It’s going to turn out that a similar mass transfer effect occurs within the mobile phase. The thing to consider here is that we want solute molecules to encounter the surface of the stationary phase as quickly as possible so that they can immediately undergo a distribution between the two phases.

For example, if we reconsider the picture for mass transport broadening in the stationary phase (Figure 38), we realize that we want the molecules at the leading edge of the mobile phase profile to quickly encounter and enter the stationary phase, otherwise they will move further ahead and broaden the distribution.

Figure 38. Representation of the movement of analyte molecules at the leading and trailing edge of the concentration distribution.

Another way to examine mobile phase mass transport broadening is to consider a capillary column as shown below.

Figure 39. Capillary column showing a molecule (black dot) that has just left the stationary phase.

The dot represents a molecule that has just left the stationary phase and is about to diffuse across the mobile phase and re-encounter stationary phase on the other side of the column. It is helpful to draw a line representing the path of the molecule, and then draw a second line for the path of the molecule if the flow rate were doubled. We could also imagine a situation in which the flow was so fast that the molecule never re-encountered the stationary phase. This would be a problem since it’s important for the molecule to encounter the stationary phase if we are to ever have a distribution occurring that leads to a separation of two compounds.
If we are using capillary columns in a chromatographic system, what does this observation above suggest about the desirable diameter for such a column? Hopefully it would be apparent that a much smaller column diameter would lead to much faster encounters with the stationary phase. So we want capillary columns of very small diameter. That is one of the reasons why the fused silica columns used today in gas chromatography are so efficient. We can not even see the opening in these columns with the naked eye. They really approach the limit of how narrow we are able to make chromatographic capillary columns.

Next we need to ask whether this effect occurs in a packed column. If we think about a packed column, we should realize that there are voids, or interstitial volume, between the particles that make up the packing. Solute molecules need to diffuse across these voids to encounter the stationary phase. The larger the void, the more time it takes to diffuse across, and the more significant the mobile phase mass transport broadening. How can we reduce the voids? If we use smaller particles, they will pack closer together and reduce the interstitial volume between the particles. Once again, we see how small particles offer a theoretical advantage when compared to large particles. Note that this has happened in every instance when particle size made a difference. Using a packing material with smaller particles is better, provided we pack a good column with minimal to no channeling.

Another critical question to consider is whether mobile phase mass transport broadening is more significant in gas or liquid chromatography. To answer this, we need to realize that we want the solute compound to diffuse across
regions of mobile phase as fast as possible. If we remember that gases diffuse about 100,000 times faster than liquids, we realize that the impact of mobile phase mass transport broadening is significantly lower for gases than it is for liquids. In fact, mobile phase mass transport broadening is the most important distinction between gas and liquid chromatography. Gases diffuse far more quickly across regions of mobile phase than do liquids. That means in liquid chromatography we need far smaller mobile phase voids to reduce the magnitude of this term. When Giddings published his important paper in 1963 on doing liquid chromatography with the efficiency of gas chromatography, this was a critical realization put forward in this paper.

**What does this mean for practical applications of liquid chromatography?** If we were to try to perform capillary liquid chromatography, it would mean that we ought to have columns with much smaller internal diameters than we use for gas chromatography. But gas chromatography already uses fused silica columns, which essentially reach the limit of practical internal diameters (remember, if we reduced this diameter even smaller, we introduce a problem of not having enough sample capacity in the column and would have a very difficult time actually introducing sample into the column), so capillary liquid chromatography is not a practical method and does not offer the same advantages of capillary gas chromatography. There are researchers who investigate aspects of capillary liquid chromatography, but it is not a commercial method and is not used widely by practitioners in the field. As far as packed column liquid chromatography, we have already seen how we end up using very small particles (1.7, 3, 5, and 10 µm). The real value of these small particles is that they reduce the interstitial volume of mobile phase between the particles, thereby reducing the time required for mobile phase mass transport. Gas chromatography can be done with much larger particles because of the much faster mobile phase mass transport.

**The last thing we could consider about mobile phase mass transport broadening is whether its overall contribution to band broadening depends on flow rate.** If we go back to our initial picture of the capillary column, we know that we want the solute molecules to encounter stationary phase as often as possible. The faster the flow, the fewer encounters, so a faster flow makes this contribution worse (this is analogous to the leading edge of the mobile phase distribution moving ahead more per unit time, thereby causing more broadening of the overall distribution). If we needed to write a term to go into our equation for \( h \), and we represent mobile phase mass transport broadening as \( C_M \) (be careful not to confuse this with \( C_M \) the concentration of solute in the mobile phase that we have used earlier), the term would take the following form:

\[
h = C_M v
\]

Notice how the relationship is analogous to what we saw with mass transport broadening in the stationary phase.