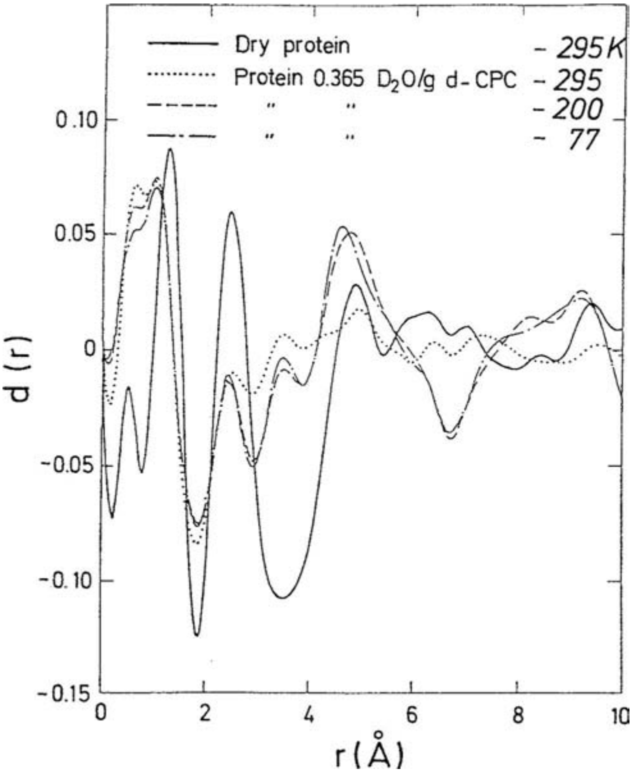

FIGURE 5 Pair correlation function *d*(*r*) for a dry d-CPC protein at 295 K and for a D_2O-hydrated ($h = 0.365$) d-CPC protein at different temperatures. *Source*: From Ref. 53.

simulations work on polypeptides and proteins (34,61) and was interpreted as resulting from some increase in the clustering of water molecules (Fig. 5). For the highest hydrated sample ($h = 0.365$), a well-defined peak appears at 3.5 Å. This is the average distance between the center of mass of a water molecule in the first hydration layer and amino-acid residues on the surface of the protein. In the case of the lowest hydrated sample ($h = 0.175$), the perturbation of the structure of protein due to water of hydration is not detectable. It is generally viewed in the literature that at full hydration ($h = 0.5$), there is a complete monolayer of water surrounding the protein (62).

Some similarity between the behavior of water close to C-phycocyanin protein and hydrophilic model systems can be stressed. In fact, for low-hydrated protein samples, no crystallization of water is detectable while, for more than one monolayer coverage, hexagonal ice is formed. Moreover, the peak at 3.5 Å is also detected. However, it should be noted that at the highest hydration level, water nucleates into hexagonal ice at low temperature; this is in contrast with hydrated Vycor where water nucleates into cubic ice.

Some other interesting findings come from the study of glass-liquid transition and crystallization behavior of water trapped in loops of methemoglobin chains (63).