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Modeling in chemical engineering

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Abstract

In its 90 year life what has chemical engineering (ChE) contributed to society? Firstly, we have invented and developed processes to create new materials, more gently and more efficiently, so as to make life easier for all.

Secondly, ChE has changed our accepted concepts and our ways of thinking in science and technology. Here modeling stands out as the primary development. Let us consider this.

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1. Chemical engineering's \$10 and \$100 flow models

I suspect that most authors put especial thought into the first sentence of a book because it sets the tone for what is to follow. In this light Denbigh's monograph (Denbigh, 1951) starts with the following sentence:

> In science it is always necessary to abstract from the complexity of the real world, and in its place to substitute a more or less idealized situation that is more amenable to analysis.

This statement applies directly to chemical engineering, because each advancing step in its concepts frequently starts with an idealization which involves the creation of a new and simplified model of the world around us. The acceptance of such a model changes our world view.

Often a number of models vie for acceptance. Should we favor rigor or simplicity, exactness or usefulness, the \$10 or \$100 model? We will look at:

- boundary layer theory,
- heat transfer and 'h',
- mass transfer and 'k_g' and 'k_ℓ',
- chemical reactors, RTD, tracer technology, and
- the troublesome fluidized bed.

We may call the 20th century chemical engineering's modeling century. This talk considers this whole development.

2. The boundary layer concept

How is the velocity of a fluid affected as it flows close to a solid surface? Throughout the years many scientists considered this phenomenon. These studies culminated in the Karman–Prandtl u vs. y relationship, see von Karman (1934),

$$\frac{u}{\sqrt{\tau_0/\rho}} = 5.75 \log\left(\frac{y\rho\sqrt{\tau_0/\rho}}{\mu}\right) + 5.56,$$

where

$$u = \frac{y\tau_0}{\mu} \quad \text{when } u < 11.84\sqrt{\frac{\tau_0}{\rho}}$$

which is shown in Fig. 1a.

However, Prandtl (1904) proposed a simpler model for the velocity profile: thus a linear velocity change with distance from the surface, or

$$\frac{\mathrm{d}u}{\mathrm{d}y} = \text{constant} \quad \text{and} \quad u = 0 \text{ at } y = 0$$

meeting nonviscous flow further away from the surface; in effect, two different types of fluid patched together. This is shown in Fig. 1b.

This combination of viscous and nonviscous fluid seemed absurd at that time, but as we shall see, it has been found to be fabulously efficient and useful for aeronautics, chemical and other branches of engineering.

Let me repeat a few words about the creator of the laminar layer model, words written by his most illustrious student, Theodore von Karman, director of the Guggenheim Aeronautical Laboratory at the California Institute of Technology (von Karman, 1954).

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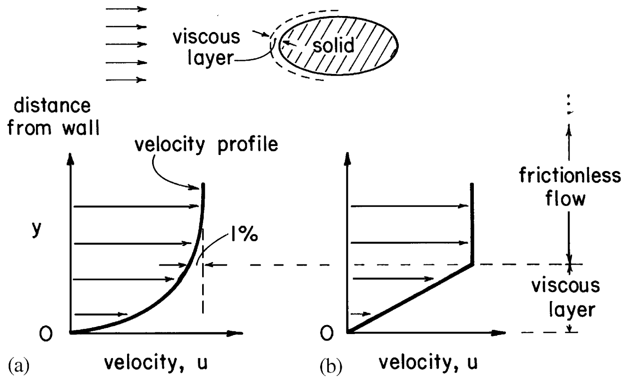


Fig. 1. Velocity profile near a wall: (a) actual profile, and (b) simplified profile.

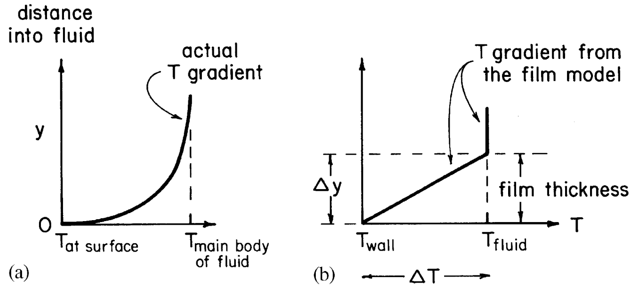


Fig. 2. Temperature by a wall: (a) actual profile, and (b) simplified profile.

