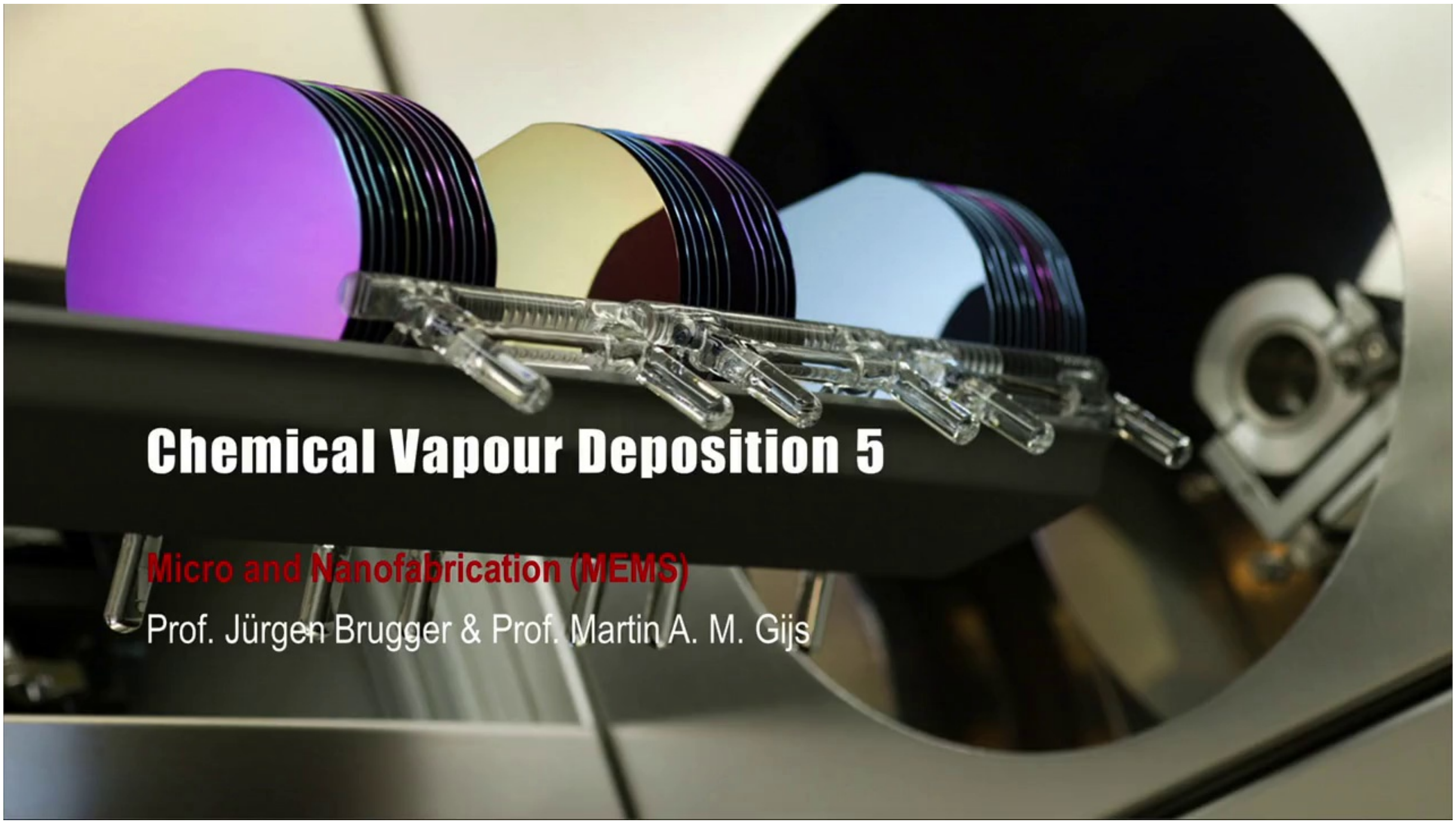

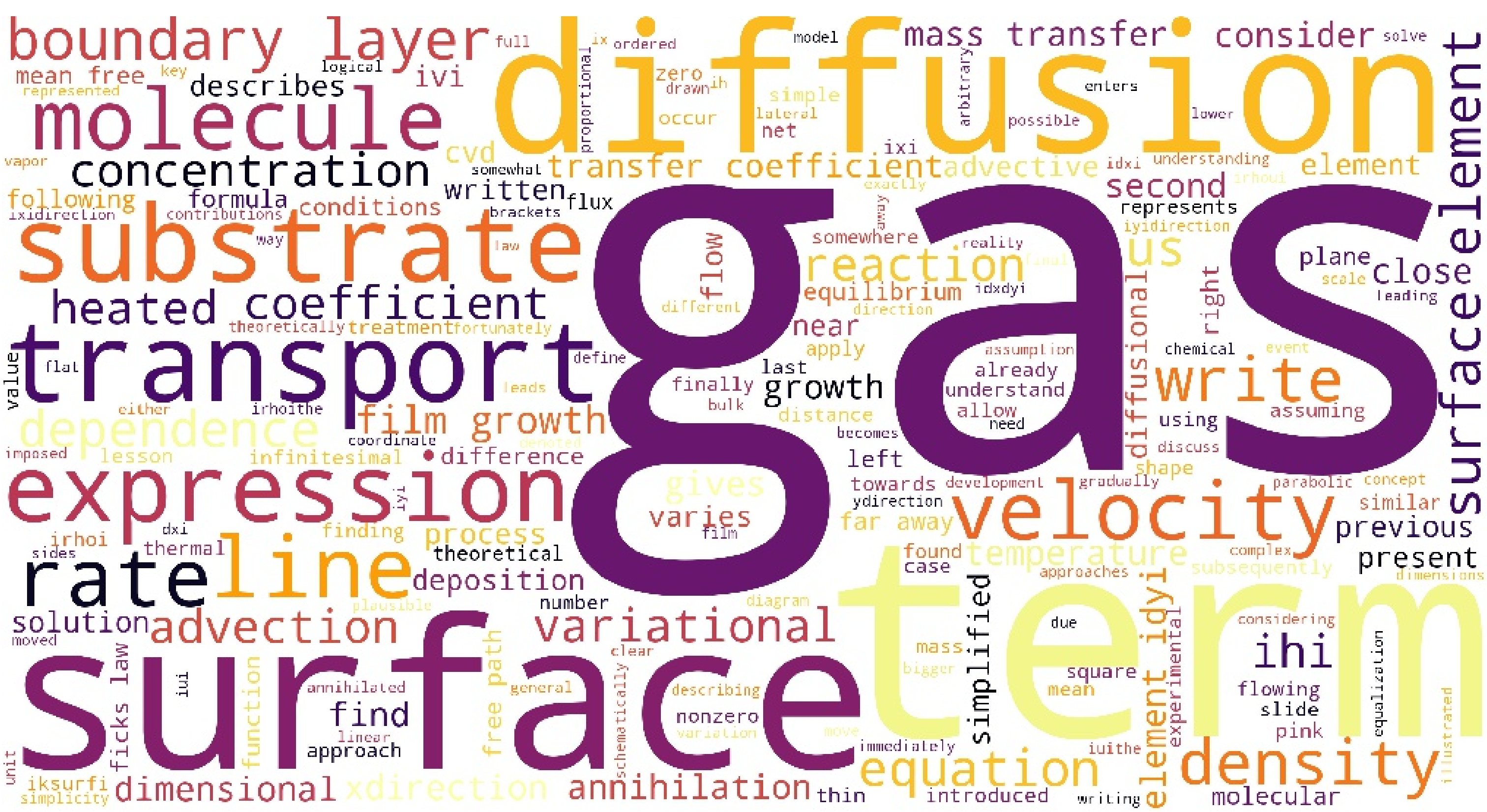

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