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The influence of temperature on the atomic structure at the electrochemical interface has been studied using in-situ surface x-ray scattering (SXS) during the formation of metal monolayers on a Au(111) electrode. For the surface reconstruction of Au(111), higher temperatures increase the mobility of surface atoms in the unreconstructed phase which then determines the surface ordering during the formation of the reconstruction. For the underpotential deposition (UPD) systems, the surface diffusion of the depositing metal adatoms is significantly reduced at low temperatures which results in the frustration of ordered structures in the case of Cu UPD, occurring on a Br-modified surface, and in the formation of a disordered Ag monolayer during Ag UPD. The results indicate that temperature changes affect the mass transport and diffusion of metal adatoms on the electrode surface. This demonstrates the importance of including temperature as a variable in studying surface structure and reactions at the electrochemical interface.