> Prandtl (1875–1953) was an engineer in training. His control of mathematical methods and tricks was limited; many of his collaborators and followers surpassed him in solving difficult mathematical problems. However he had a unique ability to describe physical phenomena in relatively simple terms, to distill the essence of a situation and to drop the unessentials. His greatest contribution is in boundary layer theory.

So here we have two models for flow close to a surface, the more precise \$100 Karman–Prandtl equation and the simple \$10 laminar layer or film model. We will see that chemical engineering embraced the \$10 model and made it a cornerstone for its developments in the 20th century.

3. Film model for heat transfer

Twelve years after Prandtl charted the path with his simple flow model, W. K. Lewis of M.I.T. (Lewis, 1916), following the ideas of Newton, Fourier, and other early workers, adopted the simple film model to represent the rate of heat transfer from a hot fluid flowing past a cold surface. This means that instead of considering a changing temperature gradient away from the cold surface, Fig. 2a, he took a straight line gradient in the film, but with no additional change beyond, as shown in Fig. 2b. Thus, close to the cold surface he said

$$\text{replace the changing}\ldots \left(\frac{\mathrm{d}T}{\mathrm{d}y}\right)_{\substack{\text{close to}\\\text{the surface}}} \xrightarrow{\text{by}} \left(\frac{\Delta T}{\Delta y}\right)_{\substack{\text{across}\\\text{the film}}}$$

in which case the Fourier heat transfer equation becomes

$$\dot{q} = kA\left(\frac{\Delta T}{\Delta y}\right)_{\substack{\text{across the}\\\text{whole film}}} = \frac{k}{\Delta y}A\Delta T.$$

Calling $k/\Delta y = h$ he finally got

$$\dot{q} = hA\Delta T,$$

where 'h' is called the *heat transfer coefficient*.

The acceptance and use of this concept led to explosive research. Thousands of research studies were reported, and are still being reported today, on 'h' for

- flow inside and outside of pipes,
- condensing fluids,
- boiling fluids,
- natural convection and
- two phase systems of all types of gases, liquids, and solids.

The resulting correlations were all made in terms of dimensionless groups, examples of which are shown below.

For the inside pipe wall (turbulent flow):

$$\underset{\text{Nusselt}}{\underline{\frac{hd}{k}}} = 0.023 \underset{\text{entrance}}{\underline{\left[1+\left(\frac{d}{L}\right)^{0.7}\right]}}$$

$$\times \underset{\text{coiled pipe}}{\underline{\left[1+3.5\frac{d}{d_{\text{coil}}}\right]}} \quad Re^{0.8} \quad Pr^{1/3} \quad \underset{\substack{\text{temperature}\\\text{dependency}}}{\underline{\left(\frac{\mu}{\mu_w}\right)^{0.14}}}$$

Single particle : $\frac{hD}{k} = 2 + 0.6\,Re^{1/2}\,Pr^{1/3}$,
Natural convection : $hL/k = A[Gr\,Pr]^B$,

$$\begin{array}{l}\text{Condensation}\\\text{Boiling}\\\text{Radiation}\end{array} \quad \ldots\text{etc.} \left\{\begin{array}{l}\text{hundreds of studies}\\\\\text{hundreds of correlations.}\end{array}\right.$$

4. Film model for mass transfer

It took another 7 years before Whitman (1923) considered applying the film model to mass transfer from a fluid to its bounding surface. With an approach similar to that used by Lewis he replaced the changing concentration profile of a component A, Fig. 3a, by a linear concentration profile as

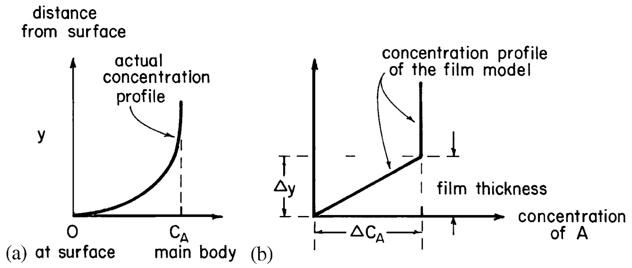


Fig. 3. Mass transfer: (a) actual profile, and (b) simplified profile.

shown in Fig. 3b. In symbols the absorption rate by the solid, or removal rate of A from the fluid is

$$\dot{N}_A = \mathscr{D} A \left(\frac{\mathrm{d}C_A}{\mathrm{d}y}\right)_{\text{at surface}} \qquad (\text{mol } A \text{ removed/s}).$$

With the linear model

$$\dot{N}_A = \mathscr{D} A \left(\frac{\Delta C_A}{\Delta y}\right) = \frac{\mathscr{D}}{\Delta y} A \Delta C_A = k_g A (\Delta C_A)_{\substack{\text{across the}\\ \text{whole film}}}$$

where k_g (or k_ℓ) is called the *mass transfer coefficient*.

