Consider a band of a compound in a chromatographic column. The band has the concentration profile shown in Figure 19.

![Figure 19](image1.png)

**Figure 19.** The representation on the left shows a band of a compound on a chromatographic column. The representation on the right shows the concentration profile of the band. The concentration is greatest at the center of the band.

The first thing to consider is what would happen to this profile if the flow of the column was stopped and the column was allowed to sit. We know from the random process of diffusion that there is a statistical preference in which more molecules diffuse away from regions of high concentration to regions of low concentration. If we were to allow this band to sit stopped in the column, it would slowly diffuse out from its central region and lead to a broadening of the concentration profile as shown in Figure 20.

![Figure 20](image2.png)

**Figure 20.** Representation of band or peak broadening that results from longitudinal diffusion. Compare to the concentration profile in Figure 19.

This observation of diffusion from a region of high concentration to one of low concentration will occur whether the band of material is sitting stationary in a column or is flowing through the column. A molecule flowing through a column has two means of movement. One is the physical flow that is taking place. But the other is still its ability to diffuse in a random manner from one point to another. All compounds moving through a chromatographic column must exhibit some degree of longitudinal diffusion broadening. Therefore, we can never get the idealized chromatogram shown in Figure 18a.

An important thing to consider is whether this phenomenon is more significant (i.e., happens faster and therefore causes more broadening, everything else being equal) in gas or liquid chromatography. To consider this, we would need to know something about the relative rates of diffusion of gases and liquids. A substance with a faster rate of diffusion will broaden more in a certain amount of time than something with a slower rate of diffusion. So the relevant
question is, which diffuses faster, gases or liquids? I suspect we all know that gases diffuse appreciably faster than liquids. Just imagine yourself standing on the opposite side of a room from someone who opens a bottle of a chemical with the odor of a skunk. How fast do you smell this odor? Compare that with having the room full of water, and someone adds a drop of a colored dye to the water at one side of the room. How fast would that color make its way across the water to the other side of the room? In fact, gases have diffusion rates that are approximately 100,000 times faster than that of liquids. The potential contribution of longitudinal diffusion broadening to chromatographic peaks is much more serious in gas chromatography than in liquid chromatography. In liquid chromatography, the contribution of longitudinal diffusion broadening is so low that it's really never a significant contribution to peak broadening.

Finally, we could ask ourselves whether this phenomenon contributes more to band broadening at higher or lower flow rates. What we need to recognize is that longitudinal broadening occurs at some set rate that is only determined by the mobile phase (gas or liquid) and the particular molecule undergoing diffusion. In the gas or liquid phase, it would be reasonable to expect that a small molecule would have a faster rate of diffusion than a large molecule. If we are doing conventional gas or liquid chromatography using organic compounds with molecular weights from about 100 to 300, the differences in diffusion rates are not sufficient enough to make large differences here. If we were comparing those molecules to proteins with molecular weights of 50,000, there might be a significant difference in the rate of diffusion in the liquid phase. If the longitudinal diffusion occurs at a set, fixed rate, then the longer a compound (solute) is in the column, the more time it has to undergo longitudinal diffusion. The compound would be in the column a longer time at a slower flow rate. This allows us to say that the contribution of longitudinal diffusion to overall peak broadening will be greater the slower the flow rate. If we use the term B to represent longitudinal diffusion broadening and v to represent flow rate, and want to relate this to h, we would write the following expression:

\[
h = \frac{B}{v}
\]

Remember that the smaller the reduced plate height the better. At high flow rates, B/v gets smaller, h is smaller, and the contribution of longitudinal diffusion to peak broadening is smaller.

We can also write the following expression for B: B = 2\(\phi D_M\)

In this case, \(D_M\) refers to the diffusivity (diffusion coefficient) of the solute in the solvent. Notice that this is a direct relationship: the faster the rate of diffusion of the solute, the greater the extent of longitudinal diffusion. \(\phi\) is known as the obstruction factor, and occurs in a packed chromatographic column. In solution, a molecule has an equal probability of diffusion in any direction. In a packed column, the solid packing material may restrict the ability of the solute to diffuse in a particular direction, thereby hindering longitudinal diffusion. This term takes this effect into account.