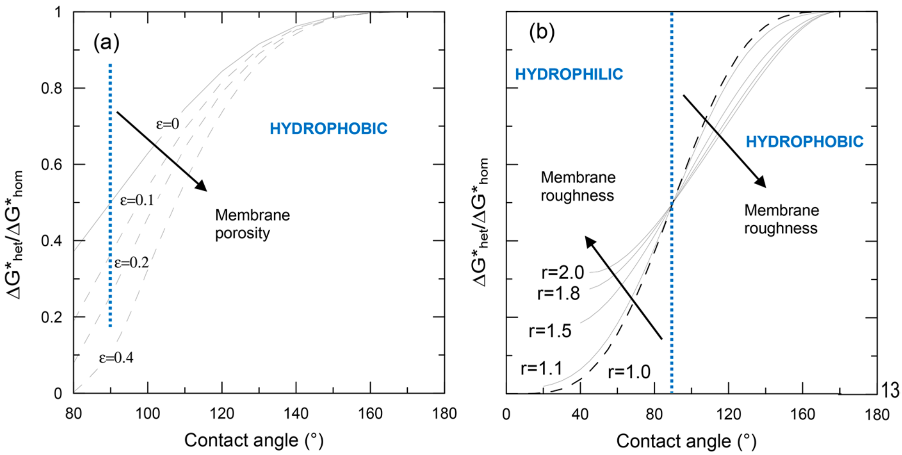

Figure 8.4 Trend of the energy barrier to the formation of a critical nucleus on a membrane as a function of contact angle (θ), for different: (a) porosity (ε); (b) Wenzel roughness coefficient (r).

1 (nucleation in homogeneous phase). For a perfectly smooth surface (r = 1) the energy ratio is expressed by eqn (8.18). Experimental investigations confirmed the enhanced nucleation rate of calcium sulphate dihydrate on heated rough stainless-steel surfaces.[26]

According to CNT, nucleation is an activated process requiring that the Gibbs free energy barrier (ΔG^*) has to be overcome in order to form a stable nucleus. The correlation between ΔG^* and nucleation rate N is mathematically expressed by the Arrhenius-like correlation:

$$N = \Gamma \mathrm{e}^{-\frac{\Delta G^*}{k_B T}} \tag{8.19}$$

where Γ is a pre-exponential kinetic factor. Therefore, the possibility of designing membranes with specific chemical, topological and structural properties offers a powerful and unique tool for controlling the nucleation stage in a crystallization process.

8.5 Membrane Crystallization of Proteins

Biological macromolecules and proteins crystallize from solutions according to the same principles and by the same mechanisms as small molecules; however, their peculiarities make their crystallization process very challenging. Due to their structural complexity, the surface of macromolecules displays a rather asymmetric and weak bonding configuration, thus significantly reducing the probability of an ordered attachment of growing units. Moreover, proteins show a significant attitude to aggregate in n-mers that diversify shape and size of lattice units and exhibit very low diffusivities so that their crystallization kinetics are extremely slow.