Again, dimensionless groups are involved in the correlations for the various mass transfer situations, as shown below (Perry & Green, 1984).

For gas absorption in columns filled with Raschig rings, and Berl saddles.

$$\text{For the gas phase}: \frac{k_g}{G_g} = 1.195\left(\frac{G_g d_p}{\mu_g(1-\varepsilon)}\right)^{-0.36} \left(\frac{\mu}{\rho \mathscr{D}}\right)_g^{-2/3}.$$

$$\text{For the liquid phase}: \frac{k_\ell d_p}{\mathscr{D}_\ell} = 25.1\left(\frac{G_\ell d_p}{\mu_\ell(1-\varepsilon)}\right)^{0.45} \left(\frac{\mu}{\rho \mathscr{D}}\right)_\ell^{0.5}.$$

5. Design consequences

These concepts of 'h' for heat transfer and 'k' for mass transfer became the heart of design methods for heat exchangers and for absorption and extraction equipment.

For heat transfer from one fluid through a wall to a second fluid this leads to the overall heat transfer coefficient U given as

$$\frac{1}{U} = \frac{1}{h_1} + \frac{1}{h_2}$$

and for a heat exchanger for counter (or parallel)-flow of two fluids a \$10 flow model assumes plug flow of the two fluids, as shown in Fig. 4. For this model the performance expression is

$$\dot{q} = UA(\Delta T)_{\ell m}, \qquad \text{where } \Delta T = T_i - t_i,$$

with the logarithmic mean ΔT is

$$\Delta T_{\ell m} = \frac{\Delta T_1 - \Delta T_2}{\ln(\Delta T_1/\Delta T_2)}.$$

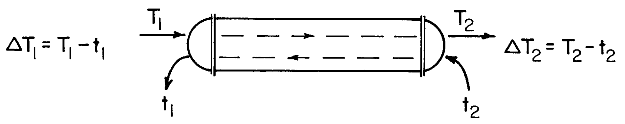


Fig. 4. Counterflow heat interchange, plug flow idealization.

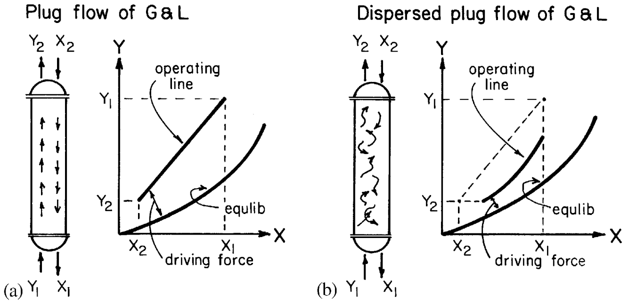


Fig. 5. Countercurrent flow mass transfer: (a) plug flow model, and (b) axial dispersion model.

It should be noted that the logarithmic mean driving force is often used to represent design of all sorts of contacting patterns—plug flow, mixed flow, laminar flow, crosscurrent flow, etc. However, we should be aware that the logarithmic mean is only correct and should only be used to represent cocurrent and countercurrent plug flow. For all other flow patterns it is incorrect, often very incorrect to use it.

For mass transfer of a component A from a gas to a liquid we have a similar development, an overall mass transfer coefficient K_g, which is defined as

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{H_A}{k_\ell}, \qquad H_A = \left(\begin{matrix}\text{Henry's law constant}\\ \text{for } A\end{matrix}\right).$$

In a packed bed tower, with countercurrent flow of gas and liquid, the design method, universally used today, is based on the crude \$10 model for the flow of gas and of liquid, the plug flow model, Fig. 5a. To be more realistic, to assume dispersed plug flow, the operating line would look different. This model is illustrated in Fig. 5b. This more realistic approach, this \$100 flow model, was championed by Vermeulen et al. (1966), but it had problems:

- It required a complex computer solution.
- We did not have reliable values for the extent of dispersion, or deviation from plug flow for gas and for liquid.
- Every time you pack a column you get a different flow behavior.