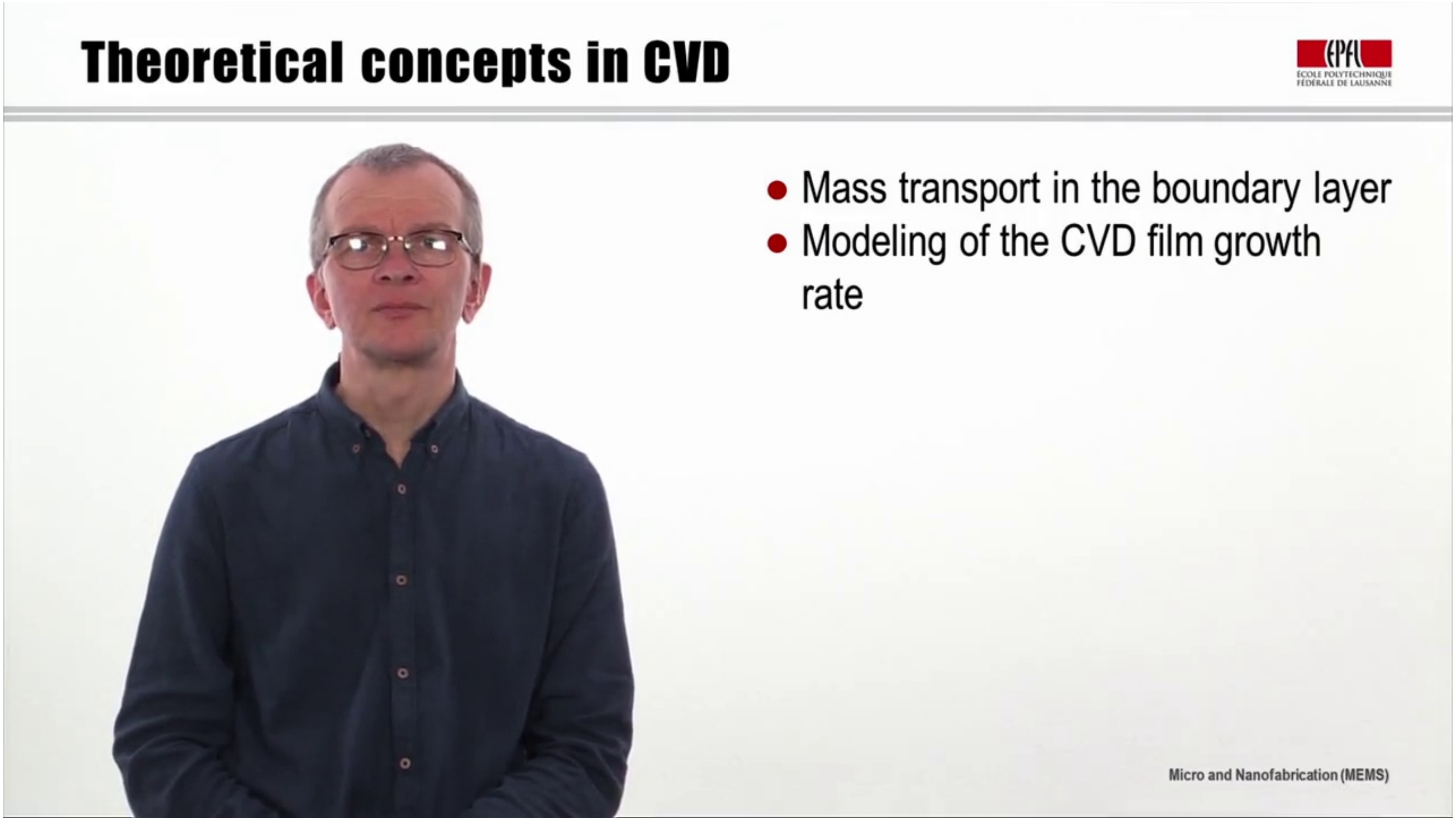
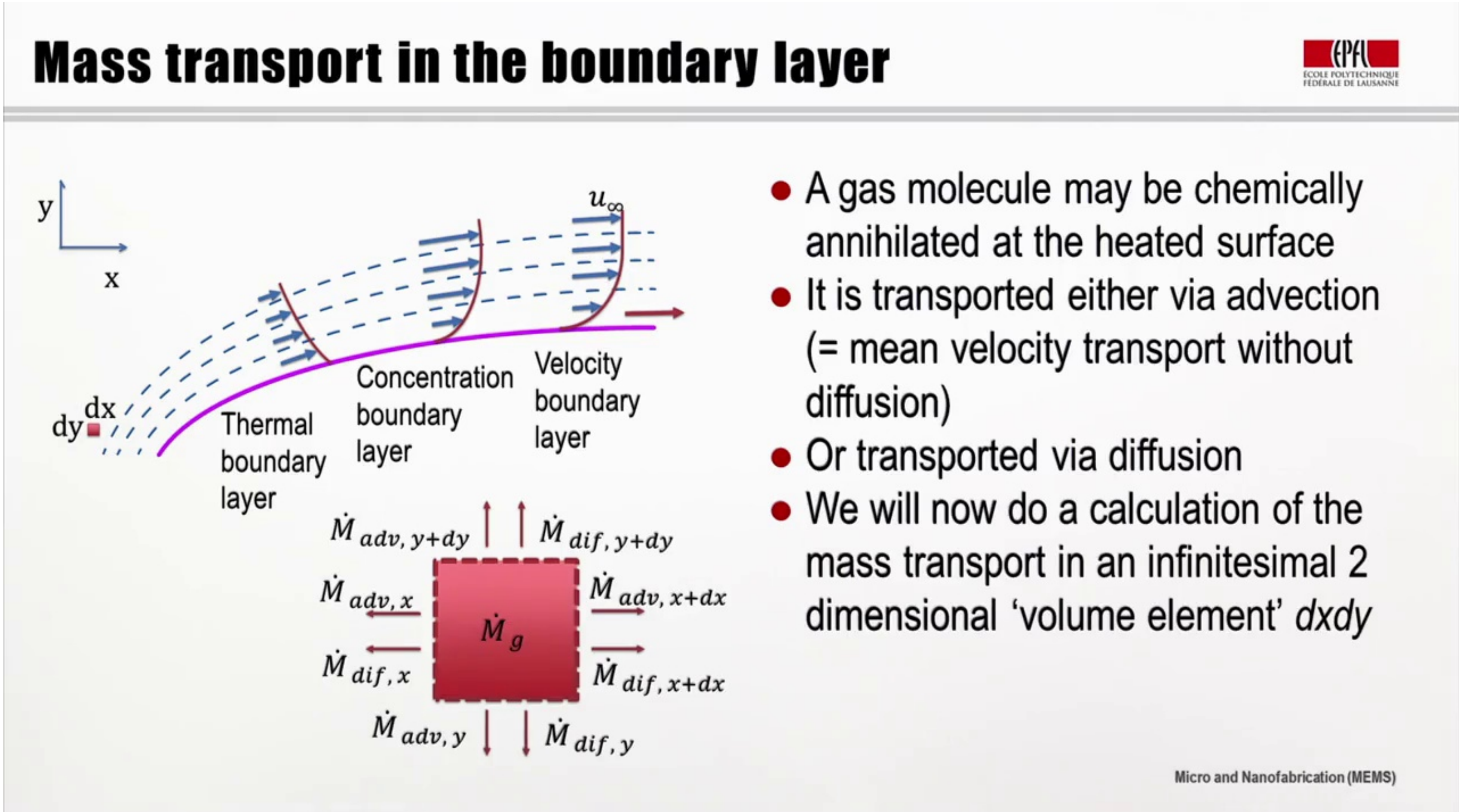
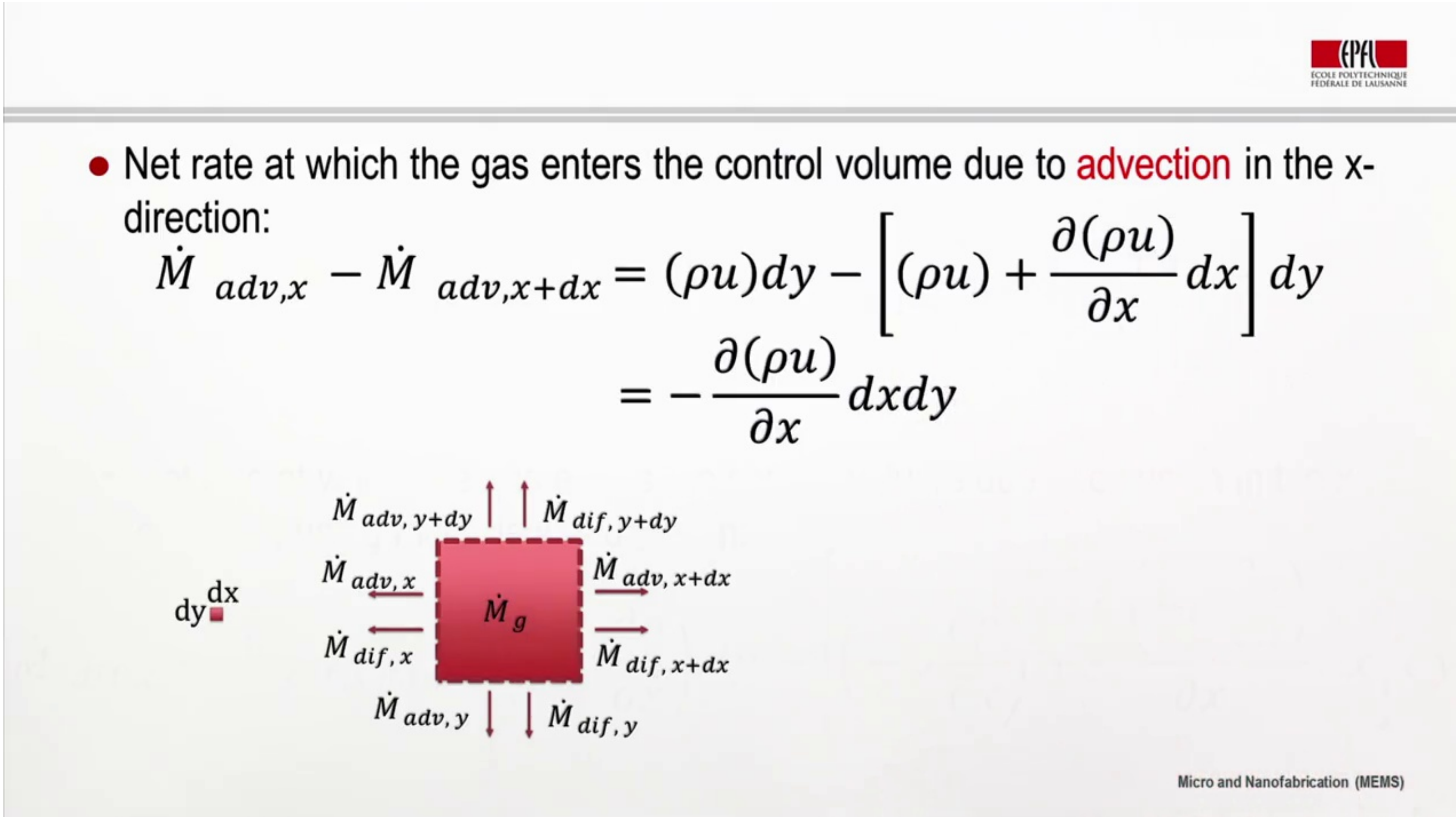


