Instructional Module on

Synthetic Fiber Manufacturing

by

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Synthetic Fiber Manufacturing

1 Introduction

The manufacture of synthetic fibers represents a huge industry, both in the United States and worldwide. In 1990, the dollar value of synthetic fibers was roughly $17 billion in the U.S. and $70 billion worldwide. Natural fibers, consisting mainly of cotton and wool, but also including silk, yielded total dollar values only slightly higher.

We sometimes forget how much of these fibers we consume, especially since the appeal of "natural" fibers of cotton and wool has grown in recent years. Despite questions of aesthetics and taste, there should continue to be a significant demand for synthetic fibers, in large part because these fibers can be tailor-made to provide specific properties that natural fibers cannot provide.

As chemical engineers, we are interested in the manufacture of synthetic fibers because we have been the principal developers of the processes used to produce the fibers and because we are usually the ones charged with overseeing and improving the manufacturing operations.

As students of chemical engineering, we are interested in the manufacture of synthetic fibers because the process involves several fundamental aspects of chemical engineering. Once we understand this process thoroughly, we will be in a position to understand other chemical processes quite easily. The goal here is to provide us students with the motivation and curiosity to learn these fundamental concepts; such motivation is supposed to stem from exposure to practical and somewhat familiar operations where the value of learning the fundamentals will become self-evident.

Figure 1.1 depicts the four main areas of fiber manufacture: pumping, filtration, fiber forming, and fiber treatment. We have purposely excluded the production of the polymer melt or solution, so that we could focus on those fundamentals associated with the transport phenomena, rather than the chemistry, of fiber production. We also point out that synthetic fibers include not only the familiar examples of nylon or polyester, but also could extend to fiber optic cables and wire, etc.

Pumping — Section 2

Filtration — Section 3

Fiber Forming — Section 4

Fiber Treatment, Miscellany — Section 5
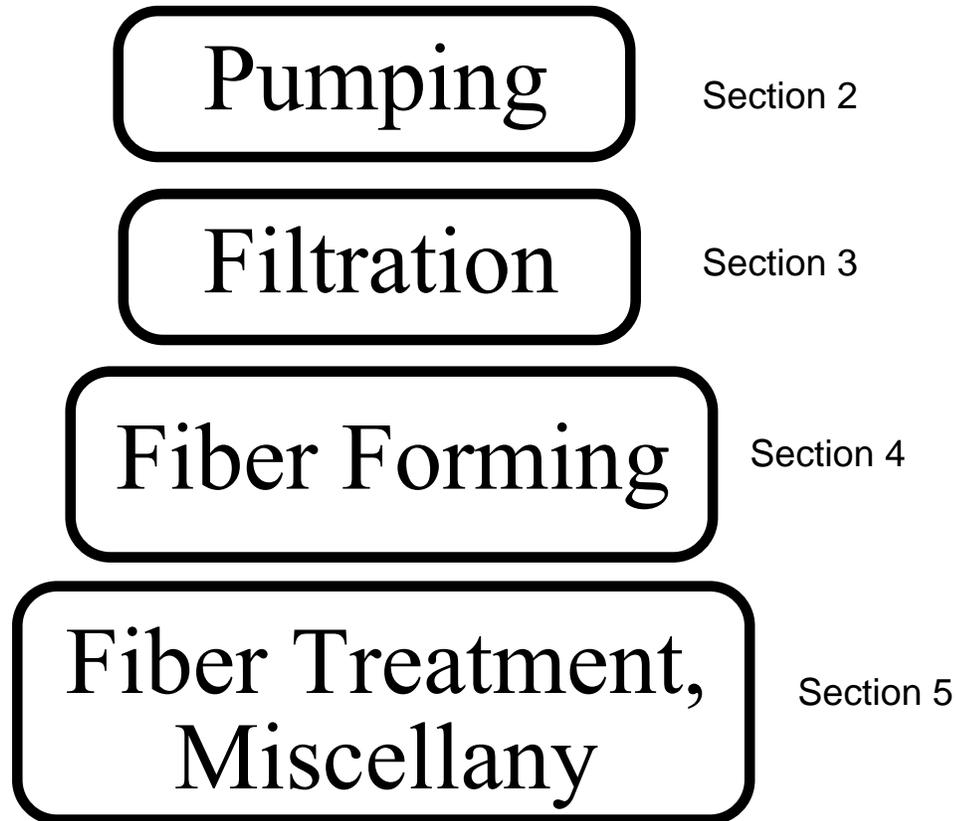
Fiber optic cables,
Nylon, polyester, orlon, rayon,
wire, tubular materials, etc.

Fig. 1.1 Synthetic Fiber Module — Principal elements

Table 1.1 depicts the principal elements of transport phenomena fundamentals which, are either described or might be included in the detailed study of the process of synthetic fiber manufacturing. Illustrated in Table 1.1 are the principal elements covered in the module, which also might be seen in the table of contents of a textbook on transport phenomena. Particularly noteworthy is the breadth of topics included in this one module, ranging from pumps and filtration to transport analogies for the three modes. The student may be less interested in this particular table than the teacher, who is often

concerned with extent of coverage. Clearly, the main goal at the present is to preserve the student's interest and curiosity by emphasizing the relevance of the topics.

Table 1.1 Transport Phenomena and Mathematics Fundamentals

SYNTHETIC FIBER MANUFACTURE MODULE

FLUID MECHANICS

Flow through tubes
Flow through packed beds
Flow perpendicular to cylinders
Drag along a cylinder
Pump selection, Filtration
Eulerian, Lagrangian perspective
Reynolds number, Viscometry

HEAT TRANSFER

Temperature rise across filter bed
Unsteady-state heat conduction
Empirical heat transfer coefficients
Quenching heat transfer
Prandtl number, Transport analogies

MASS TRANSFER

Unsteady-state diffusion of mass
Relative resistance to mass transfer
Empirical mass transfer coefficients
Schmidt number, Transport analogies

MATHEMATICS

Partial Differential Equations
Shell Balance Technique
Sensitivity Analysis

In Figure 1.2, we attempt to provide the student with some orientation and introduction to the glossary of fiber production.

Fabric This includes a description of the difference between non-woven and woven fabrics. Whereas woven fabrics have an orientation associated with them, in which the fibers are normally aligned either parallel or perpendicular to each other, non-woven fabrics do not possess any preferred fiber orientation. With synthetic fibers produced from molten polymer, non-woven fabrics can be bonded together by having the filaments laid down over one another while they are still molten. As they cool and

solidify, they are "glued" together. The fibers can be laid down in much the same way that paint appears to be laid down in a Jackson Pollock painting!

Fabric
- non-woven
- woven

Fibers
- continuous
- staple

Fibers
- natural
- synthetic

Synthetic Fibers
- carbon fibers
- Kevlar
- Spandex
- Polyester
- Nylon
- Acrylics
- Rayon
- Nomex

Fiber Manufacture
- Melt Spinning
- Dry Spinning
- Wet Spinning
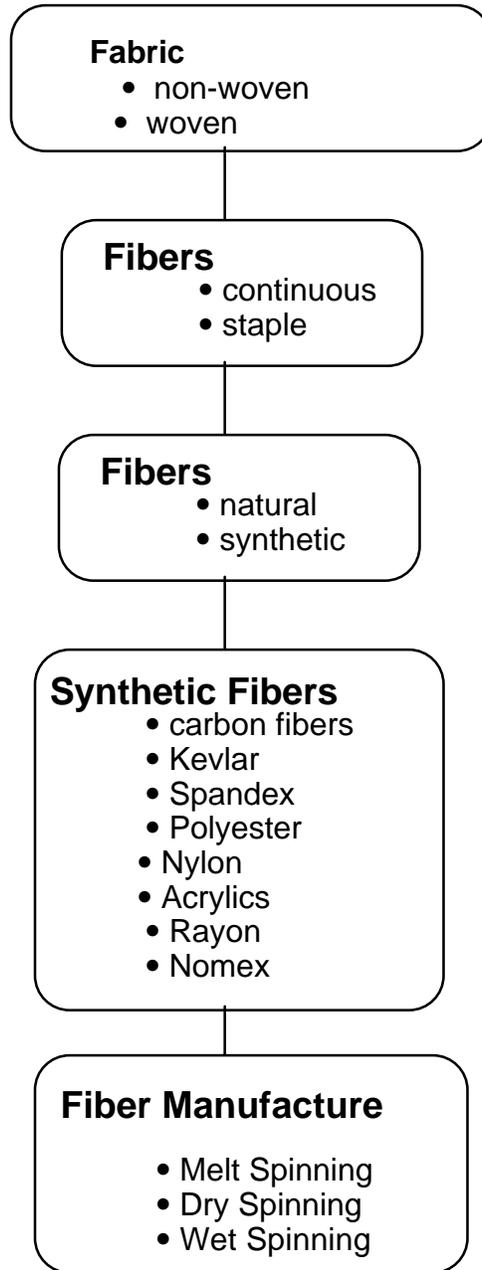
Figure 1.2 Synthetic Fibers — A Little Taxonomy

<u>Fibers</u> can be either natural or synthetic and either continuous or staple. Natural fibers, of course, can come from either animals or plants and probably the most well known example of each are wool and cotton, respectively. Their chemical structure is

polymer-based, in that a regular, repeat structure can be found in natural fibers. Synthetic fibers, too, are based on a regular polymeric structure. However, synthetic fibers are manufactured, or "synthesized," usually from oil, but sometimes from coal or natural gas. Most of the synthetic fibers are from polymers produced by step polymerization (usually, condensation polymers) but many are made from polymers produced by chain polymerization (addition polymers).

