

Does Maxwell's hypothesis of saturation of air near the surface of evaporating liquid hold at all spatial scales?

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The classical model of evaporation of liquids hinges on Maxwell's assumption that the vapor near the liquid's surface is saturated. It allows one to find the evaporative flux without any knowledge of what happens in the interface separating liquid and air. Maxwell's hypothesis is based on an implicit assumption that the throughput of the interface exceeds that of the air between the interface and infinity. If indeed so, the air adjacent to the liquid would get quickly saturated, making the interfacial flux decrease and adjust to that in the air. In the present paper, the so-called diffuse interface model is used to account for the interfacial physics and, thus, derive a modified version of Maxwell's boundary condition for the near-interface vapor density. It is then applied to a spherical drop floating in air. It turns out that the throughput of the interface exceeds that of air only if the drop's radius is $R \gtrsim 10\mu\text{m}$, but for $R \sim 1\mu\text{m}$, the two are comparable. If $R \lesssim 0.1\mu\text{m}$, evaporation is interface-driven, and the resulting evaporation rate is much smaller than the prediction of the classical model.