In the previous lesson we have introduced the concept of velocity and concentration boundary layer near a heated substrate during a chemical vapor deposition process. Now we will discuss theoretically what is the gas molecule transport from the bulk of the flow through the boundary layer towards the substrate. This transport is key for understanding the growth of the thin film on the substrate. We will subsequently present a simple model for the CVD film growth.



If we have a heated surface of an arbitrary shape like represented by the pink line, and if we apply a flow of gas it is already clear that there will be development of a thermal boundary layer in which the temperature varies; of a concentration boundary layer in which the gas concentration varies; and a velocity boundary layer in which the velocity varies. For simplicity, we will do here a two dimensional treatment and we consider an infinitesimal surface element <i>dxdy.</i> We will consider now the transport of gas molecules in and out of such element. This element is again drawn here at a bigger scale. The transport can be either by advection– that is, by an imposed ordered flow– or by diffusion from all sides. If we have somewhere in our two dimensional surface element the boundary layer of the heated surface– that means if this element would be here exactly where the pink line is– then there the gas molecules can be annihilated leading to a deposition event.



This expression represents the net rate at which the gas enters the two dimensional surface element due to advection in the x-direction. The first term represents the transport to the line element <i>dy</i> of our infinitesimal surface element with <i>rho–</i>the density of the gas– and <i>u</i>–the transport velocity in the x-direction. If we move further in the x-direction to the coordinate <i>x + dx,</i> we will have here the second line element <i>dy</i> to which the transport by advection is possible. Because we have moved over the distance <i>dx,</i> the term <i>rho-u</i> can be different. That is why we write it as a variational term, as written here in the square brackets.