All natural fibers have a finite length associated with them, ranging from about 5 to 20 cm. This could be the length of the hair on the sheep (wool) or the length of a cotton filament in a cotton plant. In order to be woven into a fabric, these filaments must first be aligned together into a continuous strand, called yarn or thread. Spinning machines are used to accomplish this. The filaments are held together by van der Waals' type forces. The thread and yarn produced in this way contain occasional filaments, which stick out away from the continuous strand; this is somewhat like branch groups on a polymer, albeit at a much larger scale. In any case, these filament branches help to provide the woven fabric with greater bulk and porosity and are associated with other positive aesthetic features of the fabric. Synthetic fibers, however, can be made into continuous filaments, which are practically infinite in length. Although the individual polymers in the filament are 1000x longer than wide, they are still usually tiny fractions of millimeters in length. A "yarn" can be made of these filaments simply by bringing the filaments together continuously as the filaments are produced. This will not produce a yarn with filaments, which occasionally stick out from the strand, however. In order to produce such a result, in some processes the continuous strands are chopped into strands of finite length, so that there is a somewhat closer match between the synthetic and the natural fibers. These chopped-up sections are called "staple," and the staple is brought together again in spinning machines which operate just like those used with natural fiber. Another difference between natural and synthetic fibers is that the natural ones are usually curlier. Two techniques have been used to make the synthetic fibers and yarn more curly: one is to pass the yarn between two heated gears which can impart a permanent crimp to the yarn, the second is to produce the synthetic filaments from two different polymers passing out of a common hole, or die. The resulting filament will exhibit varying

curliness, based on humidity conditions if the two polymers absorb water to differing degrees and if the absorption changes the shape of the filaments accordingly.

Synthetic Fibers This list brings together most of the fibers with which the students are already familiar. Most are made from condensation polymers, although acrylic is not one, and carbon fibers are made from addition polymers subjected to a pyrolysis step to kick off the hydrogen atoms.

Fiber Forming This section includes a brief forecast of what will be covered subsequently. In particular, the three principal fiber-forming processes of melt, dry, and wet spinning are described briefly. All three steps involve the formation of continuous filament strands by forcing the material through circular dies, but melt spinning involves cooling of the subsequent strand to form the solid filament, whereas dry and wet spinning involves removal of a solvent to form the solid filament. In dry spinning the solvent evaporates into a gas and in wet spinning the solvent is leached into a liquid bath.

Figure 1.3 shows a schematic of the melt spinning process, and thus illustrates the key elements listed in Figure 1.1. The molten polymer (in the case of dry or wet spinning, the spin dope) is first pumped through a filter, which removes any tiny particles that can be trapped in the tiny spinneret holes. The polymer is then forced through these tiny holes to form continuous strands of polymer filaments, or synthetic fiber. Cooling gases reduce the temperature of the filaments so that they solidify and an initial drive roll controls the initial take-up speed. The fiber may undergo subsequent heating and stretching to impart additional molecular orientation. Finally, the fiber is taken up onto bobbins at a constant speed, with a special tension control device to control the rate of rotation in order to maintain constant yarn speed.

MELT SPINNING

Filter

Spinneret

Cooling

Take-up

Stretching/molecular orientation

heater

P.S.: Stringing up system initially?

Speed Control

Final Takeup
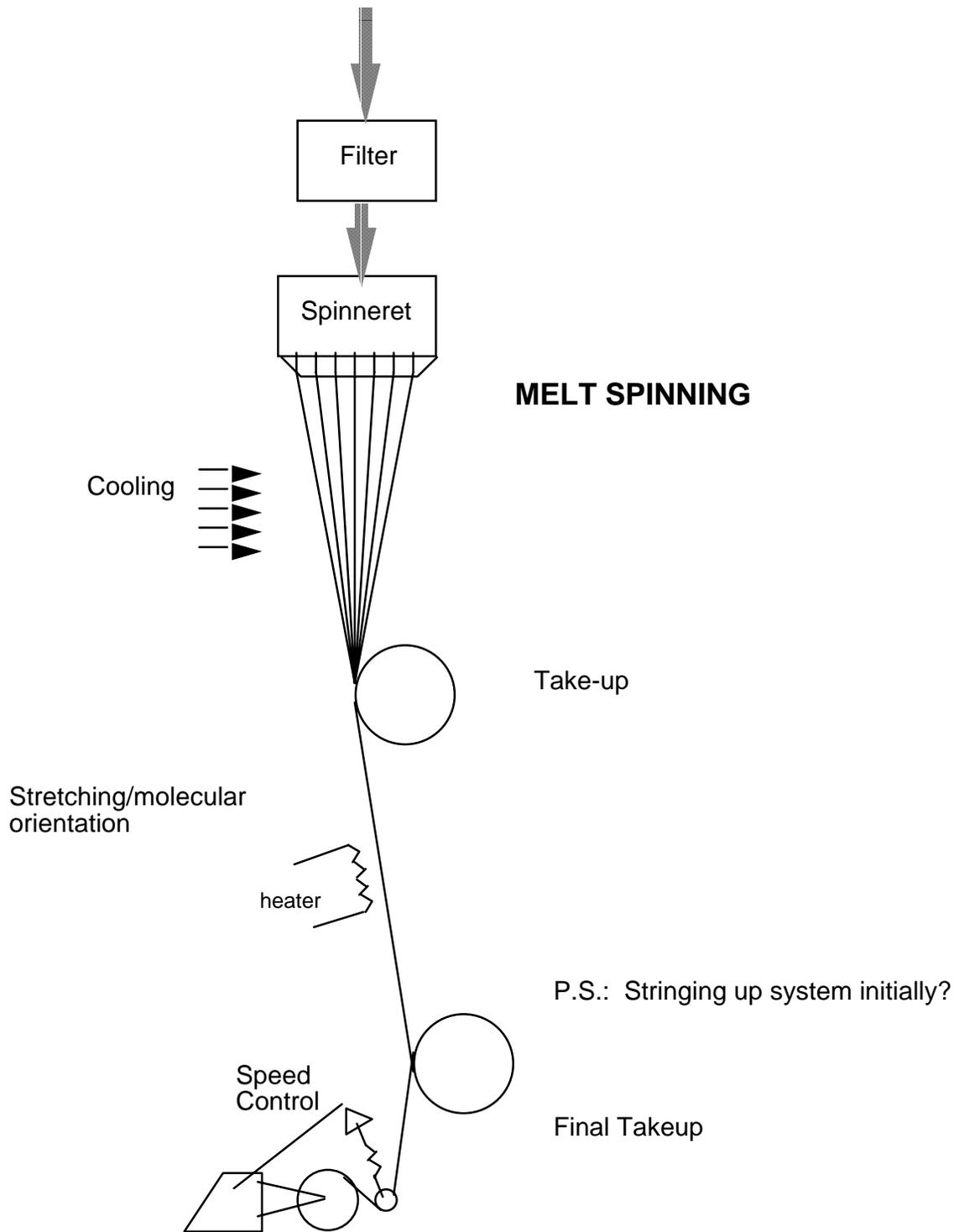
Figure 1.3 Sketch of Melt Spinning Process

2.0 Pumping

In this section, we introduce two of the main devices used to pump liquids: centrifugal pumps and gear pumps. The centrifugal pumps are general-purpose devices used to move low-viscosity liquids around in a process; gear pumps are used to pump highly viscous liquids at a controlled flow rate. In order to form synthetic fibers, a viscous liquid must be pumped through a filter bed and then through tiny spinneret holes, and both units will result in high-pressure drops along the flow direction of the viscous liquids. Finally, the flow rate must be maintained within close tolerances in order to produce synthetic fibers of uniform diameter. Gear pumps are used to provide such a closely regulated flow of the highly viscous liquid; although gear pumps could also be used to develop the high pressures required to force the material through the filter and the spinneret, it is more common to use screw extruders for this purpose.

Low viscosity liquids (water, etc.)

Centrifugal
pumps
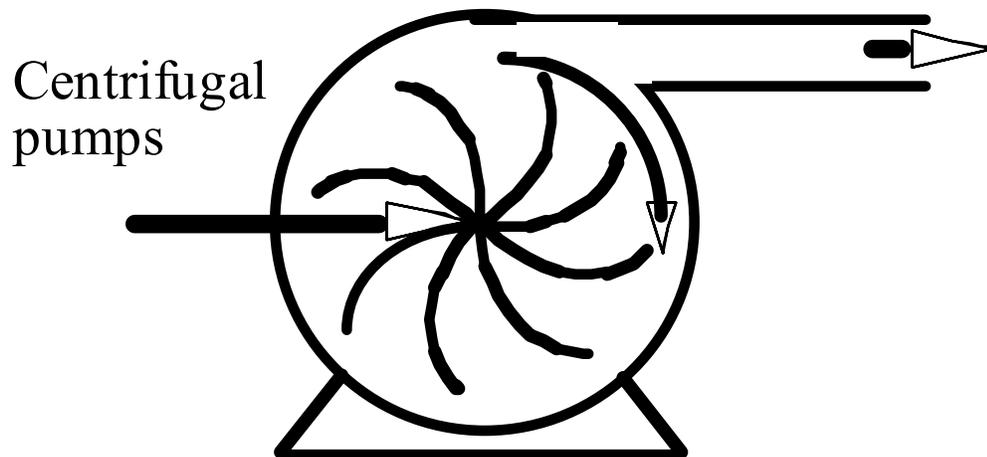
Flow rate, Q, is proportional to rotational speed and cube of impeller diameter for no downstream resistance. Pressure at outlet for choked flow condition is proportional to square of both rotational speed and impeller diameter. Viscosity is less important than liquid density in determining pump performance.

Figure 2.1 Sketch of centrifugal pump

2.1 Centrifugal pumps Perhaps the best way to understand the way centrifugal pumps work is to recall the mechanical energy balance equation. (In the present analysis, this will be Bernoulli's equation, with the additional term of shaft, or pump, work included.)

