does not require the physical transport of molecules. Mass diffusion of a solute for example, does require the physical transport of a molecule because its solid solute molecule has to move across the surface in order for mass to diffuse. However, momentum diffusion can take place due to the intermolecular forces. The fact that one molecule exerts a force on the other molecule can serve to transport momentum; molecules do not have to physically move across the surface. And for that reason the estimates for the momentum diffusion coefficient that you get are approximately equal to v_{rms} times the molecular diameter. So, they correspond to what you would get simply on the basis of the root mean square fluctuating velocity and the molecular diameter.

Therefore, the momentum diffusivity in liquids is actually much larger than the mass diffusivity in liquids because mass diffusivity is slow because it requires cooperative motion, momentum diffuse diffusivity is fast because it can take place even without the physical transport of molecules just through intermolecular forces and for this reason the momentum diffusivity in liquids can be very well estimated just based upon the root mean square fluctuating velocities and the diffusion coefficient. And therefore the Schmidt number, the ratio of the momentum diffusivity to the mass diffusivity which is μ by D is actually much larger than 1 in liquids software tend of 10^3 to 10^4 .

So therefore, there this is a significant difference between the mass diffusivity and the momentum diffusivity in liquids. Not so in gases, in gases mass and momentum diffusivity are approximately of the same order of magnitude. So, the final topic that I need to go through is thermal diffusion.

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Thermal diffusion:

$$q_{\uparrow} = B(v_{rms} e)_{z=0}$$

$$q_{\downarrow} = B(v_{rms} e)_{z=2\lambda}$$

$$q = q_{\uparrow} - q_{\downarrow} = B(v_{rms} e)_{z=0} - v_{rms} e|_{z=2\lambda}$$

$$= B \left[(v_{rms} e)_{z=0} - A \lambda \frac{d(v_{rms} e)}{dz} \right]_{z=0} - (v_{rms} e)_{z=2\lambda} + A \lambda \frac{d(v_{rms} e)}{dz} \Big|_{z=2\lambda}$$

$$= -2AB \lambda \frac{d(v_{rms} e)}{dz}$$

$$= -2AB \lambda \frac{d}{dz} \left(\sqrt{\frac{3kT}{m}} n m c_p T \right)$$

$$= -2AB \lambda \left(\frac{3}{2} \right) n m c_p \sqrt{\frac{3kT}{m}} \frac{dT}{dz}$$

$$= -2AB \lambda v_{rms} \left(\frac{3}{2} \right) c_p \frac{dT}{dz} n m$$

$$q = -k \frac{dT}{dz}$$

$$k = 2AB \lambda v_{rms} n m c_p \left(\frac{3}{2} \right)$$

$$\alpha = \frac{k}{\rho c_p} = 2AB \lambda v_{rms} \left(\frac{3}{2} \right) \frac{n m^2 c_p}{\rho c_p}$$

Once again, if we have molecules having fluctuating velocities across the surface this is the z direction, but on average the fluctuating velocities of the temperature of the molecules below the surface is greater than that above the surface. So, let us say that there is a temperature gradient across the surface. In this case if you maintain the temperature gradient so this could for example be a small section of a fluid in which you enforce the temperature gradient because this is a hot surface, drink the other way around. This has a higher temperature the hot, and this has a lower temperature the cold. You have two surfaces one heated one cold and there is a temperature difference across the two. And if you take a small section within this and then expand out that section it will look something like this. There is some temperature variation across the surface. The molecules below have a higher fluctuating energy and the molecules above have a lower fluctuating energy due to which as the molecules move across the surface there is a net transfer of energy across the surface due to this molecular motion.

Once again the reason for this transfer of energy is because the molecules below the surface come on average from a distance of the order the mean free path below the

surface where the temperature is higher. Whereas, the molecules above the surface come at some distance above the surface where the temperature is on average lower; so what is the heat flux due to these molecules? The heat flux going upwards is equal to the average energy of the molecules going upwards times the fluctuating velocity times some unknown constant. So, they were equal to some constant times the product of the fluctuating velocity times the energy density at the locations that is equal to minus $A \lambda$.

Note that in this case if the temperature is varying the rms fluctuating velocity also varies across the surface. If you recall the rms fluctuating velocity was equal to root of $3 k T$ by m and the mean free path was equal to 1 by root two $\pi n d$ square. So, the number density does not change the mean free path does not change, but since the temperature changes the fluctuating velocity also changes. So therefore, this is the flux going upwards, the flux going downwards is equal to v times v_{rms} times the energy density the flux is equal to a velocity times the density of that quantity at the location $A \lambda$.