- Net rate at which the gas enters the control volume due to advection in the x-direction:

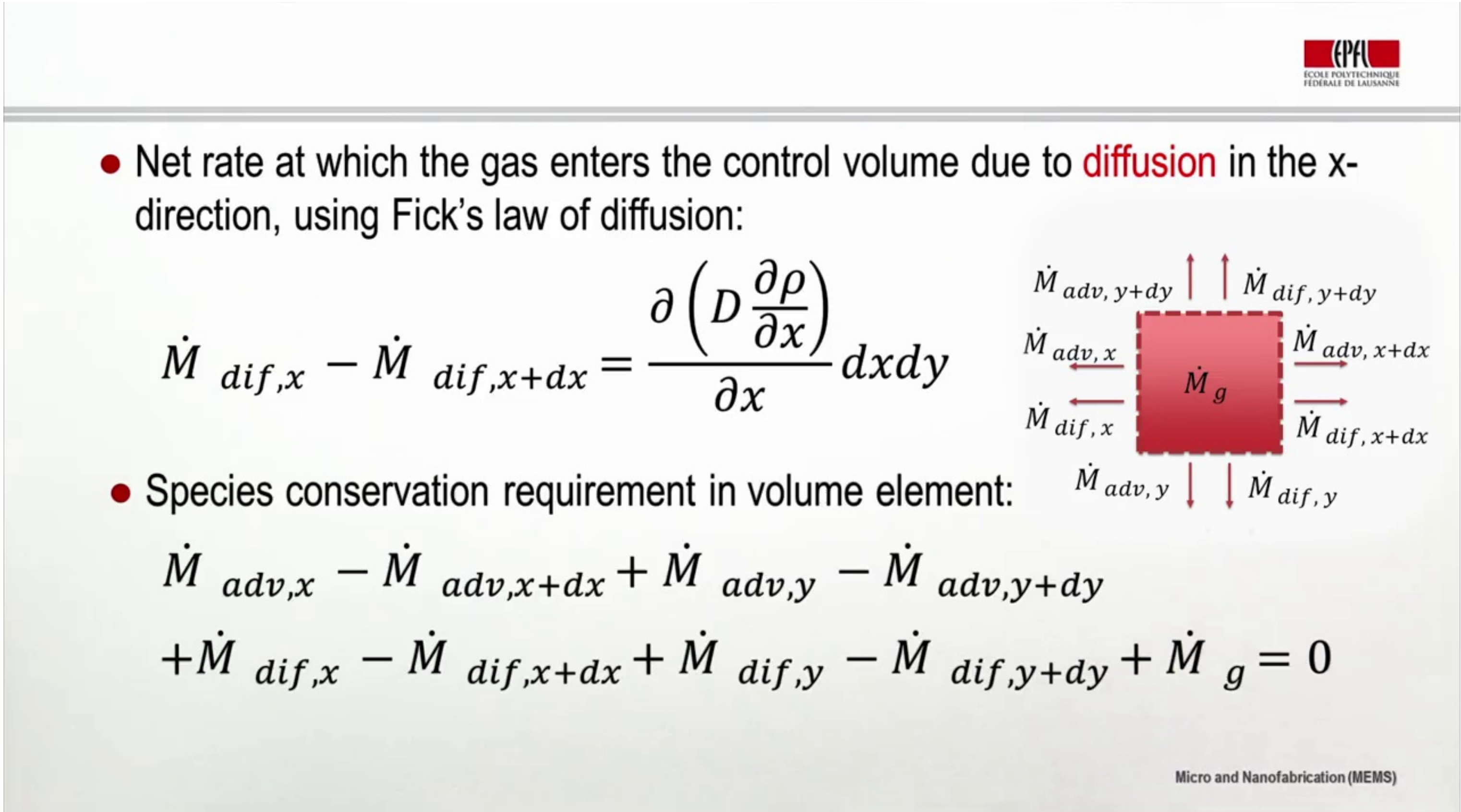
$$\dot{M}_{adv,x} - \dot{M}_{adv,x+dx} = (\rho u)dy - \left[(\rho u) + \frac{\partial(\rho u)}{\partial x}dx\right]dy$$
$$= -\frac{\partial(\rho u)}{\partial x}dxdy$$

- Net rate at which the gas enters the control volume due to diffusion in the x-direction, using Fick's law of diffusion:

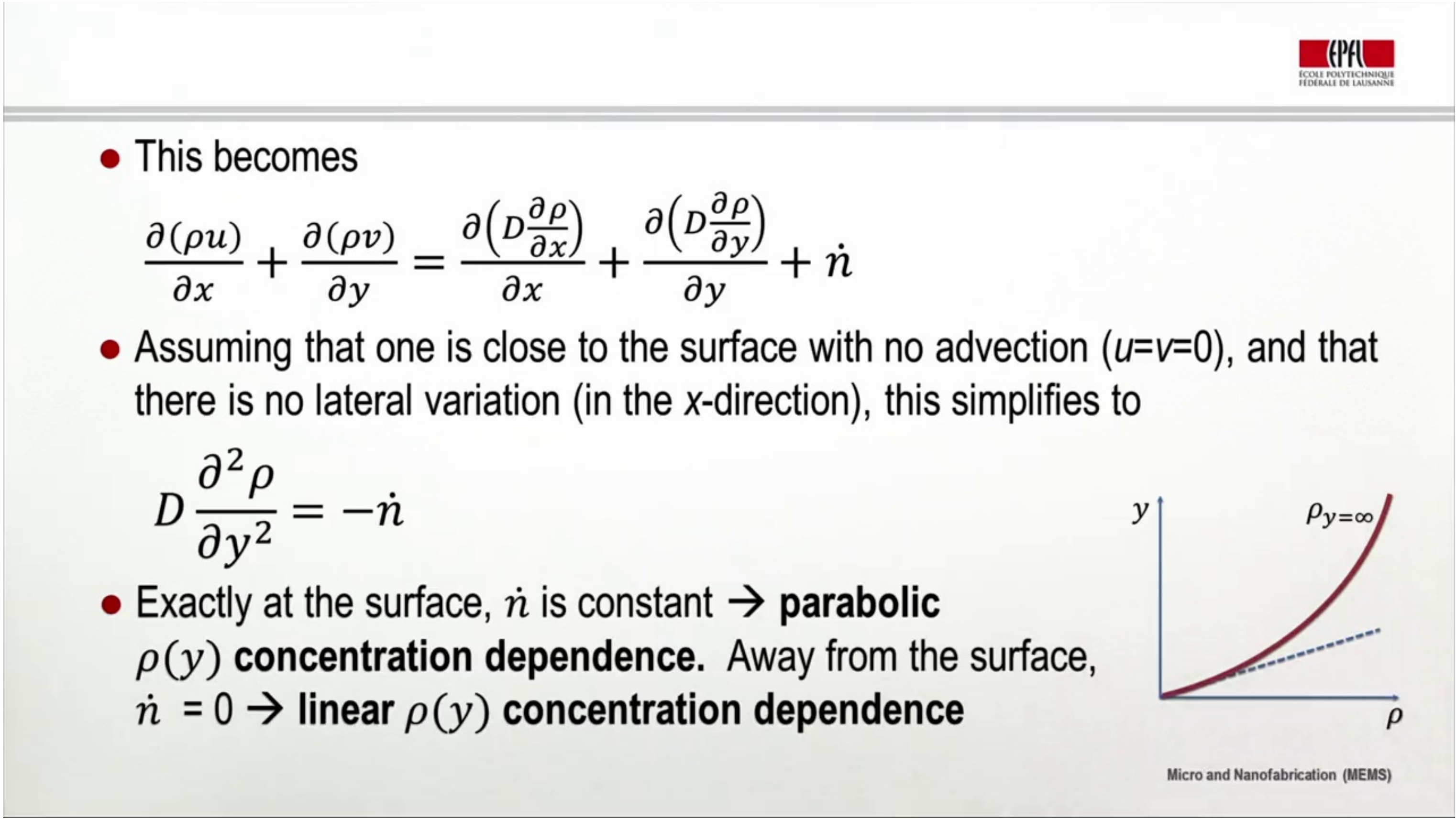
$$\dot{M}_{dif,x} - \dot{M}_{dif,x+dx} = \left(-D\frac{\partial \rho}{\partial x}\right)dy - \left[\left(-D\frac{\partial \rho}{\partial x}\right) + \frac{\partial\left(-D\frac{\partial \rho}{\partial x}\right)}{\partial x}dx\right]dy$$