The mechanical energy balance (MEB) equation is:

$$\frac{\Delta u_b^2}{2} + g\Delta z + \int_{p1}^{p2} \frac{dp}{\rho} + lw_f + W_s = 0 \qquad (5\text{-}1)$$

Recall that this equation is valid, under steady-state conditions, along a streamline of the liquid. Since we are dealing with a liquid of relatively low viscosity, we can ignore the viscous term, lw_f, and, with constant density, the integral term simplifies, so the modified MEB equation (Bernoulli's equation with shaft work included) becomes:

$$\frac{\Delta u_b^2}{2} + g\Delta z + \frac{\Delta P}{\rho} + W_s = 0 \qquad (5\text{-}2)$$

Referring to Figure 2.1, we see what amounts to a spiral fan, with the inlet at the fan axis and the outlet in a line tangential to the tip of the rotating fan. The fan, or impeller, is usually of uniform thickness or width and is sandwiched in a casing formed by two parallel disks, which are sealed at the edges with a short, squat cylinder with one exit tangential to the cylinder. In operation, the liquid enters along the axis, into the "eye" of the impeller and both the pressure and velocity are relatively low at this entrance. As the liquid travels through the pump, the rotating impeller (previously, spiral fan) imparts shaft work to the liquid as the liquid develops higher, mainly θ-direction, velocity. As a matter of fact, within the pump,

$$\mathbf{v} = 0\ \mathbf{e_r} + (V_R)(r/R)\ \mathbf{e_\theta} + 0\ \mathbf{e_z} \qquad (5\text{-}3)$$

Where V_R is the θ-direction speed of the liquid at the tip of the impeller (which should only be slightly less than the actual tip speed, depending on the design of the pump) and $\mathbf{e_r}$, $\mathbf{e_\theta}$, and $\mathbf{e_z}$ are the orthogonal unit vectors in the r, θ, and z directions, respectively. The reason that v_θ varies linearly with r/R is geometric; think of the example of a rock

attached to a string as you swing the rock around your head—the θ-direction velocity of the string at any radial position varies as r/R. This means that the amount of motor power delivered to the impeller is concentrated towards the outer parts of the impeller, because the shaft work is proportional to the square of the velocity, from Equation (5-1). Getting the liquid out to a radial position halfway towards the exit requires only one-fourth of the power and two-thirds out still less than half (only 4/9) of the power. At the tip of the rotating impeller, most of the pump power or shaft work has gone into increasing the velocity of the liquid; the MEB equation shows that this arises in the kinetic energy term. If the liquid encounters no resistance downstream of the pump—let's say that it goes directly into a vertical fountain with no additional change in cross-sectional area of the exit tube—then very little pressure is "developed" by the pump. Again, pursuing the fountain example, you will recall calculations in physics about how the height reached by a ball thrown into the air can be calculated from the conversion of kinetic energy at the bottom to potential energy at the top, and you realize that the same thing could be done here. You could, theoretically, calculate the impeller tip speed from the height of the vertical fountain. Of course, you quickly realize that problems with friction inside the pump, changing tube sizes, and friction with the air would likely render the calculation too inaccurate. But you do realize that the same principle can be applied here. In the typical setting, the fluid does encounter resistance downstream of the pump. In the extreme, the resistance is infinite (the valve is closed!) and now the pump is used to develop pressure, instead of velocity. If we now apply the MEB equation from the impeller entrance to a point just past the rotating impeller, where the liquid velocity is zero, the change in kinetic energy, KE, is zero, but the change in potential energy, ÆP/r is equal to the shaft work, W_S (per unit mass of liquid pumped).

Before we move on to some of the design equations with centrifugal pumps, we should briefly mention some other pumps for low-viscosity liquids:

Straight-through pumps: Axial fan and turbine pumps are typical of these units, although they are more commonly used with gases.

Piston/cylinder pumps: Multi-stroke units are used as metering pumps, where a constant flow rate, though pulsating, is needed; single-stroke units are typified by infusion

pumps, which are useful in medical applications where medicine has to be titered into a patient over a sufficiently long time period that replenishing the stroke volume produces no problem.

Airlift pumps: These produce vertical, two-phase flow and, although they are not energy efficient, are relatively cheap and can be used with highly corrosive liquids. Drip coffee makers work on this principle, moving the hot water to the top by vaporizing a portion of the water and the resulting steam bubbles rise in a tube, dragging and pushing the hot water upwards.

2.2 Gear Pumps These pumps are also aptly named, since they consist of two intermeshing gears. One intriguing part of these pumps is that, for most people, the flow goes in a direction different from that first thought. Referring to the sketch on the diagram, we see two rotating gears, set in a Figure-Eight chamber, with the fluid being carried around the outside periphery of each gear before meeting again to be pumped away. As a matter of fact, the fluid is carried in discrete packets as it moves towards the exit. Each packet moves at a speed directly proportional to the rotational speed of each gear, so the total volumetric flow rate is proportional to the rotational speed of the pump.

High viscosity liquids (molten polymers, etc.)
Gear pumps
Positive Displacement

Flowrate, Q, is proportional to rotational speed.
Pressure buildup, within a wide range, depends on downstream resistance and not Q. The liquid viscosity must be high enough so that liquid does not leak back around the gears.
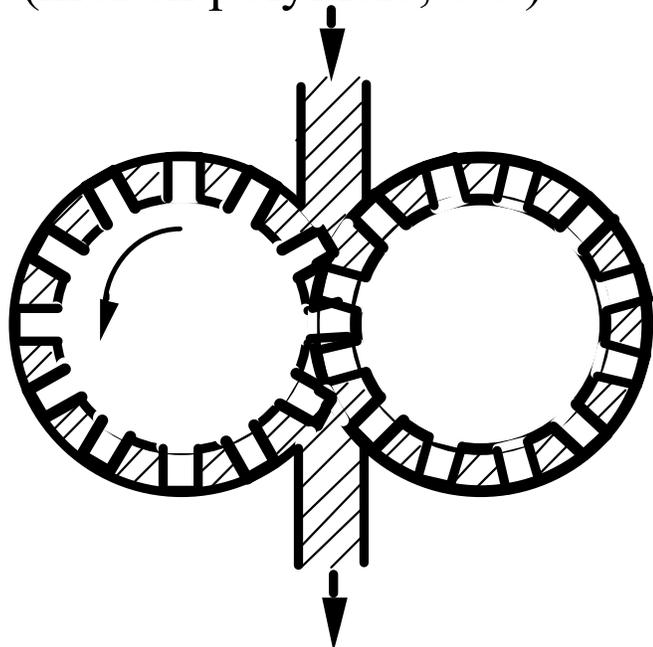
Figure 2.2 Sketch of section of a gear pump

Although the gear teeth are shown in the diagram as square-toothed, they can also be sinusoidal. If the gears are sinusoidal, then the output flow rate from one gear will vary sinusoidally, from zero to a maximum value. Corresponding output from the other gear will also be sinusoidal, but the phase difference will be exactly π. This means that sum of the two outputs will be a steady, or uniform, flow because the two flows will exactly balance each other. While this is not exactly like destructive wave interference learned in physics in the study of light and sound waves, since we have a uniform maximum output remaining, it does appear similar.

In fiber spinning operations, the gears are normally square-toothed, with a relatively large number; say 40 or more, teeth per gear. The gears are usually designed to operate over a relatively narrow range of rotational speeds and many utilize a standard diameter, so additional capacity, or flow rate, are obtained by choosing gear units of varying thickness. This would be analogous to centrifugal pumps being designed for higher flow rates by using impellers of greater thickness. For other applications, such as pumps for heavy oils and lubricants, one normally finds fewer teeth per gear (perhaps eight or so) and a sinusoidal shape to the teeth.

With gear pumps, the clearance between gear teeth and barrel of gear housing is important, because, with an adverse pressure gradient, the liquid can leak back through the pump through this clearance. This is one of the reasons that gear pumps used in fiber spinning, which may be exposed to opposing pressures of a 1000-psi, are square-toothed. The flow between the teeth tips and the barrel is nearly Coquette, which the student will recall as flow between parallel plates. One can calculate the amount of leakage by taking into account the difference between the drag flow, produced as one moving parallel produces a linear velocity profile and flow in the pumping direction, and the adverse pumping flow, which produces a parabolic type of flow in the opposite direction. This difference can be shown to depend strongly on this distance between the teeth tips and the barrel.

3.0 Filtration

Starting up a spinning line is a complex operation and one wants to minimize the frequency. It also is time-consuming to replace spinneret plates and filter beds. Inclusion of particles, whether they are thermally degraded polymer or small chips of metal, can lead to imperfections along the filament and potential points where the filament may break. Worse still, the particle may become attached to the entrance to a tiny spinneret hole and this could reduce the flow to that hole and thus the diameter of the resulting filament; this smaller filament will cause the yarn to take up dye differently and the resulting non uniformity will show up in the final fabric. Another problem with partial blockage of flow is that the blockage may be nearly complete, leading to breaking of the filament, which is usually only a very slight problem, since there are so many filaments, although gradual oozing of the melt through the nearly blocked hole can be a very major problem. It becomes a major problem because the polymer, as it oozes out the hole, will gradually travel to neighboring holes and interfere with the filaments from them as well. The only solution for this problem is to shut down the line and remove and clean the spinneret plate.

Since there can be up to 1000 holes in a spinneret plate, the large number means that the filtration process must be completed to very exacting standards. Similarly, because one wants to operate the line for long periods of time between shutdowns, one wants to use a filter medium which can trap a large number of particles without causing excessive pressure drop or blinding of the filter. This brings us to the first part of filtration, deciding between filter screening and entrapment among small particles.

3.1 Screen Filtration

Before the mid 1960's, draft beer was sold in large containers, called kegs, under refrigerated conditions. Draft beer, which had not gone through a high temperature pasteurization step to destroy the yeast and any bacteria, had to be consumed within a short time of its brewing and had to be kept refrigerated prior to consumption, in order to avoid problems with further fermentation. Purists liked the draft beer because they

claimed that the pasteurization step, which was necessary for beer sold in small containers at room temperature, would destroy some of the delicate flavors of the beer. In the 1960's, the beer manufacturers found that one could substitute an extremely fine filtration process for the pasteurization step, since all the yeast and bacteria could be simply filtered from the beer. The relatively small molecular species producing the delicate flavors could pass through the very tiny filter holes. The resulting beer could be packaged under sterile conditions and could then be sold in cans or bottles stored at room temperature. This is an example of very fine screen filtration, where the requirements for filtration of the yeast and bacteria could be carefully determined. Of course, the yeast does tend to pile up on the filter screen and blind it periodically, requiring replacement of the filter screen.

