The transmembrane flux is expressed as:[19]

$$\frac{J_i^{\mathrm{D}}}{D_{ie}^{\mathrm{K}}}+\sum_{j=1\neq i}^{n}\frac{p_j J_i^{\mathrm{D}}-p_i J_j^{\mathrm{D}}}{D_{ije}^{0}}=-\frac{1}{RT}\nabla p_i \tag{8.3a}$$

$$J_i^{\mathrm{v}}=-\frac{\varepsilon r^2 p_i}{8RT\tau\mu}\nabla P \tag{8.3b}$$

$$D_{ie}^{\mathrm{K}}=\frac{2\varepsilon r}{3\tau}\sqrt{\frac{8RT}{\pi M_i}} \tag{8.3c}$$

$$D_{ije}^{0}=\frac{\varepsilon}{\tau}PD_{ij}^{0} \tag{8.3d}$$

where J^{D} (mol m^{-2}s) is the diffusive flux, J^{v} the viscous flux, D^{K} the Knudsen diffusion coefficient (m^2 s^{-1}), D^0 the ordinary diffusion coefficient, M_i (kg mol^{-1}) is the molecular weight, p (J m^{-3}) the partial pressure, R the gas constant (8.314 J mol^{-1} K^{-1}), T the temperature, P the total pressure, μ (m^2 s^{-1}) the gas viscosity, r (m) the membrane radius, ε the membrane porosity and τ the membrane tortuosity. Subscript "*e*" indicates the effective diffusion coefficient.

Although DGM is strictly derived for an isothermal system, it is successfully applied whenever a membrane crystallizer is operated under relatively small thermal gradients (10–50 °C); in this case, the average temperature across the membrane is assumed as T value.

8.4 Heterogeneous Nucleation on Membranes

Membrane crystallization combines the principles of mass and heat transport through microporous hydrophobic membranes with the theory of heterogeneous nucleation promoted by polymeric films.

Transport phenomena related to the removal of solvent or to the controlled addition of anti-solvent have been elucidated in Section 8.2. In this section, the classical nucleation theory is adapted to the case of porous or rough membranes in order to clarify – from a mathematical point of view – the relationships existing between the physico-chemical properties of the polymeric surface and the nucleation kinetics.

The formation of clusters (or nuclei) from solution can be imagined as resulting from collision and aggregation of a certain number of solute molecules moving among the molecules of solvent. At the early stage these clusters have a large probability to dissolve; however, under specific conditions, nuclei are able to reach a critical size characterized by the same probability (50%) to grow or to dissolve (critical nuclei). According to the classical nucleation theory (CNT),[22] crystallization is an activated process and requires overcoming an energy barrier (whose peak corresponds to the Gibbs free energy for a critical nucleus).