Micro and Nanofabrication (MEMS)

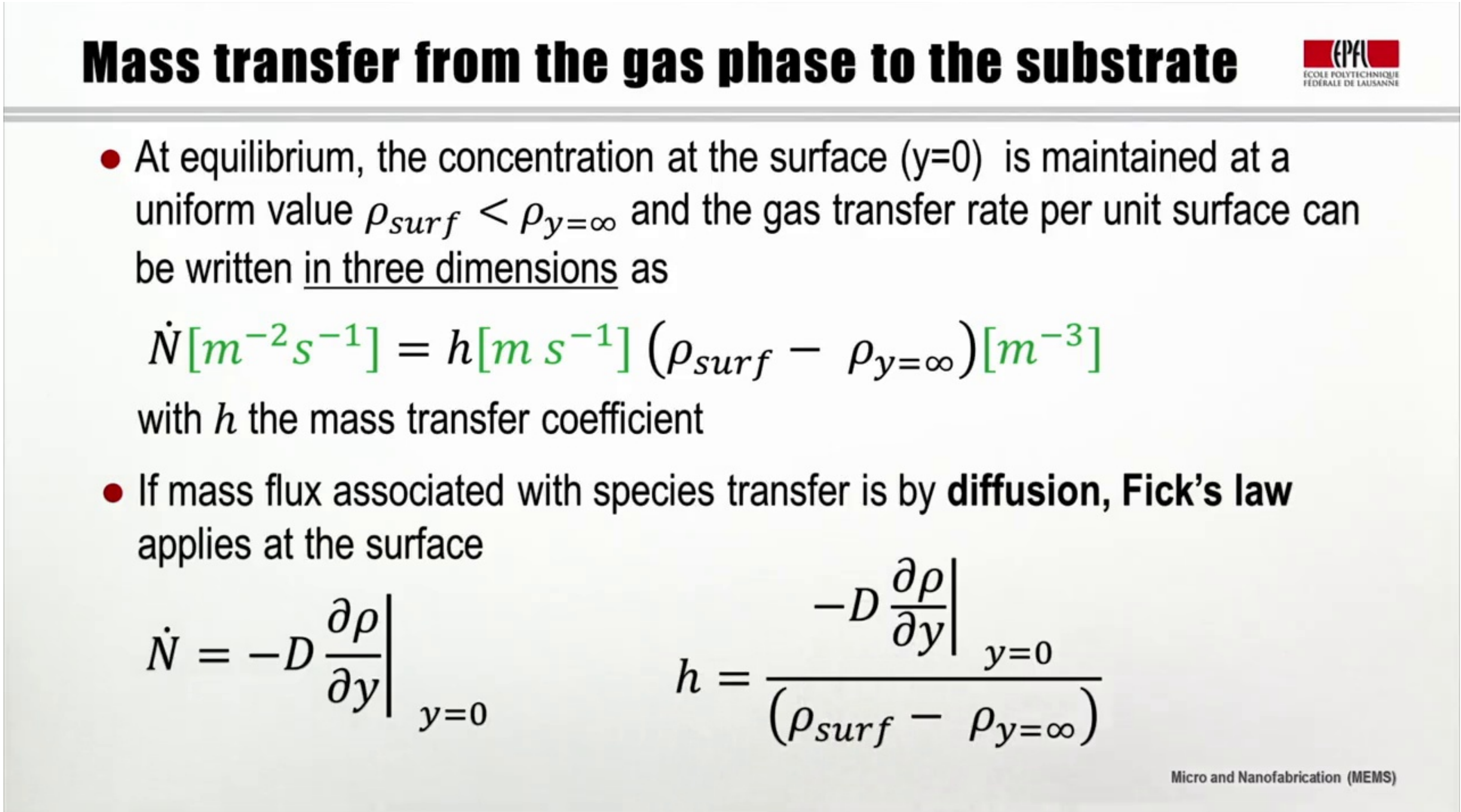
For describing the diffusion through the two dimensional surface element we write Fick's law of diffusion for the transport to the first line element <i>dy.</i> And using a similar variational approach as before, the second term describes the transport by diffusion through the second line element <i>dy.</i>



Here we have written the net transport through the surface element by diffusion in the x-direction. We can do a similar treatment for the y-direction and we define the advection velocity in this direction by <i>v.</i> This gives us eight terms: four advective terms and four diffusional terms. The last term in the equation describes the annihilation of the mass, which is only non-zero when the heated substrate is present in the surface element.



Writing all these contributions in the the <i>x-</i> and <i>y</i>-direction down, gives us the final equation with the two advection terms and the two diffusional terms and the annihilation term. So this is the equation we need to solve in general. Fortunately we can write this complex equation in a simplified way by assuming that one is close to the surface where there are no advective terms– that means close to the surface <i>u</i> and <i>v</i> are zero– and by considering that there is no lateral variation in <i>x</i>, which is a plausible assumption as we have a flat substrate so there is no dependence in the <i>x</i>-direction on the gas density. This equation is then simplified to this one where we only have a variational term in <i>y</i> and the annihilation term. The solution of this last equation is simple. Immediately at the surface where annihilation of the gas can occur– where this term is non-zero– this gives us a parabolic shape. Somewhat away from the surface this term becomes zero and this gives a line. The solution is schematically illustrated here in this diagram. This is the linear solution close to the substrate. In reality, we will have a concentration which gradually approaches the value for the density of the gas that is far away from the substrate, as denoted by the full line here.