Screen Filter   (Drip coffee maker)

suspension (liquid plus particles)

particles

screen

Examples: oil filter, chemistry lab, air filter, water filters

clearfiltrate
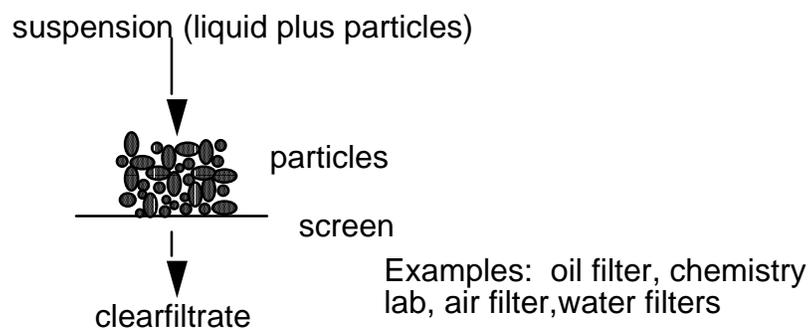
Fig. 3-1 Screen Filtration

Screen filtration can be accomplished under batch or continuous operation. For example, a rotary filter, with continuous scraping of filter particles from the surface of a rotating screen, can provide continuous filtration. With batch filtration, as described above for the beer example, the operation can be conducted under a) constant pressure, in which the volumetric flow rate decreases with time or b) constant flow rate, in which the pressure drop increases with time, as the filter becomes loaded with particles. Commercially, one frequently encounters operations requiring the filtration of particles, which are rigid and incompressible, unlike bacteria. With these liquid/particle systems, the particles build up on the screen, forming a filter cake. If the resulting filter cake is

indeed incompressible, equations (from <u>Momentum, Heat, and Mass Transfer</u>, 3rd ed., by
C. O. Bennett and J. E. Myers, McGraw-Hill, New York, (1982), p. 233) for the filtration
process are:

$$\theta_f = \frac{K_1}{2P}V_f^2 + \frac{K_2}{P}V_f \qquad \text{(3-1)}$$

Where θ_f is the filtration time, V_f is the volume of filtrate, P is the pressure difference
(usually upstream gage pressure for atmospheric filtration) and K_1 and K_2 are
characteristics of the filtration, suspension concentration, and particle size and shape. K_1
and K_2 relate to the resistance of the collected particles and screen, respectively, and
would normally be determined by experimentation, although Bennett and Myers do
provide equations to relate the values to such variables as specific cake resistance,
concentration, and viscosity of fluid.

For filtration at a constant volumetric rate q_0, the equation is:

$$ÆP = K_1 q_0^2 \theta + K_2 q_0 \qquad \text{(3-2)}$$

Where K_1 and K_2 are the same as for constant pressure filtration. Thus, one can predict
constant flow rate filtration performance from constant pressure data and vice versa. All
of this is predicated on incompressible filter beds, however, and at least half, if not more,
commercial slurries exhibit compressible bed performance. Although one can attempt to
account for this by a dependence of specific cake resistance on pressure, the final design
normally requires close experimental verification anyway.

3.2 Deep-bed filtration

Deep Bed Filter

filtered partices

sand particles

Suspension

very coarse sand

Delaware (Lewes/ Rehoboth Beach)

Ocean City (fine sand)

support grid

Clear filtrate

Advantages: High Capacity, doesn't blind

Design requires experimentation

Polymer melts use deep bed filters
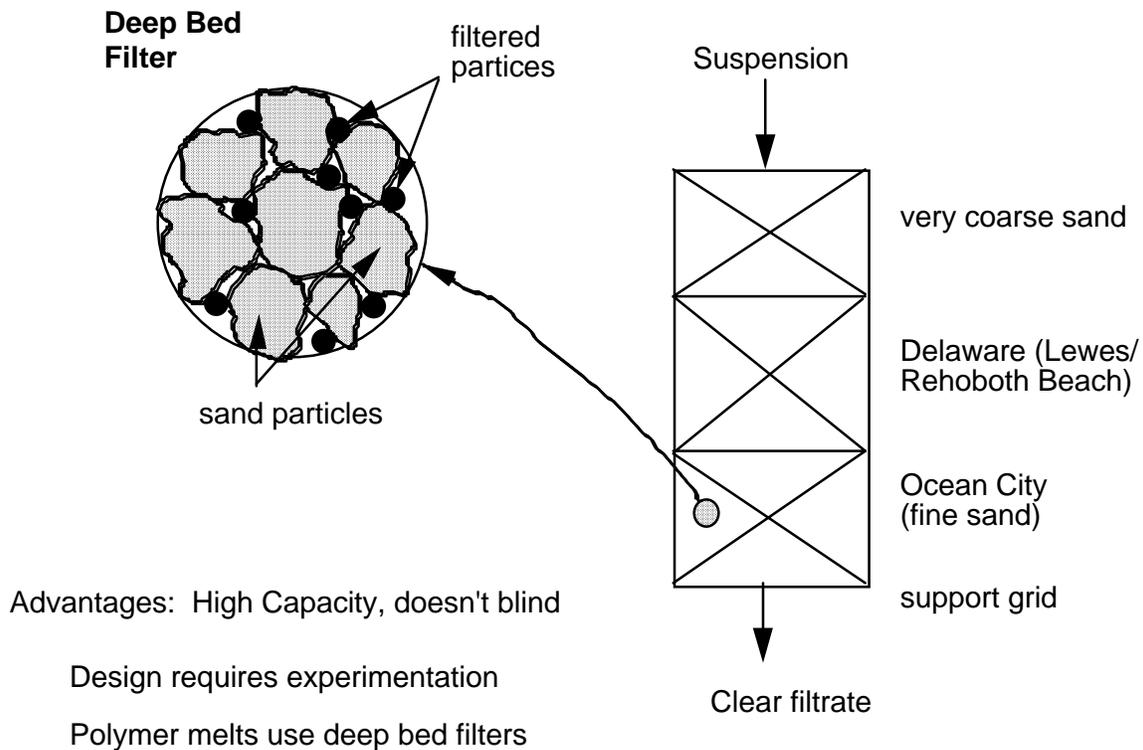
Fig. 3-2 Deep-bed Filtration

With deep-bed filtration, illustrated by Fig. 3-2, the particles to be captured are entrapped in the interstices among particles held in a deep bed. The sizes of the interstices are roughly the same order as the size of the particles in the bed, so, in order to maximize the capacity of the bed, the particles are laid down in such a way that a gradient of particle sizes exists in the bed. Larger bed particles at the top, or beginning, of the bed will tend to trap the larger particles and smaller bed particles at the bottom of the bed will trap the smaller ones. The example on the sketch shows a gradation in sand particle sizes produced by taking the sand from different locations along the eastern seaboard. In practice, although sand is frequently used in such deep-bed filters, it usually is riverbed sand and not salt-water sand, because the former tends to be more free of extraneous materials.

The pressure drop for laminar flow (which will certainly exist for molten polymer melts and polymer spin dopes) can be calculated from the mechanical energy balance

equation, MEB, and the Kozeny-Carman equation. The MEB (from Bennett & Myers) is written as:

$$\frac{\Delta u_b^2}{2} + g\Delta z + \int_{p_1}^{p_2} \frac{dp}{\rho} + lw_f + W_s = 0 \qquad (3\text{-}3)$$

u_b is the bulk, or average velocity, Δz is the change in elevation, p is pressure, ρ is density, lw_f the lost work due to friction, W_s is the shaft work introduced to the system. The Kozeny-Carman equation is:

$$f_p = \frac{150}{Re_p} \qquad (3\text{-}4)$$

Where

$$f_p = \frac{D(lw_f)\varepsilon^3}{Lu_{bs}^2(1-\varepsilon)} \qquad (3\text{-}5)$$

And

$$Re_p = \frac{D(u_{bs})\rho}{\mu(1-\varepsilon)} \qquad (3\text{-}6)$$

f is the friction factor, D the particle diameter, u_{bs} is the superficial liquid velocity, L is the length of the bed, ρ is the liquid density, and ε is the void fraction of the bed.

On account of the high liquid viscosities, pressure drop through the bed can be enormous. This can lead to significant temperature increase, since one can demonstrate from thermodynamics:

$$\Delta H = \Delta P/\rho \ + \ Cp\Delta T \ = \ 0 \qquad\qquad (3\text{-}7)$$

The enthalpy change is zero since the operation is adiabatic and there is no shaft work in the process. Temperature increases of 20 F° are readily possible.

4.0 Spinning

As mentioned previously, fibers are formed by the extrusion of the polymer melt or spin dope through tiny holes in a spinneret plate. Such a plate may contain 1,000 holes or more. Textile fibers are relatively fine, so the diameter of the hole may be only a few mils, (one mil is 0.001 inches or 25.4 μm). The thickness of the filament is generally not given in linear dimensions, but rather in terms of mass per length. For some reason the fiber industry has adopted the terms denier and denier per filament, dpf, to express the filament size. One dpf corresponds to a mass of 1 g in a length of 9000 meters! If the density of the polymer is 1 g/cm^3, this would correspond to a diameter of 1.2 x 10^{-3} cm, or about half a mil. Typically, textile fibers are in the range of 3 to 15 dpf. Recall that one g is roughly 1/30 of an ounce.

In melt spinning, the filaments are normally drawn down, or stretched, just downstream of the spinneret holes. The stretch is of the order of 2 to 3x, so the spinneret hole may be 50 to 75% larger than the filament diameter when it is first cooled. Additional post-formation stretching may also be used, however, so that the final filament diameter may be one-half or less than the diameter of the spinneret hole.

The spinneret hole is usually only slightly longer than its width, in part to minimize pressure drop at the plate. But the plate still has to be strong enough to withstand the upstream pressure. For this reason, the melt passes through a conical section before reaching the final spinneret hole, so that the plate can be relative thick (see Fig. 4.1). Pressure drop through this converging section is very difficult to calculate for these polymeric materials, because the extensional flow rheology is usually not well characterized. One can readily visualize the alignment of the polymer molecules in the converging section, where the polymer undergoes a severe stretching step. Ignoring this pressure loss, let us focus on the spinneret hole itself.

