

2.2. Mixing with Deformation.

The first attempts to identify the mixing mechanism in very viscous liquids were undertaken by Spencer and Wiley [15]. They postulated that mixing proceeds by some sort of continuous deformation be called "streamline mixing". Due to Spencer and Wiley [15] mixing consists of two processes: increasing the contact area between liquids being mixed and distributing that interface throughout the mixed volume. For the simple shear (figure 2.3) Spencer and Wiley [15] found the relationship for the contact area:

$$A = A_0 \cdot \sqrt{1 - 2 \cdot \left(\frac{\partial v_x}{\partial y} \cdot t \right) \cdot \cos \alpha_x \cdot \cos \alpha_y + \left(\frac{\partial v_x}{\partial y} \cdot t \right)^2 \cdot \cos^2 \alpha_x}, \quad (2.5)$$

where $\cos \alpha_x$ and $\cos \alpha_y$ are the direction cosines of the normal to the initial surface.

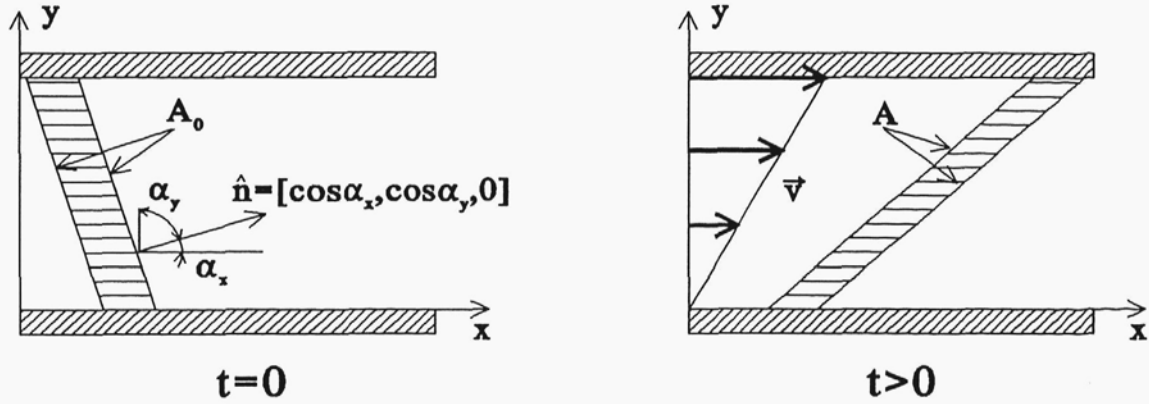


Figure 2.3. Mixing in a simple shear flow.

Equation (2.5) indicates that the area of the deformed surface is proportional to the undeformed surface area and depends on the initial orientation of material element. Consequently, the energy required to develop area to the certain value should depend on the initial orientation. Spencer and Wiley [15] applied equation (2.5) to find the initial orientation which assures the most efficient area generation in the considered shear flow:

$$\alpha_x = \arctg\left(\frac{A_0}{A}\right), \quad \alpha_z = 0, \quad (2.6)$$

Equation (2.6) shows that the infinitely small increase of the interfacial area can be obtained most efficiently for $\alpha_x=45^\circ$, whereas the infinitely large increase of the area requires $\alpha_x=0^\circ$ to be most efficient.

It is very important to know how the newly created surface is distributed over the system.

Spencer and Wiley [15] handled the problem by matrix method, dividing the system volume into N discrete cells of the same size and assigning numbers from 1 through N to these cells. Then they defined a distribution matrix for each unit mixing operation $[D_{ij}]$, where D_{ij} is that fraction of the tracer material originally in the i-th cell which is to be found in the j-th cell after the mixing operation. Thus each "distribution matrix" is directly related to the flow pattern in the system.