We now consider that we are in equilibrium conditions and that the density of the gas near the surface is lower than the density of the gas far away, which is logical during a deposition process. We can then write the gas transfer rate per unit surface in three dimensions as following. This is the difference between the surface and the far away concentration of the gas. And this is <i>h– </i> the mass transfer coefficient. As close to the surface of the substrate there are no advective terms, Fick's law of diffusion should apply which, by equalization to this expression, leads to the value for the mass transfer coefficient <i>h.</i> We see that <i>h</i> is proportional to the diffusion coefficient.

Expression for D and the mass transfer coefficient h

- Flow of molecules through a surface in the gas per unit area and time

$$\overrightarrow{\rho_- \, v} \;\Big|\; \overleftarrow{\rho_+ \, v}$$

$$J[m^{-2}s^{-1}] = v[m\,s^{-1}]\,(\rho_- - \rho_+)[m^{-3}]$$

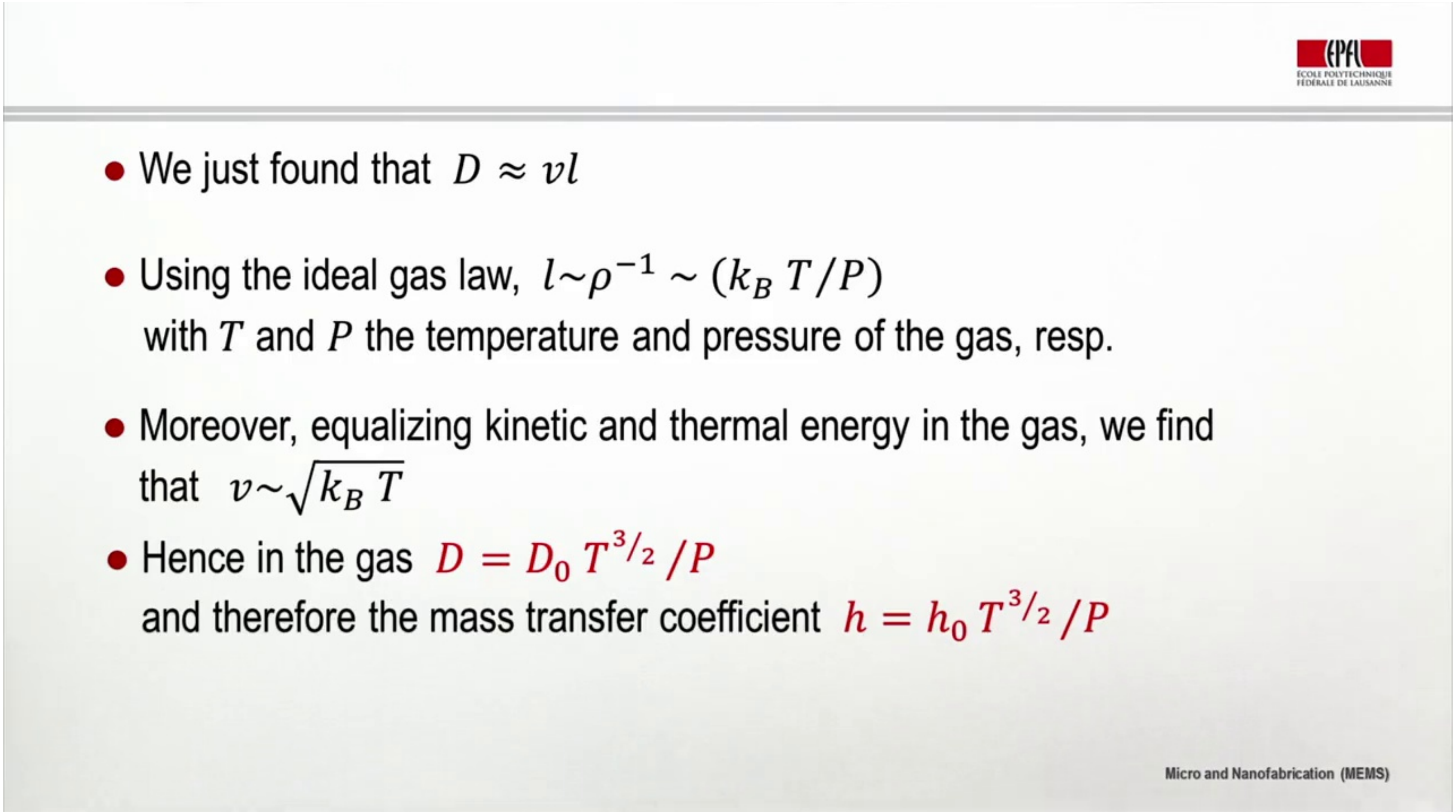
$$= -v\left(\frac{\partial \rho}{\partial x}\Delta x\right) \approx -vl\left(\frac{\partial \rho}{\partial x}\right)$$

with l the mean free path in the gas

- Comparing with Fick's law, we find that $D \approx vl$

Micro and Nanofabrication (MEMS)

We will now find an expression for the diffusion coefficient. If we consider somewhere in the gas plane with a gas density <i>rho</i> minus at the left and a gas density <i>rho</i> plus at the right of that plane and if <i>v</i> is the molecular velocity, we can write down the effective number of molecules flowing through the plane by this expression. It is the difference between molecules flowing from left to right and right to left. We can now follow again, a variational approach to write down this difference in which we subsequently equalize the variational distance <i>delta x</i> by <i>l,</i> which is the molecular mean free path in the gas. Comparing this expression with Fick's law we find that diffusion coefficient is given by the velocity of the molecule times the mean free path of the molecule.



Here we repeat the expression we just found for the diffusion coefficient. We can write the mean free path in the gas as function of the temperature and pressure of the gas using the ideal gas law. And we can write the molecular velocity– which is here– by the square root of the thermal energy. This provides then the following expression for the diffusion coefficient: <i>T^1.5</i> and <i>P^-1.</i> Therefore the mass transfer coefficient has the same dependence.