An important question here is whether one can use the Hagen-Poiseuille equation to compute the pressure drop in such a short tube. To help answer this question, we first compute the entrance length, which is approximately equal to the axial distance downstream from a tube entrance at which the momentum boundary layers merge at the

center axis, where a fully parabolic profile is established. This distance, from <u>Transport</u> <u>Phenomena</u>, by Bird, Stewart, and Lightfoot, Wiley, New York, (1960), p. 47, is

$$L_e/D \;=\; 0.035\ Re \qquad\qquad (4\text{-}1)$$

Where L_e is the entrance length, D is the tube diameter and Re is the Reynolds number.

Spinnerets —Melt Flow--momentum transport

melt flow

spinneret
plate

I. D. = 2 to 10 mils
(1 mil = 0.001 in)

spinneret holes
500 to 1500 holes per plate
This produces "yarn" with up to 1500 filaments
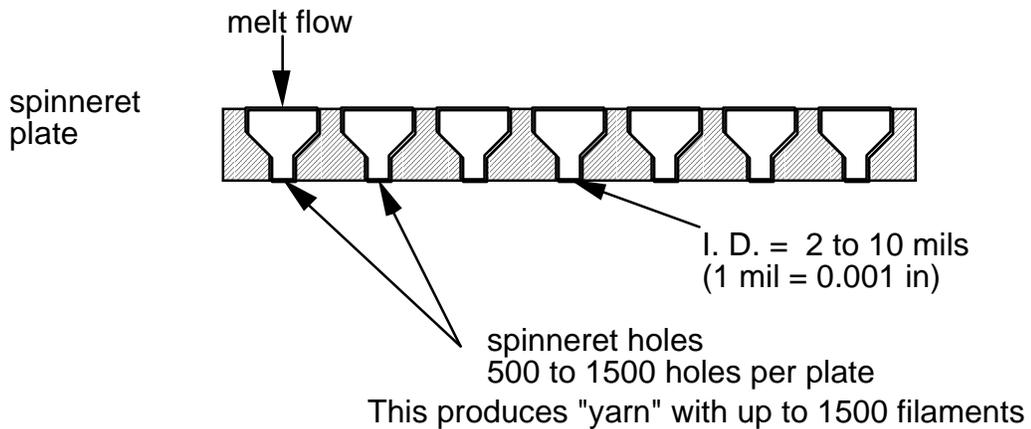
Flow in spinneret hole: (momentum transport)

     Hagen-Poiseuille equation for flow (flow in a tube)

$$Q = (\pi D^4/128\mu)(-\Delta P/L)$$

where Q is volumetric flow rate, D is diameter of hole, L is length of hole,
²P is pressure drop across hole, and μ is viscosity of polymer melt.

Note that Q is: proportional to ²P
          inversely   "   to L
            proportional to D^4

Net force on fluid in tube = ²P(šD²/4) = shear stress x tube wall area

$$\tau_{rz}\big|_w$$
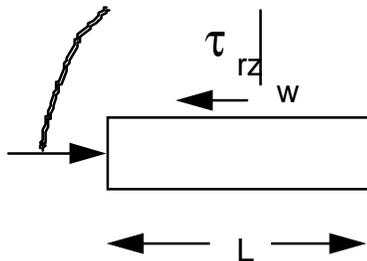
$$= \tau_{rz}\big|_w \times \text{š } D\, L$$

$$\text{where } \tau_{rz}\big|_w = \mu\,(dv_z/dr)\big|_w$$

L

{can derive the Hagen-Poiseuille equation}

Fig. 4.1 Flow in spinnerets

For a representative calculation, we consider nylon melt, with a viscosity of 200 Poises, being spun from a hole 10 mils in diameter at a final spinning speed of 2,000 ypm and a stretch of 5x between the spinneret and the final take-up. This means that the bulk velocity, u_b, in the spinneret hole is 400 ypm. The Reynolds number, for a specific gravity of about one, is:

$$Re = u_b\, D/\nu \quad = 0.077 \qquad\qquad (4\text{-}2)$$

so the entrance length calculated from Eqn. 4.1 is less than 3 thousandths of the diameter of the hole. Therefore, we can safely use the Hagen-Poiseuille equation to calculate the pressure drop. The equation is:

$$\frac{\Delta P}{L} = -\frac{32\,\mu\,u_b}{D^2} \qquad\qquad (4\text{-}3)$$

For the nylon example we just explored, the pressure drop is predicted, for a length of 3.0 mils, to be 2200 psi. This pressure drop might be a bit excessive in practice, but the method of calculation remains illustrative. One part of the calculation, which was not taken into account, is the power-law behavior of most polymer melts and polymer solutions. Such behavior usually is revealed by a shear-thinning response, in which the apparent viscosity decreases as shear rates increase. This would lead to significantly lower pressure drops for the spinneret plate.

As the polymer exits the spinneret hole, it tends to swell and this swell is especially noticeable at low filament tensions. Apparently, the polymer molecules must coil under the shearing action within the hole and, as it exits, the polymer molecules are free to uncoil, as seen by an expansion of the polymer stream jetting out of the hole. This phenomenon is referred to as "die swell," and can even amount to a doubling or more of stream diameter. Newtonian fluids can also be shown to exhibit a swelling at the exits of tubes, even at very low Re; the predicted extent of swell is about 14% for Newtonian fluids. Since, in fiber spinning, the filaments are under tension, the extent of die swell is considerably reduced. Furthermore, the extent of swell appears to have no influence of

final filament properties. In order for the filaments to undergo stretching, some power must go into the stretching motion immediately downstream of the spinneret plate, but the amount of this power is negligible, as described in the next section.

4.1 Melt Spinning

In the spinning of molten polymers, such as nylon, polyester, and polypropylene, melt spinning begins with a cooling of the molten filament after it leaves the spinneret. At the same time, the filament is pulled downwards towards the take-up section and this resulting tension in the molten filament provides a stretching action in the molten filament itself. In most melt spinning operations the degree of stretch is of the order of 3x, which means that the velocity of the initially cooled, or solid, fiber is about three times the average velocity of the melt coming out of the spinneret. For some filaments, this initial stretch is very important in helping to establish properties in the polymer, which depend on whether one deals with the properties in the fiber axis direction or in the fiber radius direction. This directional dependence of properties is called anisotropy and the usual example is that of a slab of wood, in which strength and fracture properties along the grain are quite different from properties across the grain. (With many fibers, however, these properties are controlled downstream, where the fibers are reheated, stretched further, and cooled again.)

In any case, the polymer melt, once it comes out of the spinneret hole, starts to cool down and also starts to stretch out. Because the "apparent viscosity" of the melt increases rapidly as the melt cools, most of the stretching takes place in a region relatively close to the spinneret hole whereas "most" of the cooling takes place well away from this hole. But these terms and descriptions are not exact and are not easily quantified. The real advantage in using these descriptions is that it permits us to make a simplifying assumption as we analyze the melt spinning process. The assumption is: We can separate the stretching and cooling operations into two separate distinct regions, with the first occurring relative close to the spinneret (say, within 10% of the distance to the first take-up, or speed-control roll), and the second over the remaining distance to the first

take-up roll. If need be, we could return later to this assumption to determine its degree of accuracy, but let us accept it for the moment.

The stretching region, within which the relatively long polymer molecules become aligned along the filament axis, might be characterized by very complex rheology. Within the field of polymer processing, rheology deals with the relationship between stress and the history of strain; for Newtonian fluids, you can recall that the fluid stress is proportional to the instantaneous rate of strain (the shear rate). We are not really too concerned with the polymer melt rheology here, however, since it will not likely be important in determining the power required for the first drive or take-up roll. Frictional and interfacial stresses are likely to be far more important. Therefore, in terms of design considerations, we can probably ignore that part of the melt-spinning process in which the initial, post-spinneret stretching of the polymer melt occurs and focus instead on the cooling step of the melt spinning operation.

Energy Transport/Melt Spinning

Cooling of Hot Filament Downstream of Spinneret

Cooling
Air @ T_∞
v

Cross-sectionalview to
show heat flowing
radially outward
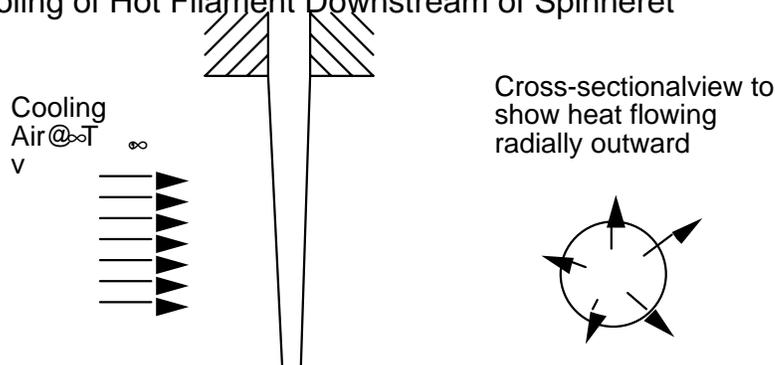
$$\frac{\partial T}{\partial \theta} = \frac{\alpha}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)$$

(partial differential equation)

dependent variable = T, temperatureindependent
variables = θ, time & r, radial position

Boundary conditions: (a) Initially (t = 0), the temperature is uniform at all points within the molten filament at To.
(b) at the center point of the filament, the temperature is not infinite
(c) at the outside radius of the filament, the temperature is identical to surrounding fluid temperature (infinite h).