So this \$100 approach has been lost in history.

For heat exchanger design we get similar flow complications if we try to account for deviations from plug flow.

6. Reflections on the first 50 years of chemical engineering

Prandtl's simple model was taken up by Lewis for heat transfer, and by Whitman for mass transfer, and it led ultimately to the core of the unit operations. Our profession has really blossomed as a consequence of this simple concept. Can you imagine what heat and mass transfer studies would be like without 'h' and 'k'? A desert.

7. Chemical reactors

In the first half of this century two flow models dominated the design of flow reactors, *plug flow* and *mixed flow*. Fig. 6 shows, for the reaction given, if a plug flow reactor would need a length of 1 m, then for mixed flow you would need a length of 1000 m to produce the same product.

It would be unwise to only use these flow models, since real reactors behave somewhere between these two extremes. How do we deal with this? The $100 approach says evaluate the velocity field within the reactor, or better still, the $1000 approach says evaluate the three-dimensional fluctuating velocity field, and then use your computer to tell you what would happen; in essence, use computational fluid dynamics. What an ugly procedure!

In so complicated a world what should we do? It was the genius of Danckwerts (1953) who proposed a ridiculously simple flow model to tell how a vessel would act as a chemical reactor. He said, introduce a pulse of tracer into the fluid entering the reactor and see when it leaves. This exit concentration–time curve is called the *residence time distribution* curve, or RTD curve, see Fig. 7.

This information tells how the reactor would behave—exactly for linear reaction kinetics, and as a close approximation for more complex reaction kinetics. How wonderfully little information is needed! No need to measure what is happening within the reactor.

This proposal of Danckwerts led to an explosion of research, and to the development of all sorts of models to represent these response curves. Fig. 8 shows one class of these models, the one to represent the flow in pipes and in other long narrow vessels. Lots of research, lots of publications and lots of Ph.D. theses resulted from this concept, mainly in the late 1950s, the 1960s and the 1970s.

The study of the RTD of flowing fluids, and its consequences is called *tracer technology*. Chemical engineers and medical researchers are those who are most interested in this subject, to the chemical engineer to represent the behavior of reactors, to the medical doctor to represent the movement and distribution of fluids and drugs in the body, to diagnose disease, etc.

8. Fluid sciences

Let us briefly summarize the science and technology of fluid flow.

In the 19th century two completely different approaches were used to study the flow of fluids. First there was the theoretical study called *hydrodynamics*, which dealt with

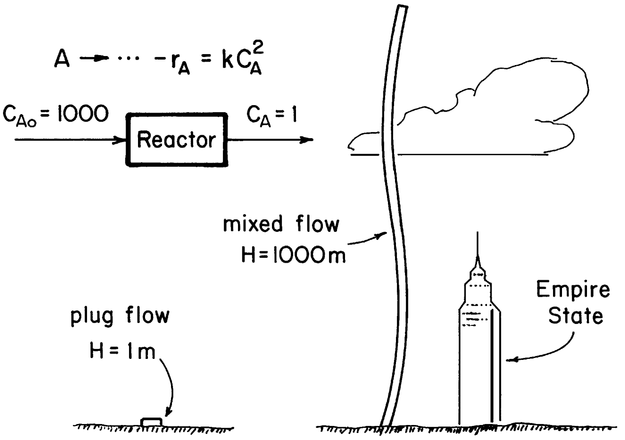


Fig. 6. Volumes needed for the two ideal flow patterns: (a) plug flow model, and (b) mixed flow model.

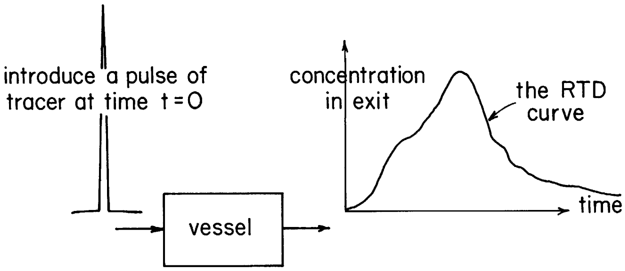


Fig. 7. Key to the tracer method for determining the flow pattern in vessels and reactors.

the ideal frictionless fluid (that imaginary stuff). This was a highly mathematical exercise dealing with what is called irrotational flow, velocity potentials and stream functions.

