

1. formation of a homogeneous solution by melt-bending the polymer with a high-boiling, low-molecular weight solvent;
2. casting of the solution;
3. cooling of the cast solution to induce phase separation and solidification of the polymer;
4. removal of the solvent (typically by extraction) to produce the membrane structure.

TIPS allows isotropic microporous structures to be obtained.

According to the operational principle of a membrane crystallizer, the mass transfer through a microporous hydrophobic membrane must take place in vapor phase. Dusty gas model (DGM) theory is conventionally used to describe the transport of gases in a porous medium:¹⁹ under the assumption of negligibility of surface diffusion¹ and in absence of viscous resistance (no filtration of liquid), the transmembrane flux is determined by the Knudsen diffusion resistance (due to collisions between molecules and membrane walls) and by the ordinary diffusion resistance (due to collisions among diffusing molecules).²⁰ Predominance or coexistence of these different mechanisms is determined by the Knudsen number (Kn) that compares the mean free path (λ) of diffusing molecules to the mean pore size (d_p) of the membrane.

Specifically, if the free mean path of the diffusing gas is small with respect to the average membrane pore diameter, $\text{Kn} < 1$ and molecule–molecule collisions predominate over molecule–wall collisions. *Vice versa*, in the so-called “Knudsen diffusion regime” ($\text{Kn} > 1$), the mean free path of the gas is large with respect to the average membrane pore diameter and molecule–wall collisions predominate over molecule–molecule collisions.

Kinetic theory of ideal gases calculates λ (m) as:

$$\lambda = \frac{k_B T}{P \sqrt{2} \pi \sigma^2} \quad (8.1)$$

where k_B is the Boltzmann constant ($1.380 \times 10^{-23} \text{ J K}^{-1}$), T (K) is the absolute temperature, P (J m^{-3}) the pressure, and σ is the collision diameter of the molecule (*i.e.* 2.7 Å for water, 3.7 Å for air).

Membrane modules are usually not deaerated; therefore, water vapour diffuses in air and, in this circumstance, the free mean path $\lambda_{w/a}$ can be evaluated at the average membrane temperature \bar{T} as:²¹

$$\lambda_{w/a} = \frac{k_B \bar{T}}{\pi [(\sigma_w + \sigma_a)/2]^2 P \sqrt{1 + (M_w / M_a)}} \quad (8.2)$$

where σ_a and σ_w are the collision diameters, and M_a and M_w (g mol^{-1}) the molecular weight for air (average) and water, respectively. At room temperature, the mean free path of diffusing water vapour is in the order of $10^{-1} \mu\text{m}$, that is comparable to the typical pore size of microporous membranes; as a consequence, both diffusional mechanisms have to be considered.