Solution (presented analytically):

$$Y = 2 \sum_{i=1}^{i=\infty} \frac{\exp(-a_i^2 X)}{a_i\, J_1(a_i)} J_0(a_i n)$$

Solution (presented graphically):

2nd parameter = Biot number

Y

Dimensionless
temperature

Dimensionless
radial position

X, Dimensionless time
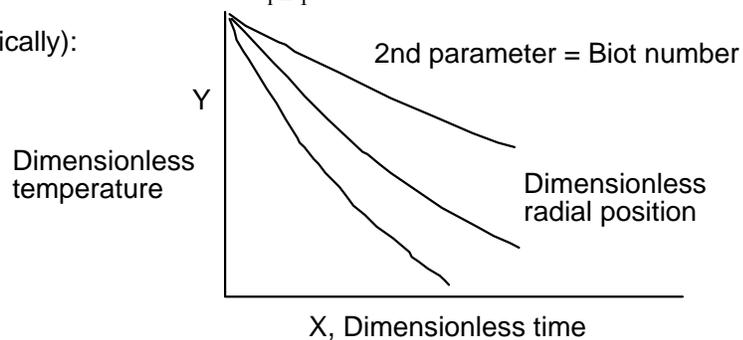
Biot number: Tells us whether <u>resistance</u> to heat transfer is mainly inside the filament (polymer melt) or outside the filament. (air film)

Effect of velocity of cooling air, v ∞; wind chill factorestimating h, heat transfer coefficient for air film
Eulerian perspective (fixed in space)Lagrangian perspective (moving with material)

Fig. 4-2 Cooling of filaments in melt spinning

Perhaps the most important design consideration in the melt spinning process is the cooling of the filaments, Fig. 4-2. In order to simplify our analysis, we restrict our focus to the point where the filaments have reached a uniform diameter (recall that we

previously asserted that this is a relatively short distance) and that they are at some initial temperature, which will be somewhat cooler (by about 20 C°) than the melt temperature at the spinneret exit. At this point, the temperature within the filament will depend on radial position, with the maximum occurring at the center, on the filament axis. We shall invoke an approximation of a flat temperature profile, in which the temperature does not vary with r, at this initial position in order to utilize existing mathematical solutions. An important part of learning engineering is to learn how to take "appropriate shortcuts" which save time with little sacrifice in accuracy. This is one example. The melt spinning process is steady: viewing the spinning thread lines at a fixed position (the so-called Eulerian perspective) shows that nothing appears to change with time. If one situates oneself on the moving threadlike (figuratively, of course) there does certainly appear to be time dependence to the temperature of the filament. This viewpoint of moving with the material is called the Lagrangian perspective. Whereas the Eulerian perspective requires you to measure the threadlike temperature as a function of r, radial position within the filament, and z, axial position along the filament, in order to follow the cooling, the Lagrangian perspective allows you to follow the cooling as a function of r and t, where t is time. Zero time should be some convenient reference—here it would correspond to locating yourself on the filament at the end of the stretching region and at the "beginning" of the cooling region. This is equivalent to the cooling of an infinite rod, which is fixed in space. The governing differential equation, which can be derived, easily using shell balance techniques, is:

$$\frac{\partial T}{\partial \theta} = \frac{\alpha}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) \tag{4-4}$$

Where θ is time and α is the thermal diffusivity of the polymer. The student will readily recognize this as a partial differential equation, since the temperature T depends on both r and θ. In order to solve the equation quantitatively, one must specify initial and boundary conditions. The boundary is naturally R, the outside radius of the filament. The initial condition (= 0) is simply:

$$T(r,\theta) = T_O \quad \text{for } r < R \qquad (4\text{-}5)$$

where T_O is a constant. We need two boundary conditions, corresponding to $r = 0$ and $r = R$. At $r = 0$,

T remains finite

although some prefer to say:

$$\frac{\partial T}{\partial r} = 0 \qquad (4\text{-}6)$$

Based on symmetry arguments. At $r = R$, the heat arriving at the surface by conduction from within must match the heat leaving by convection:

$$-k\frac{\partial T}{\partial r} = h(T - T_\infty) \qquad (4\text{-}7)$$

At $r = R$ and all $\theta > 0$. k is the thermal conductivity of the filament (we shall assume that this conductivity does not change as the polymer solidifies. h is the heat transfer coefficient governing the heat transfer from the surface to the surrounding air. h can be estimated from various correlations if information about the velocity and direction of the cooling air is given. An example of such a correlation for heat transfer from a cylinder in crossflow is given by Churchill and Bernstein (J. Heat Transfer, **99**, 300 (1977)):

$$Nu_D = 0.3 + \frac{0.62Re_D^{1/2}Pr^{1/3}}{[1+(0.4/Pr)^{2/3}]^{1/4}}[1+(\frac{Re_D}{28\,200})^{5/8}]^{4/5} \qquad (4\text{-}8)$$

where Nu_D is the Nusselt number, hD/k, (k is the thermal conductivity of the fluid in crossflow and D is the cylinder or fiber diameter) and Re_D is the Reynolds number based on the fluid in crossflow. Pr is the Prandtl number, ν/α, and is also based on the crossflow fluid. The student will recall that an important advantage of presenting correlations in terms of dimensionless variables like Nu (dimensionless heat transfer

coefficient) and Re (inertial stresses divided by viscous stresses) is that the resulting expression is often simpler, revealing more clearly the relationships among such variables.

We shall also assume that the heat of fusion is negligible, primarily because we want to simplify the calculation. This assumption, especially for crystalline polymers, could be very poor, however, and could lead an underestimate of the cooling time by a factor of two.

As engineers, or even as normal, sane people, we would not want to solve the differential equation for every single set of geometries, thermal diffusivities and initial and boundary conditions. We can avoid this needless energy expenditure if we express the differential equation in dimensionless form:

$$\frac{\partial Y}{\partial X} = \frac{\partial^2 Y}{\partial n^2} \qquad (4\text{-}9)$$

where:

$$Y = \frac{T_\infty - T}{T_\infty - T_o}, \; n = \frac{r}{R}, \text{ and } X = \frac{\alpha\,\theta}{R^2} \qquad (4\text{-}10)$$

Y is called the unaccomplished temperature change, since it starts at unity at time zero and declines from there. n is the normalized radial position, and X is dimensionless time, sometimes called the Fourier number. One final dimensionless group, m, (also equal to 1/Bi) expresses the relative resistance outside the filament to that within the filament:

$$m = \frac{k}{h\,R} \qquad (4\text{-}11)$$

Finally, the initial and boundary conditions become:

$$Y = 1 \qquad \text{at } X = 0 \text{ and } 0 < n < 1; \qquad (4\text{-}12)$$

$\partial Y/\partial n = 0$ X at n = 0 and > 0.   (4-13)

$- m\partial Y/\partial n = Y$ at n = 1 and X > 0.   (4-14)

The solution, Y(n, X) is then valid for any case of unsteady-state heat conduction within a cylindrical geometry with a uniform initial temperature and convective heat transfer from the surface to a surrounding fluid at a uniform temperature T_o. The solution is shown in graphical form on the slide and is available in almost all transport textbooks. The resulting charts are known variously as "Gurney-Lurie Charts" or "Heissler Charts," depending on which reference or form of charts you use. An analytical solution for a slightly less general case is given below. Note that, by use of dimensionless variables, we have successfully created a result which is applicable to a broad range of geometries and material properties. For the special case in which heat transfer resistance from the surface of the fluid to the surrounding fluid is negligible, one can set h, the heat transfer coefficient, to infinity (this, of course, is equivalent to setting the temperature of that surface to that of the surrounding fluid for all $\theta > 0$) and the analytical solution is:

$$Y = 2 \sum_{i=1}^{i=\infty} \frac{\exp(-a_i^2 X)}{a_i \, J_1(a_i)} J_0(a_i n) \qquad (4-15)$$

where J_0 is the zero order Bessel function of the first kind and a_i is the ith root of $J_0(a_i) = 0$. This solution is presented in the transport text Momentum, Heat, and Mass Transfer, by Bennett and Myers, 3rd ed., p. 286.

A solution for nonzero m, or finite heat transfer resistance to the crossflow fluid, is

$$Y = 2 \sum_{i=1}^{i=\infty} \frac{J_1(a_i)\exp(-a_i^2 X)}{a_i \left(J_0^2(a_i)+J_1^2(a_i)\right)} J_0(a_i n) \qquad (4-16)$$

where J_0 and J_1 are Bessel functions of the first kind (zero and first order, respectively), and a_i is the ith root of $a_i J_1(a_i)/J_0(a_i) = Bi$.

Key elements that you have learned in this section include:

- Difference and relationship between Lagrangian and Eulerian perspective,
- Existence of unsteady-state heat conduction charts,
- Heat transfer resistance within objects relative to resistance outside these objects,
- Value of dedimensionalization as a means to obtain more general solutions to complex equations,
- A typical heat transfer correlation for heat transfer coefficient, h,
- Spinning of synthetic fibers with a melt spinning process is conceptually simple, involving little more that the extrusion of molten polymer through fine holes and solidification of the resulting filaments by cooling.

Dry Spinning

Here, the polymer is dissolved in a solvent which evaporates after the solution (spin dope) leaves the spinneret.

Acrylics: Orlon, Acrilan, etc.
• Lower temperature process than melt spinning
• For polymers that are not readily melted

Mass Transport

Drying Air @ T_O, v_O

solvent evaporation
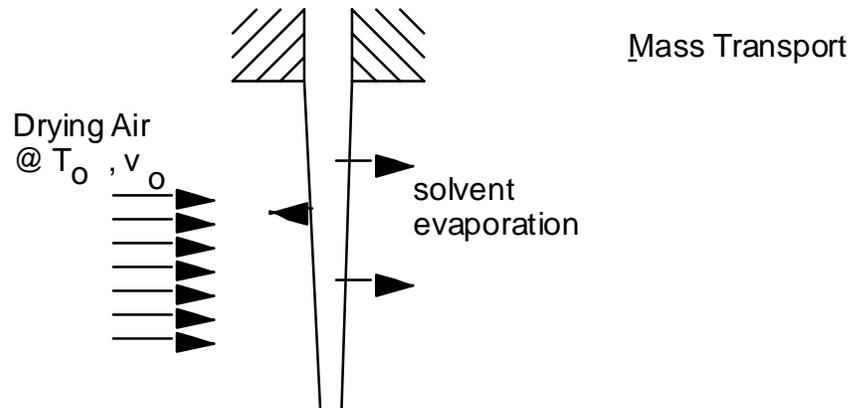
Partial Differential Equation (compare with PDE for melt spinning!

$$\frac{\partial C}{\partial \theta} = \frac{D_{AB}}{r} \frac{\partial}{\partial r}(r\frac{\partial C}{\partial r})$$

where D_{AB} is the mass diffusivity of the solvent in the polymer solution, and C is the concentration of the solvent (as a function of time θ and radial position r.

Boundary conditions for differential equation:

$C (r,0) = C_O$ for r< R and $\theta = 0$,

$\frac{\partial C}{\partial r} = 0$ at r = 0 and $\theta>0$,

$-D_{AB}\frac{\partial C}{\partial r} = k (C - C_\infty)$

at r = R and $\theta>0$.