Calculation of the film growth rate

- Diffusion flux of molecules through the boundary layer

$$\dot{N}_1[m^{-2}s^{-1}] = h[m\,s^{-1}]\left(\rho_{surf} - \rho_{y=\infty}\right)[m^{-3}]$$

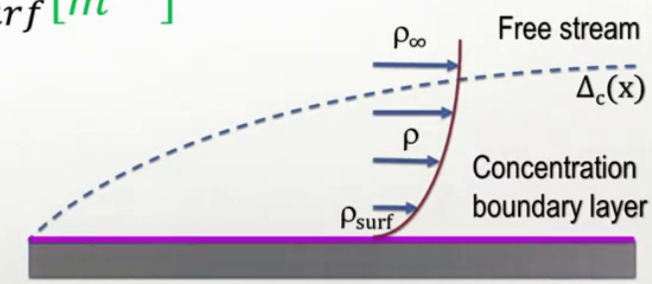
- Flux of reacted molecules consumed by the surface reaction

$$\dot{N}_2[m^{-2}s^{-1}] = -k_{surf}[m\,s^{-1}]\rho_{surf}[m^{-3}]$$

with k_{surf} the surface reaction rate

- In equilibrium, $\dot{N} \equiv \dot{N}_1 = \dot{N}_2$, giving

$$\rho_{surf} = \rho_{y=\infty}\left(\frac{h + k_{surf}}{h}\right)^{-1}$$



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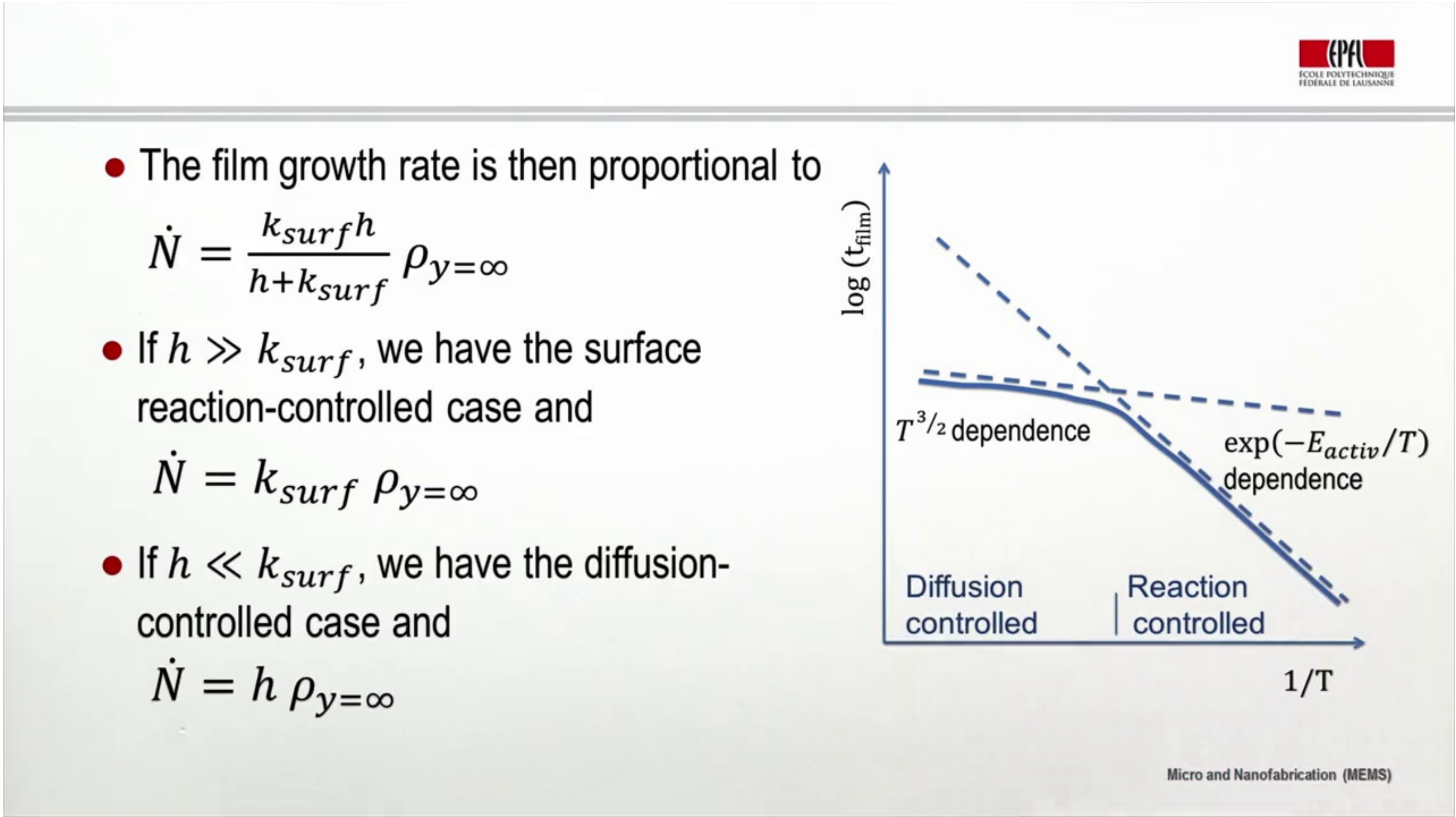
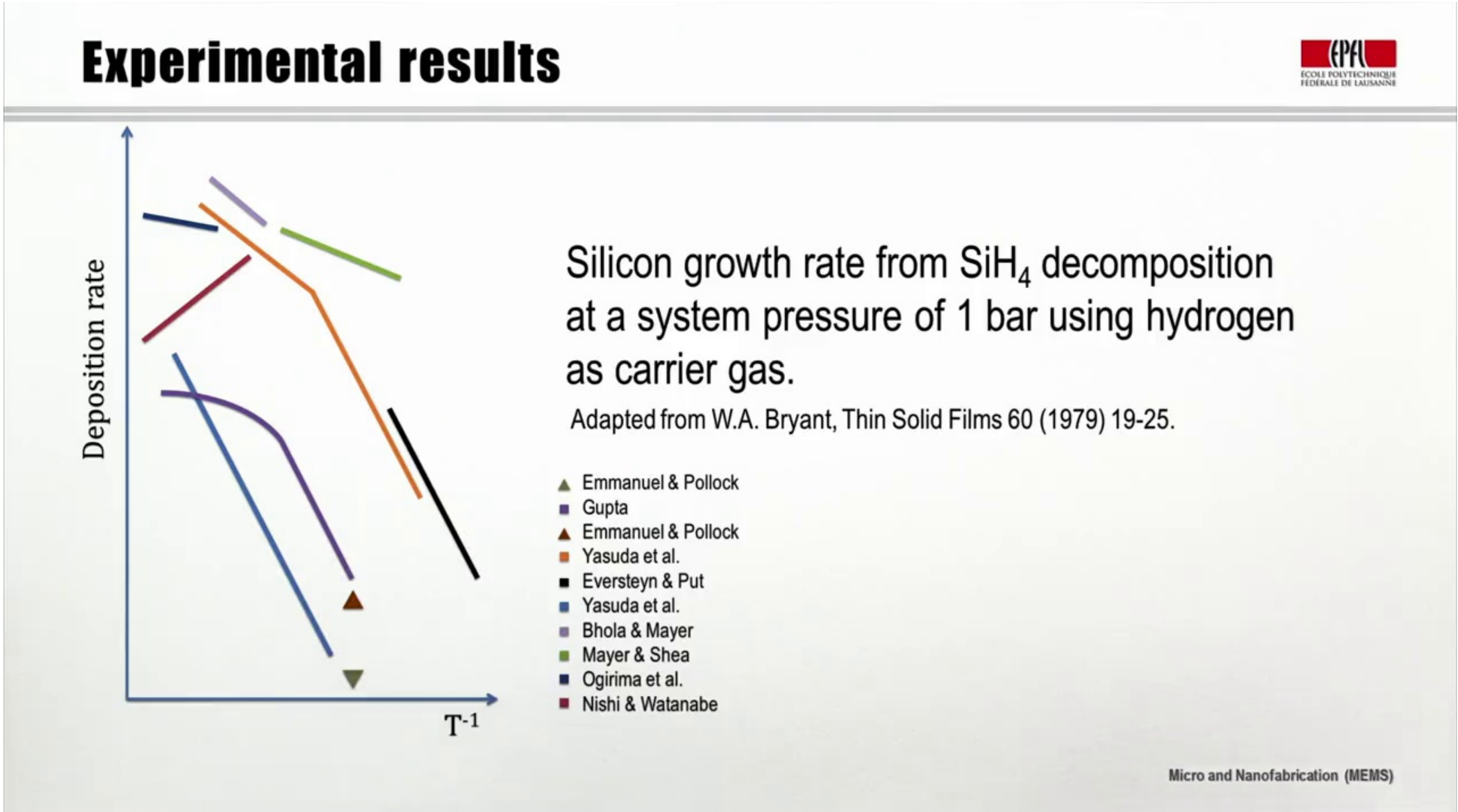
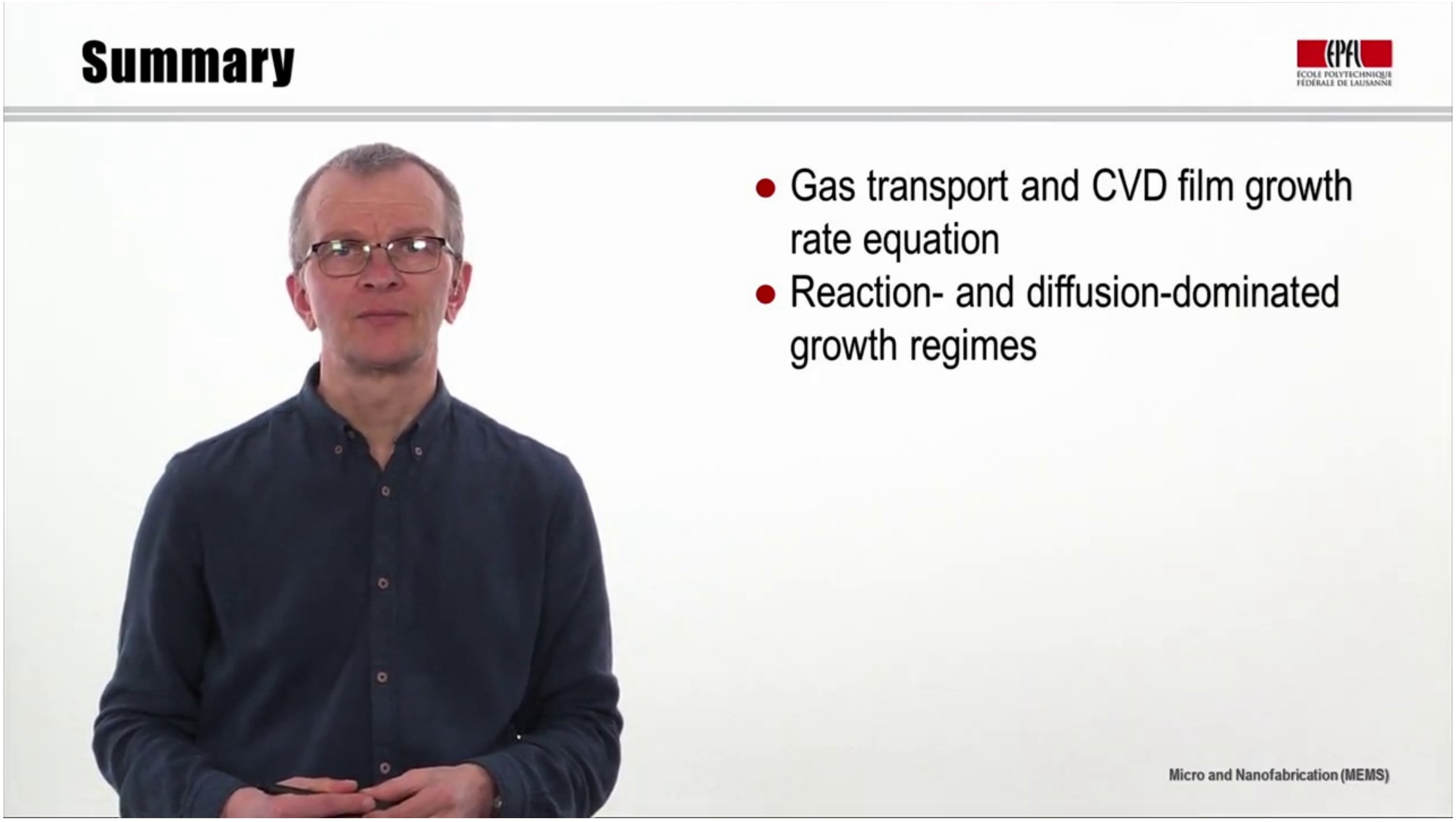
We present here again, the formula we have found before for the diffusional flux of molecules through the boundary layer. The second formula describes the flux of reacted molecules that are consumed by the surface reaction, with <i>ksurf</i> the surface reaction rate. In equilibrium both fluxes should be the same and this allows us to find an expression for the gas density at the surface in function of <i>h</i> and <i>ksurf.</i>



By substitution in the first formula of previous slide, we find the following expression for the growth rate. If the mass transfer coefficient by diffusion is much higher than the surface reaction rate, we obtain the film growth rate in the reaction-controlled case from this expression. Under these conditions there is no dependence on <i>h</i> as sufficient gas is provided everywhere for the reaction to occur. In the opposite case, we have diffusion-controlled film growth and this evidently depends on <i>h.</i> These theoretical findings allow us to understand the Arrhenius-type plot for the thin film growth, which we have already introduced before, with here the exponential temperature dependence and here the T^1.5 dependence.



Finally on this slide we have plotted a number of experimental data of the growth of silicon on a heated substrate. Here one has used silane as a gas and this gas is diluted in hydrogen as a carrier gas. The experimental curves indeed are in line with the result of previous theoretical finding.



In this lesson we have discussed gas transport by diffusion in the boundary layer near the substrate during a CVD process. We then have written a simplified expression for the mass transport towards the substrate as limited by diffusion. Finally, assuming equilibrium conditions, we have compared a reaction- and diffusion-limited growth rates which have allowed us to understand the dependence of CVD film growth rate as a function of temperature.