And now we of course know what to do the total flux q is equal to q upwards minus q downwards which is equal to B into $v_{rms} e$ at z is equal to minus $A \lambda$ minus. Now, we have to substitute. So, you get this quite easily as B into $v_{rms} e$ at z is equal to 0 . Once again retaining terms only up to linear order in the expansion plus A , I am sorry minus. Then I could subtract out $v_{rms} e$ at z is equal to 0 plus x is equal to 0 . And once again the values add z is equal to 0 will cancel out, and the net result that I will get is that q is equal to $3 AB \lambda$ we are deep with the negative sign.

Now, in order to relate this to Fourier's law of heat conduction, I have to express the root mean square saturating velocity as well as a thermal energy in terms of the temperature. Therefore, minus $2 AB \lambda d$ by $d z$ of root of $3 k T$ by m into thermal energy will be equal to $n C_v$ times T ; where C_v is a specific heat constant volume. $n C_v T$ is the energy per unit volume, the internal energy per unit volume. And when I take the derivative of this since this is proportional to T to the $3/2$ power I will get minus $2 AB \lambda$. I will get a factor of $3/2$ because I have at equal three halves power in this expression here there is a T to the half here this T here. And then I will get $n C_v$ times root of $3 k T$ by m times $d T$ by $d z$.

So, that is going to be the flux of thermal energy across the surface; $n C_v$ is the number density times C_v is the specific heat per unit mole, if I were to write it in the traditional form in the form of the specific heat per unit mass which you are used to then I have to have the factor of the molecular mass here $n m C_v T$. In which case I will have the molecular mass coming in here, so now it should be understood that m times n ; so C_v is the curve is the specific heat per unit mass.

So, this is approximately equal to $-\frac{2}{3} \lambda n v_{rms} C_v \frac{dT}{dz}$ (Refer Time: 19:58) times the number density times the molecular mass. So, from this if you draw an analogy with $-k \frac{dT}{dz}$ where k is thermal conductivity you will find that k is equal to $\frac{2}{3} \lambda n v_{rms} m C_v$ times some constant. So, to within a constant this is thermal conductivity. This is thermal conductivity to within constant factors. So, this gives me an expression for thermal conductivity you have got from molecular expressions. The thermal diffusivity is equal to $\frac{k}{\rho c_p}$, and therefore I will have here $\frac{2}{3} \lambda n v_{rms} m C_v$ into this factor of $\frac{1}{\rho c_p}$ into $n m C_v$ by ρC_v .

Note that the density ρ just equal to n times m . So, these two factors actually cancel out and I have a ratio of specific heats here. As you know for gases the ratio of specific heats is basically $\frac{c_p}{C_v}$ is equal to γ . So, this is just equal to $\frac{1}{\gamma}$ which is a constant number it is equal to $\frac{3}{5}$ or $\frac{2}{3}$ depending upon whether its mono atomic or diatomic gases.

So, these are all constant numbers; that means, that to within a constant thermal diffusivity is also proportional to the mean free path times the fluctuating velocity. And that is once again because in the case of gases the transfer of energy also takes place due to the physical transfer of molecules across the surface.

Once again you can use kinetic theory calculations to get more exact expressions for this thermal diffusivity.

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Thermal conductivity,
Spherical gas molecules:

$$k = \frac{75}{64d^2} \left(\frac{k}{\pi m} \right)^{3/2}$$

$$C_v = \frac{3k}{2m}$$

$$\alpha = \frac{k}{\rho C_p} = \frac{75}{64d^2 \rho} \left(\frac{k}{\pi m} \right)^{3/2} \frac{1}{\left(\frac{k}{m c_p} \right)}$$

$$= \frac{75}{64d^2} \sqrt{\frac{k}{m}} \left(\frac{k}{m c_p} \right)^{1/2}$$

$$= \frac{75}{64} \frac{1}{m^{3/2}} \left(\frac{k}{\pi m} \right)^{3/2} \left(\frac{k}{m c_p} \right)^{-1/2}$$

$$\propto v_{rms} \lambda$$

Prandtl number = $\frac{\mu}{\alpha}$

Liquids:

Organic liquid

Liquid metals

Very high k

For example in the case of spherical molecules; the thermal conductivity is given as $\frac{75}{64 d^2} \frac{k}{\pi m} \sqrt{\frac{k T}{\pi m}}$. So, that is the expression for thermal conductivity in a mono atomic gas; where C_v is equal to $\frac{3k}{2m}$ $\frac{3}{2} k$ is the specific heat per unit based upon the number of moles; so if you divide by the molecular mass will be divided by unit mass.