Compare mass transfer coefficient, k, with heat transfer coefficient, h.

Note similarity to melt spinning

Usually, there will be no stretching to produce molecular orientation.

Recall Eulerian and Lagrangian perspective.
   Think of baking bread on a conveyor belt moving through an oven, vs. using an enclosed oven.

Fig. 4-3 Solvent Evaporation in Dry Spinning

4.2 Dry Spinning

Unlike melt spinning, both dry and wet spinning use solvents in which the polymer dissolves, see Fig. 4-3. The resulting solution or suspension is a viscous "spin dope." This process necessarily introduces another species, which is subsequently removed, and therefore is more expensive than conventional melt spinning processes. It is used in cases where the polymer may degrade thermally if attempts to melt it are used or in cases where certain surface characteristics of the filaments are desired—melt spinning produces filaments with smooth surfaces and dry spinning produces filaments with rough surfaces. The rougher surface may be desirable for improved dyeing steps or for special yarn characteristics.

The term "dry spinning" is a bit misleading, since the polymer is certainly wet by a solvent. Presumably, the intent here was to distinguish the two methods of solvent removal for the two cases of dry and wet spinning. The solvent in dry spinning is a volatile organic species and this solvent starts to evaporate after the filament is formed, which is immediately downstream of the spinneret. Whereas melt spinning involved solidification by cooling, dry spinning produces solidification of the polymer by solvent removal.

Several commercial fibers, including acrylic fibers such as Orlon™, are made by a dry spinning process. You may recall that these acrylic fibers are popular as substitutes for wool fibers. In any case, the spinning step which defines, in large part, the spinning process is that of solvent removal from the filaments. In the case of Orlon, the polymer, polyacrylonitrile, is dissolved to a polymer concentration of 20 to 30 wt% in a dimethylformamide solvent. Warm gases (air? — probably not, on account of the need for solvent recovery) are passed through the fiber bundle in the region just downstream of the spinneret. This begins to look very much like the cooling crossflow in melt spinning. The solvent encounters both a diffusional resistance within the fiber and a convective resistance in moving from the surface of the filament to the crossflow gases. Within the filament, the material property of greatest importance is D_{AB}, the diffusivity of the solvent A through the filament B. Here, we can characterize the diffusive flux of the solvent by:

$$N_A = -D_{AB} \frac{dC_A}{dr} \qquad\qquad (4\text{-}16)$$

which is your familiar Fickian Diffusion equation. We use the ordinary derivative here because the process is steady and we have not yet begun to use the Lagrangian perspective. One point to emphasize here is the similarity of this equation to the Fourier heat conduction equation. If we then adopt the Lagrangian perspective, we have:

$$\frac{\partial C}{\partial \theta} = \frac{D_{AB}}{r} \frac{\partial}{\partial r}\left(r \frac{\partial C}{\partial r}\right) \qquad\qquad (4\text{-}17)$$

Comparison with the unsteady heat conduction equation reveals the equation to be identical with the exception that α is replaced by D_{AB} and T by C. Both α and D_{AB} have dimensions of length squared over time or units of cm^2/s. The initial and boundary conditions are also practically identical to the heat transfer case, with the assumption of uniform concentration profile at time zero, and zero concentration gradient on the filament centerline and matching diffusive and convective flux at the filament surface:

$$C(r,0) = C_o \quad \text{for } r < R \text{ and } \theta = 0, \qquad\qquad (4\text{-}18)$$

$$\frac{\partial C}{\partial r} = 0 \qquad \text{at } r = 0 \text{ and } \theta > 0, \qquad\qquad (4\text{-}19)$$

and

$$-D_{AB} \frac{\partial C}{\partial r} = k(C - C_\infty) \quad \text{at } r = R \text{ and } \theta > 0. \qquad\qquad (4\text{-}20)$$

Instead of heat transfer coefficient, h, we have mass transfer coefficient, k. Correlations for k, expressed in terms of a dimensionless mass transfer coefficient, Sh (for Sherwood

number) as a function of Re_D and Sc, are also available. Sc is the ratio of momentum diffusivity to mass diffusivity, ν/D_{AB}, (for the cross flow fluid) and is comparable to the Prandtl number, ν/α. Note that ν and D_{AB} are the momentum diffusivity and mass diffusivity of the gas in crossflow, and not of the polymer solution. One correlation (Transport and Unit Operations, 3rd ed., by C. J. Geankoplis, Prentice Hall, Englewood Cliffs, (1993), p 450) for k is:

$$Sh = 0.600\ Re^{0.513}\ Sc^{1/3} \qquad (4\text{-}21)$$

where $Sh = (kD/D_{AB})$. The reader may want to compare other correlations with this one to determine the consistency of different predictions and to determine whether the appropriate the correlation applies to the range of variables used.

Just as we dedimensionalized the heat transfer equations, we can do the same for solvent diffusion. The resulting equations then are exactly identical to those for unsteady heat conduction.

$$\frac{\partial Y}{\partial X} = \frac{\partial^2 Y}{\partial n^2} \qquad (4\text{-}22)$$

$$Y = \frac{C_\infty - C}{C_\infty - C_0},\ n = \frac{r}{R},\ \text{and}\ X = \frac{D_{AB}\,\theta}{R^2} \qquad (4\text{-}23)$$

$$m = \frac{D_{AB}}{k\,R} \qquad (4\text{-}24)$$

Of course, T is replaced by C, α by D_{AB}, h by k. Therefore, the same solution (graphical or analytical) is obtained and the same charts can be used to obtain quantitative predictions of the fiber spinning process. One can readily calculate, therefore, the Fourier number, X, required for the solvent concentration at the filament centerline to become

less that 1% of the original value (Y < 0.01). From this value for X, the actual time (in a Lagrangian sense, remember) can be calculated. Finally, by multiplying this time by the yarn speed, the length of the solvent recovery section is obtained directly. The analogy here might be that of using a conveyor belt in a tunnel oven to bake bread. We can calculate the length of the tunnel oven, once we know the time to bake the bread and the speed of the conveyor belt.

Key elements learned in this section include:

- Equivalence of fundamental equations for heat transfer and mass diffusion,
- Similarity (and difference?) between convective equations for heat transfer and those for mass transfer,
- Manufacture of synthetic fibers by volatilization of solvent from fibers produced as spin "dope" is extruded through small holes.

4.3 Wet Spinning

Fibers produced by wet spinning include rayon and Kevlar™. Rayon was originally developed as a synthetic substitute for silk and Kevlar was produced as a high-strength fiber for use in various aerospace and specialty-use applications. Furthermore, many comercial acrylic fibers are also produced by wet spinning.

Wet Spinning

Here, the polymer is dissolved in a solvent which is <u>extracted</u> into a liquid (usually water) after the solution (spin dope) leaves the spinneret.

Rayon, Kevlar (air gap wet spinning)
- Lower temperature process than melt spinning
- For polymers that are not readily melted

<u>Mass Transport</u>

air gap (Kevlar)

solvent is leached (or extracted) from polymer filaments into liquid
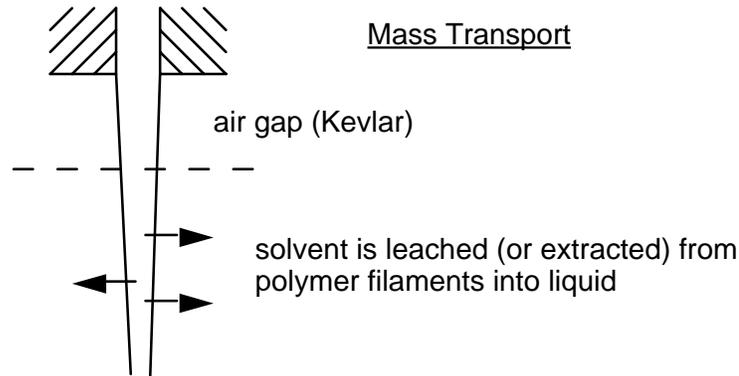
Slow yarn speed compared to dry spinning because the viscosity of the surrounding fluid, water, is 100x times the viscosity of the surrounding fluid (air) during dry spiinning. This causes high drag forces on the yarn, leading to very high yarn tensions.

Partial Differential Equation is the same as that for dry spinning. Boundary conditions?

$$\frac{\partial C}{\partial \theta} = \frac{D_{AB}}{r} \frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right)$$

Boundary layer analysis, in order to quantify drag force and mass transfer coefficient.

Fig. 4-4 Wet Spinning — Solvent Removal by Extraction or Leaching

As with dry spinning, the polymer is dissolved or suspended in a solvent, to form a viscous "spin dope" and filaments are formed by extrusion through tiny holes in a spinneret plate. Kevlar, for example, will degrade thermally if attempts are made to melt it, and thus a solvent must be used. The term wet spinning more accurately depicts the process than does dry spinning, because the solvent is extracted or, perhaps more appropriately, leached, from the filaments by another liquid. In most cases, the second liquid is aqueous.

A major difference between wet spinning and either melt or dry spinning is that one is spinning into a fluid (liquid) with a much higher viscosity. Because this higher viscosity can translate into high shearing stresses on the surfaces of the filaments, the

tension in the filaments can become quite high. For example, towing a buoy by a long line behind a boat can produce very high tensions in the line when compared with towing the same buoy by a short line. For long baths, the tension can become sufficiently high that the filaments might break, as their tensile strength is exceeded. To avoid this danger, much lower spinning speeds must be used. Whereas melt spinning may utilize spinning speeds of 2,000 yards per minute (80 mph), spinning speeds in wet spinning are usually less than 300 ypm.

Another difference with dry spinning is the capability of using many more spinneret holes in the case of wet spinning. The total number can approach 60,000 in a single spinneret plate, if the spinning is done directly into a coagulating or extracting liquid. Because the liquid is present, the filament forms a type of skin almost immediately and the potential for the filaments to touch and fuse is practically eliminated, compared with dry or melt spinning.