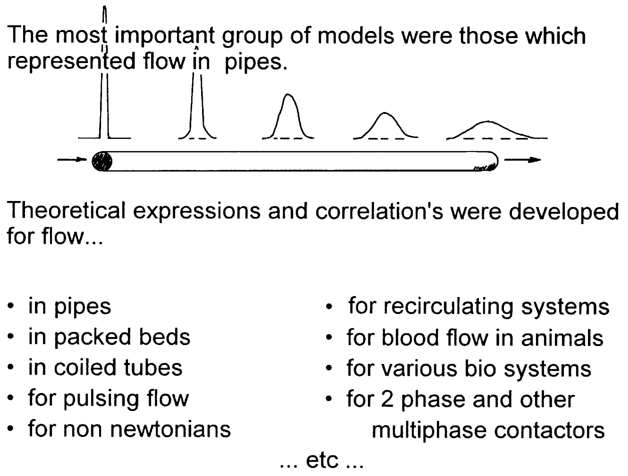
On the other hand, you had *hydraulics* developed by civil engineers, who amassed mountains of tables, all obtained from experiments on pressure drop and head loss of fluids flowing in all sorts of open and closed channels—made of concrete, fresh wood, slimy old wood, etc.

Reflecting on the situation at the beginning of the 20th century, Prandtl (see Tietjens, 1934) said

> Hydrodynamics has little significance for the engineer because of the great mathematical knowledge required for an understanding of it and the negligible possibility of applying its results. Therefore engineers put their trust in the mass of empirical data collectively known as the "science of hydraulics".

Prandtl (1904) was the genius who patched together these completely different disciplines with his simple boundary layer model. The result is modern *fluid mechanics*. The left side of Fig. 9 shows the pioneers in this development, the types of problems solved, the terms used, and so on. I call this Type 1 problem of fluid flow.

Then in 1952 Danckwerts introduced a completely different type of study of fluids which I call *tracer technology*.



The most important group of models were those which represented flow in pipes.

Theoretical expressions and correlation's were developed for flow...

- in pipes
- in packed beds
- in coiled tubes
- for pulsing flow
- for non newtonians
- for recirculating systems
- for blood flow in animals
- for various bio systems
- for 2 phase and other multiphase contactors

... etc ...

Fig. 8. The dispersed plug flow model is used to represent many reactors and vessel types.

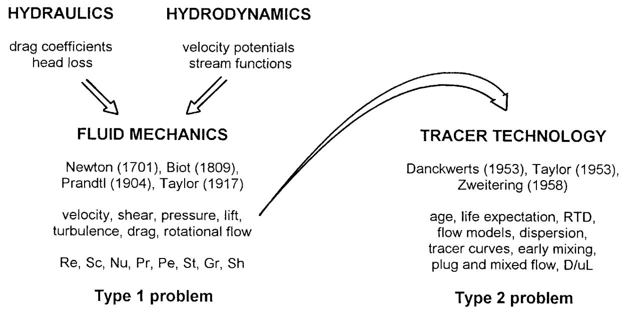


Fig. 9. The two distinctly different types of fluid mechanics problems.

The right side of Fig. 9 shows the names of the pioneers and the terms used in this type of study. I call this Type 2 problem of fluid flow. Both these types of problems started with a simple approximation of the complex real world. Note how completely different are these two branches of fluid flow. It is interesting to note that there are dozens upon dozens of books on Type 1 problem, as well as courses in every academic institution in the world on this type of problem. However, there is not a single book in print today devoted to the Type 2 problem even though it is important in the study of chemical reactors, in physiology, in oceanography, in dealing with the flow of ground waters, rivers, and oceans. How curious.

Also note that the Type 2 branch of the subject was developed as a \$10 approximation of what is a very complicated mathematical model, one which involves stochastic computational fluid dynamics.

9. Models for chemical reactions

There are two broad classes of models for chemical reactions, the LHHW and the CRE. Let us discuss these.

9.1. The LHHW models

Since the beginning of the century chemists have used the Langmuir–Hinshelwood models to represent the rates of chemical reactions. The chemical engineer, following the lead of Hougen and Watson's 1947 book (Hougen & Watson, 1947a), built on this approach developing what is called the Langmuir–Hinshelwood–Hougen–Watson (LHHW) models.

