

Determination of Wetting Transitions in Binary Mixtures at Three-Phase Coexistence Using the Transition-Matrix Monte Carlo Method and Finite-Size Scaling

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The transition from partial to complete wetting of a surface by a fluid is known as the wetting transition, and is of immense practical importance. While there has been considerable theoretical work on this subject, there has been comparatively less simulation work, due to the computational demands of conventional methods when applied to study this interfacial phenomenon. Here, we demonstrate how the wetting transition at three-phase coexistence can be located efficiently, via simulation, in a straightforward manner.

To this end, we use the combination of the grand-canonical transition-matrix Monte Carlo (TMMC) method and finite-size scaling [1-6]. The former is used to calculate precisely the free energy barrier (apparent interfacial tension) between phases at three-phase coexistence as a function of system size. Finite-size scaling is subsequently used to extrapolate the apparent interfacial tensions to their thermodynamic limits. It can be shown from thermodynamic arguments [7] that the relative magnitudes of the interfacial tensions, as embodied in a spreading coefficient, determine whether partial or complete wetting occurs.

To illustrate the methodology, we determine the wetting temperature for a series of binary Lennard-Jones mixtures with varying degrees of miscibility at three-phase coexistence involving two liquids and a vapor. In particular, we focus on the wetting of the two liquids by the vapor. While we focus on simple fluid mixtures in this work, the methodology is completely general, and can be applied to more complex fluids.

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