In the case of Kevlar the spin dope is relatively warm, about 100°C, and forms a viscous, liquid crystal. The solvent is sulfuric acid, at a concentration of about 80 wt% (20 wt% polymer). These liquid crystals are easily oriented by a stretching motion, but they can lose their orientation, presumably by Brownian motion, once the stretching is stopped. Therefore, during the spinning process, the filaments are first extruded through an air gap, where the filaments undergo strains of 2 to 3x, which produces a high degree of molecular orientation in the filaments, and then they are suddenly "quenched." This air gap is of the order of one inch. It also allows the spinneret plate to be warm (100°C) while the extraction bath can be cool (ca 15°C). The hot filaments then strike the cooling bath where the filaments are quenched and much of the orientation is locked in by the rapid cooling action. Subsequent to the quench step, the solvent is extracted, which requires a relatively long bath contact time. But the initial quenching step is crucial, since it allows for the oriented molecules to be "frozen" into position. This orientation is particularly important to the high-strength properties of Kevlar—the filaments, on a weight basis, are significantly stronger that steel. If one attempts to use the same process to produce Kevlar filaments of large diameter, the core of the filaments can lose its orientation, because the quench time to reach the core will increase with the square of the

filament radius. The filament skin, or the outer part of the filaments, however, will have the orientation locked in and a high degree of orientation will exist there. This produces a so-called "skin-core" effect, in which the average properties of the filaments, expressed as tensile strength per unit cross-sectional area, will decline on account of a decreased average orientation.

Kevlar, with its focus on strength development via "air-gap" wet spinning, is somewhat unique within the process of wet spinning. As with melt- and dry- spinning, the controlling part of the process is associated with development of the filament structure, either by cooling of the filament or by removal of the solvent. The equations for diffusion in wet spinning are identical to those for dry spinning, with the exception that the fluid passing outside the filaments is a liquid and not a gas. Also, the flow may not be across the filaments, but even, partially, along the filaments. Therefore, the correlations and nature of the flow surrounding the filaments will result in different values for the surface mass transfer coefficient. Whether this will change the relative resistance dramatically will depend on the particular fiber to be produced and its dimensions and properties. Note that the same graphical solutions described earlier can be used.

To design a wet-spinning process, it may be necessary to predict the transport of momentum, heat, and mass in the region adjacent to the filament just downstream of the spinneret. One can use a so-called "boundary-layer" analysis to do this. Treatment of such an analysis is beyond the scope of the present discussion of fiber spinning, but a brief description of the analysis is appropriate. One form of boundary-layer analysis involves von Karman integral boundary-layer techniques. The boundary layer starts at zero thickness at the first point where the fiber contacts the extracting liquid, and grows gradually radially outwards from each filament as one proceeds downstream. The velocity profile inside the boundary layer is assumed and all of the velocity change between the filament and the surrounding fluid is contained within this "momentum" boundary layer. Similarly, thermal and diffusional boundary layers contain all the changes in temperature and concentration, respectively. Based upon approximations of these velocity profiles, frequently assumed to be turbulent, the variation in filament drag

with position can be predicted, along with local heat and mass transfer coefficients. The student is referred to the text Transport Phenomena, by Bird, Stewart, and Lightfoot, Wiley, New York (1960) for additional details of such integral boundary-layer techniques.

Key elements of the wet spinning process include:

• Similarity of governing equations to melt and dry spinning,

• Lower spinning speeds in wet spinning,

• Structure development in air-gap spinning of Kevlar and skin-core effects,

• Qualitative introduction to boundary-layer concepts.

5.0 Fiber Treatment & Miscellany

In order to start up a fiber spinning line, the filament bundle must be "strung up" along the process path. The first stage of the spinning process is vertically downwards, so gravity will tend to pull the line downwards. The line is caught with a large vacuum nozzle and, almost simultaneously, the line beneath the nozzle is cut with scissors. The line now is sucked into the nozzle, which functions exactly like a home cannister style vacuum cleaners, with the fiber piling up in a large drum. The suction at the nozzle keeps the spinning line under tension.   The line is then passed over pairs of drive rolls, described below, and then over certain stretching/orientation steps, if needed. Finally, the line is taken to a take-up device which winds the fiber bundle onto bobbins. In order to maintain a uniform takeup speed, the rotational speed of the bobbins must decrease as additional fiber is laid on it and the average diameter increases. This decrease in rotational speed is controlled by keeping the tension constant in the takeup line. The tension is sensed by deflection of an idler wheel located between the last drive roll and the take-up machine. The idler wheel is located on a type of cantilever beam, so that the deflection is a measure of the tension in the line. The position of the wheel, and thus the line tension, is maintained constant by adjustment of the take-up speed.

The drive rolls are always characterized by having non-parallel axes. This permits the threadline to advance in the axial direction on the rolls as the line is strung multiple

times around the rolls. The rolls, which are usually highly polished, permit no slip on the surface on account of the multiple wraps on each pair of rolls and the tension in the line. This is somewhat like the calculation of frictional force for a rope wound around a post, a calculation the student probably performed in a statics course.

Because the drive rolls permit good speed control for each pair of rolls, it is possible, by having the second pair of drive rolls moving faster than the first, to control the degree of stretch the fiber undergoes between the two pairs of rolls. This stretch, which may range from a few percent to 20 or 30%, helps to impart desired molecular orientation, and thus desired mechanical properties, to the fiber bundle. Sometimes it is necessary to heat the bundle to a temperature above Tg, the glass transition temperature, but below the melt temperature, in order to facilitate significant stretches without imparting excessive line tension. Usually, the strain gives the fiber a higher modulus (stress over strain), or stiffness, in the axial direction and higher tenacity, or strength to break per unit cross sectional area.

Stretching and Orientation
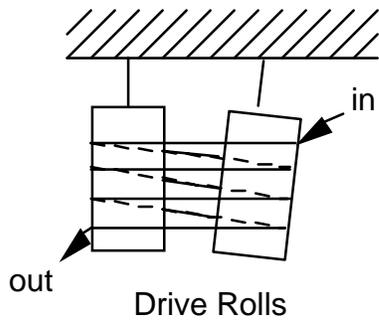
Provides excellent control of yarn speed, recall friction for rope wound around a post

3500 ypm

Drive Rolls

Stretching —— between two pairs of drive rolls, with second pair driven faster

in

out

V_1

heat
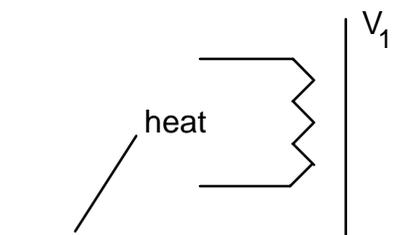
$\dfrac{V_2}{V_1} - 1$ = "stretch" or strain

Recall mechanics:
 stress α strain,
Hookean elasticity

To temp > T_g =

V_2

Glass Transition Temperature (but below melt temp)

Here we have <u>permanent</u> deformation, which orients the polymer molecules in the same direction as the stretch. This produces higher modulus (stress/strain) and higher strength

Speed control of take-up device:
    This speed is adjusted in response to the tension in the yarn; speed increases as tension decreases. Tension is detected by measuring deflection of an idler wheel that is spring-mounted.

Fig. 5-1 Fiber Stretching and Orientation

Table 5.1 summarizes several areas which would be convenient for post-presentation elaboration, or, perhaps, illustrative asides. For example:

<u>Analytical solution of Partial Differential Equations</u> The diffusion equation is seen frequently in the physical sciences, and presents a nice starting point for mathematical topics, including techniques of separation of variables, inhomogeneous boundary conditions, etc.

Table 5.1 Topics for Elaboration

● Analytical Solution of PDE (partial differential equations)

● Graphical Presentation of Results — Gurney-Lurie Charts, Heissler Charts

● Continuous cylinder of uniform radius vs.Melt spinning result
        (declining radius); Fiber optic cables,
● Short cylinders: cooling cans of soda, pasteurizing foods, polymer
      resin particles

● Other geometries or applications

        Slabs — Cooling of float glass, cooling of metal slabs

        Brick = special case (three slabs), Newman's Rule

        Spheres — drying of porous spheres, cooling of molten pellets, etc.

● Convection currents inside object, if a fluid

Gurney-Lurie & Heissler Charts These charts depict very nicely several physical results of unsteady-state conduction and diffusion.   These include the "nearly exponential" decline of unaccomplished change with time and, similarly, the dependence on the square of characteristic dimension, via the Fourier number. Similarly, the relative resistance effect can be seen clearly, along with quick calculations to indicate quantitatively, when a lumped-parameter model, where, for example, internal resistance could be neglected, would be appropriate.

Application to Other Cylindrical Geometries Direct applications could include glass fiber-optic cable and extrusion of rod-shaped polymer material, although one could extend the calculations to food processing, such as sterilization times for cans of food placed in a steam oven, or cooling of cans of soda, etc.

Complications of Declining Radius and Finite Heat of Fusion The student can recall that these complications were removed during our treatment so that we could

proceed with the analysis. One could account for the declining radius by patching together successive solutions of uniform diameter and uniform temperature to approximate the smoothly varying geometry with one varying in steps. This would require knowledge of the extensional rheology as a function of temperature, however. Similarly, one would have to know the heat of fusion in order to account for its effect. If the total amount of heat to be removed by fusion is of the same order as that of the sensible heat, then the Fourier time calculation is likely to be too short by a factor of two or so.

Extension to other Geometries These would include infinite slabs, for example in the manufacture of float glass or cooling of metal slabs or ribbons of steel. Extension of the infinite slabs to Newman's rule so that three-dimensional bricks can be treated by using three separate one-dimensional solutions. Spheres are also very important, for example, in the removal of unreacted monomer, VCM (vinyl chloride monomer), from PVC (poly-vinylchloride) spheres made by suspension polymerization or drying of porous spheres, and cooling of molten metal pellets, etc.

Convection Currents Inside an Objects The time to cool a soda can will be less than that calculated from the charts because convection currents will become established with the can that will hasten heat transfer from the can. This is somewhat like the familiar example from heat transfer courses which states that ice cubes can be made more quickly from tepid water than from cold water on account of the establishment of such convection currents, which will more than compensate for the greater amount of heat to be transferred. The author does not recall seeing any confirming experimental results, however.