These models were cumbersome to use, but were based on the mechanism of action of molecules, such as:

- adsorption of reactants onto active sites on the solid surface,
- reactions of attached molecules
  - with adjacent attached molecules (dual site)
  - with free molecules (single site)
  - by decomposition alone
- desorption of product molecules from the surface.

For a typical equation, say for a first-order reversible reaction, $A \rightarrow R$, dual-site mechanism, surface reaction controlling, no product in the feed, the performance equation for plug flow of gas through the packed bed catalytic reactor is:

$$\begin{aligned}\frac{C}{\pi}\left(\frac{W}{F}\right) = {} & \left[\frac{(1/\pi + K_A n_{A0} + K_I n_{I0})^2}{(1+1/K)} + \frac{2(1/\pi + K_A n_{A0} + K_I n_{I0})(K_R - K_A)n_{A0}}{(1+1/K)^2} + \frac{(K_R - K_A)n_{A0}^2}{(1+1/K)^3}\right] \ln\left(\frac{n_{A0}}{n_{A0} - (1+1/K)x}\right) \\ & - \frac{(K_R - K_A)^2 x^2}{2(1+1/K)} - \frac{2(1/\pi + K_A n_{A0} + K_I n_{I0})(K_R - K_A)x}{(1+1/K)} - \frac{(K_R - K_A)^2 n_{A0} x}{(1+1/K)^2}.\end{aligned} \tag{1}$$

This is a rather awkward complicated equation.

One of the two major problems with this approach is that many possible mechanisms can and do fit any set of data. For example, Hougen and Watson (1947b) show that 18 different mechanisms can be proposed by the simple reaction:

$$\underset{\text{codimer}}{C_8H_{16}} + H_2 = C_8H_{18}.$$

Sad to say, not even with the most detailed experimental program has anyone been able to choose among these models.

Since these models extrapolate differently, this means that one cannot predict what to expect in new conditions so your choice of this or that mechanism is arbitrary and may not represent reality.

The second problem with the LHHW models is that they completely ignore possible heat and mass transfer resistances such as:

- film mass transfer from gas to particle surface,
- pore diffusion in the particle,
- film heat transfer,
- nonisothermal particles.

Now the chemist deliberately chooses conditions where he can study chemical kinetics free from physical resistances. However, the chemical engineer, dealing with reactor design, has to consider these contributions.

9.2. The CRE models

In 1956 a new approach was introduced, called *chemical reaction engineering* (1958). This approach used a simple nonmechanistic based kinetic form (often *n*th order) combined with heat and mass transfer effects (Thiele modulus, Prater–Weisz nonisothermal criteria).

As an example, for the reaction leading to Eq. (1) the CRE approach gives

$$r'_A = k' C_A \varepsilon,$$

where ε, the effectiveness factor, depends on the nonisothermal Thiele modulus. This relationship is based on values for

- the particle size, L;
- the effective diffusion coefficient of gas in catalyst pores, $\mathscr{D}$;
- the thermal diffusivity of the solid, k;
- the heat of reaction, ΔH_r.

The CRE approach was found to be simpler and more general, and so found favor and was widely accepted by the profession. It is the class of model used today.

10. Creators of models

Who discovered America? The Egyptian reed boat explorers, the Mongol wanderers, Lief Ericsson and his Viking bands or Christopher Columbus? The earlier discoveries were isolated events which were not followed up on and were forgotten by history. But Columbus' was different. It was used, it changed society's thinking and action, so we credit him with the discovery.

So it is with the film model and the boundary layer idea. Certainly, earlier works were reported in this area, for example: Newton (1701), Biot (1809), Peclet (1844), Reynolds (1874), Stanton (1877), and Nernst (1904).

But Prandtl's 1904 article (Prandtl, 1904) changed our thinking in engineering. He was our Columbus.

Let me give you a picture of what engineering was like early in the century. Until 1912, ASME had only recorded eight papers in all areas of heat transfer in the previous 32 years of its history, not one of which was on films, boundary layers or "*h*" (Layton & Leinhard, 1988). The very first book on engineering heat transfer was the well known 1933 volume by McAdams (1933). Thus, these concepts are all relatively recent and all part of this century's creations.

May I end up by suggesting the following modeling strategy: always start by trying the simplest model and then only add complexity to the extent needed. This is the $10 approach, or as Einstein said,

> "Keep things as simple as possible, but not simpler".

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