So, this is the expression for thermal diffusivity in a gas for a mono atomic gas you can see well here that the coefficients vary, so from this I will get thermal diffusion coefficient as $\frac{k}{\rho C_p}$ which will be equal to $\frac{75}{64 d^2} \frac{k}{\pi m} \sqrt{\frac{k T}{\pi m}}$; number density is n and I will get $\frac{k}{\rho C_p}$ into $\sqrt{\frac{k T}{\pi m}}$. And, if I take this root of $\frac{k T}{\pi m}$ into $\frac{k}{m c_p}$ into $\frac{1}{n}$ over the number density; so you can see that this becomes within a constant $\frac{1}{n d^2} \sqrt{\frac{k T}{\pi m}}$ times $\frac{k}{m c_p}$. $\frac{k}{m c_p}$ because, c_p was defined on the basis of per unit mass, so this is actually dimensionless k is defined as energy per unit mole, whereas $m c_p$ defined as energy per unit mass multiplied by the molecular mass you will get energy per unit mole.

This is proportional to the mean free path and this is proportional to the molecular fluctuating velocity. So, to within proportionality constant this is the same as this is exactly proportional to v_{rms} times the mean free path. And that is because the mechanism of transfer is the same relates for gases or liquids. And that is the reason that the Prandtl number is equal to $\frac{\mu}{\alpha}$ it is a constant for gases.

Now what about liquids? In the case of liquids thermal diffusivity actually depends upon the mechanism of energy transfer. So, for example, if you had; so in gases energy transfer has to take place due to the physical motion of molecules across the surface, not so in liquids; the mechanism differs. So, in the case of organic liquids for example, in to some extent even and water and so on this will take place due to the contact forces, the intermolecular forces between the molecules.

So, if you have a higher temperature at one location and lower temperature another location, the intermolecular forces between the molecules can transfer the energy from one molecule to the other. It does not require the physical motion of molecules for energy transfer to take place. Due to this like momentum transfer energy transfer is in fact faster than mass transfer, because mass transfer requires the physical motion of molecules, whereas energy transfer and momentum transfer do not in general.

In fact in liquid metals actually, the energy transfer is not due to the intermolecular forces, but rather in metals you have these molecules which share a sea of electrons around them. And this transfer through the sea of electrons around these molecules you know that in metals for example; the outer shell electrons are all shared between all the metal molecule atoms in solid sits in the lattice in molten metal's it is in a liquid state where these molecules are fluctuating motion, but we have electrons around them. And these electrons are able to transport energy much faster than due to intermolecular forces. And due to that you have very high thermal conductivities.

Due to the transfer through these liquid metals very high thermal conductivities in very high diffusivities; that means, the Prandtl number for these liquid metals actually pretty low because thermal diffusivity is very high compared to the momentum diffusivity. Momentum diffusivity does require the intermolecular forces, whereas transfer of fluctuating energy does not.

In the case of thermal diffusion it depends on the details of the mechanism of diffusion. In cases like organic liquids or non polar liquids the transfer is relatively low because that requires transfer of energy from molecules one molecule to another whereas, in cases like liquid metals the transfer can be very fast. And therefore, for liquid metals for example, the Prandtl number is very low, whereas the Prandtl number for organic molecules and so on is relatively high.

So, in the previous four lectures I have tried to give you a physical understanding of diffusion. How these constitutive relations arise from a molecular picture. In the case of gases we have managed to get these coefficients, fairly accurately just based upon simple arguments. The diffusion coefficient in all cases, mechanism of diffusion is due to the physical transport of molecules. Diffusion coefficient therefore is proportional to the mean free path times the rms fluctuating velocity. All three diffusivities are comparable; therefore the Prandtl and Schmidt numbers are all of order one.

And therefore, in gases the diffusion coefficients for all three are comparable to about 10^{-5} meter square per second at normal temperatures. Liquid the picture is different mass diffusion is slow because it requires cooperative motion and I gave you an example of a formulas that can be used to estimate those. Momentum diffusion is relatively faster, the kinetic kinematic viscosity for water there is only about 10 times lower than that for gases. And the reason for that is because momentum is transported due to intermolecular forces rather than due to the physical transport of molecules.

In the case of energy transfer it depends on the details of the mechanism. In non polar molecules, organic molecules, conductivity is relatively low. In the case of liquid metals for example, the conductivity is relatively high because the transfer takes place due to the electron gas around the molecules. And this also gives you some idea of the magnitudes of the diffusion coefficients. The dimensionless numbers, the Prandtl number, the Schmidt number and so on.

So, this completes our discussion of molecular diffusion. The next lecture I will start off solving problems using this using a continuum approximation for these fluid flows. And I will try to give you some idea of how the balance between convection and diffusion determines the macroscopic transport properties in these systems. And so we will continue this in the next lecture; a new topic how do we actually solve, how do you actually first of all design differential equations then solve those differential equations to get the average transport rates. I will see you in the next lecture.