Mohr et al. [12] adopted the concept of interpreting mixing as an increase of the interfacial surface area. They defined the striation thickness as shown in figure 2.4 and then expressed it in terms of the interfacial area:

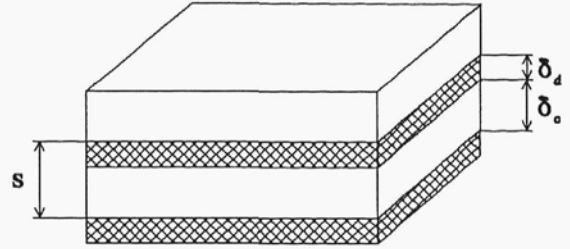


Figure 2.4. Definition of striation thickness proposed by Mohr.

$$s = \delta_d + \delta_c = \frac{2 \cdot V}{A} = \frac{2}{a_v} \quad (2.7)$$

In equation (2.7) V denotes the mixture volume and a_v stands for the interfacial area per unit volume. Introducing equations (2.5) and (2.7) into the shear stress continuity condition:

$$\tau = \mu_c \cdot \left. \frac{dM_c}{dt} \right|_A = \mu_d \cdot \left. \frac{dM_d}{dt} \right|_A \quad (2.8)$$

leads to:

$$s = \frac{S_0}{M_c \cdot \phi_d} \cdot \frac{\mu_d}{\mu_c} \quad (2.9)$$

In equations (2.8) and (2.9) M_c is the amount of shear imposed on the major component by the system boundaries; it is calculated as the product of the shear rate and the mixing time. M_d denotes the total amount of shear transferred from the "major" component to the "minor" component forming dispersed phase and ϕ_d is the volume fraction of the "minor" component. Mohr et al. [12] have pointed out that equation (2.9) is valid when the minor component is more viscous ($\mu_d/\mu_c > 1$); in such a case the spots of the minor component are relatively less deformed than the matrix of the major component. When however $\mu_d/\mu_c < 1$ the ratio of viscosities in equation (2.9) should be replaced by unity because the minor, less viscous component can never be deformed more rapidly than the surrounding liquid.

Later, Mohr [16] extended his analysis over the case of tensile deformation and obtained the following expression for the interfacial area:

$$A = A_0 \cdot \sqrt{\left(\frac{\cos \alpha_x}{X}\right)^2 + \left(\frac{\cos \alpha_y}{Y}\right)^2 + \left(\frac{\cos \alpha_z}{Z}\right)^2}, \quad (2.10)$$

where X , Y and Z denote the relative changes of distances between the same particles in x , y and z directions caused by non-zero values of velocity gradients: $(\partial v_x/\partial x)$, $(\partial v_y/\partial y)$ and $(\partial v_z/\partial z)$.

This simple theory was used by Mohr et al. [17] to relate mixing performance in a single screw-extruder to screw geometry and degree of pressure flow. The distribution patterns of the "minor" tracer liquid in the cross section of extruded rods were found to be in a qualitative agreement with the theoretical predictions. Another success of the theory of Mohr is presented by Schrenk et al. [18]. They have shown that in the case of pressure driven, laminar flow through a rotating tube, measured and calculated values of the striation thickness remain in a good quantitative agreement. The importance of effects of deformation, orientation and redistribution of the intermaterial area in mixing of very viscous liquids was also confirmed in special cases by Shearer [19] and Erwin[20].

The theory of Mohr was further developed by Ranz, Ottino and Macosko [21,22,23] by including the effects of molecular diffusion and chemical reaction.

In this context it is very interesting that the Mohr's interpretation of the effect of viscosity ratio on mixing was seriously criticized already in 1972 by Murakami et al. [24]. The theory was examined experimentally by the authors using a cone rotor type mixer to generate the uniform shear. The authors concluded that the effect of viscosity ratio on the striation thickness might be negligible in the range of $0.6 < \mu_d/\mu_c < 3$. In the range of viscosity ratio $\mu_d/\mu_c > 3$ and $\mu_d/\mu_c < 0.6$ Murakami et al. [24] observed formation of uneven streaks and spots of the "minor" component, which completely changes interpretation of mixing; the relation between the shape of these spots and viscosity ratio is extremely different from that for insoluble liquids. All these observations are contrary to Mohr's predictions. Only when the viscosity ratio was equal to one, were the experimental results in good agreement with the theoretical results.

2.3. Mixing with Diffusion and Reaction.

Transport processes occurring at the molecular level such as molecular diffusion and chemical reaction were generally neglected in the early studies of mixing in very viscous liquids. The rate of molecular mass transfer was considered to be too slow and acting over