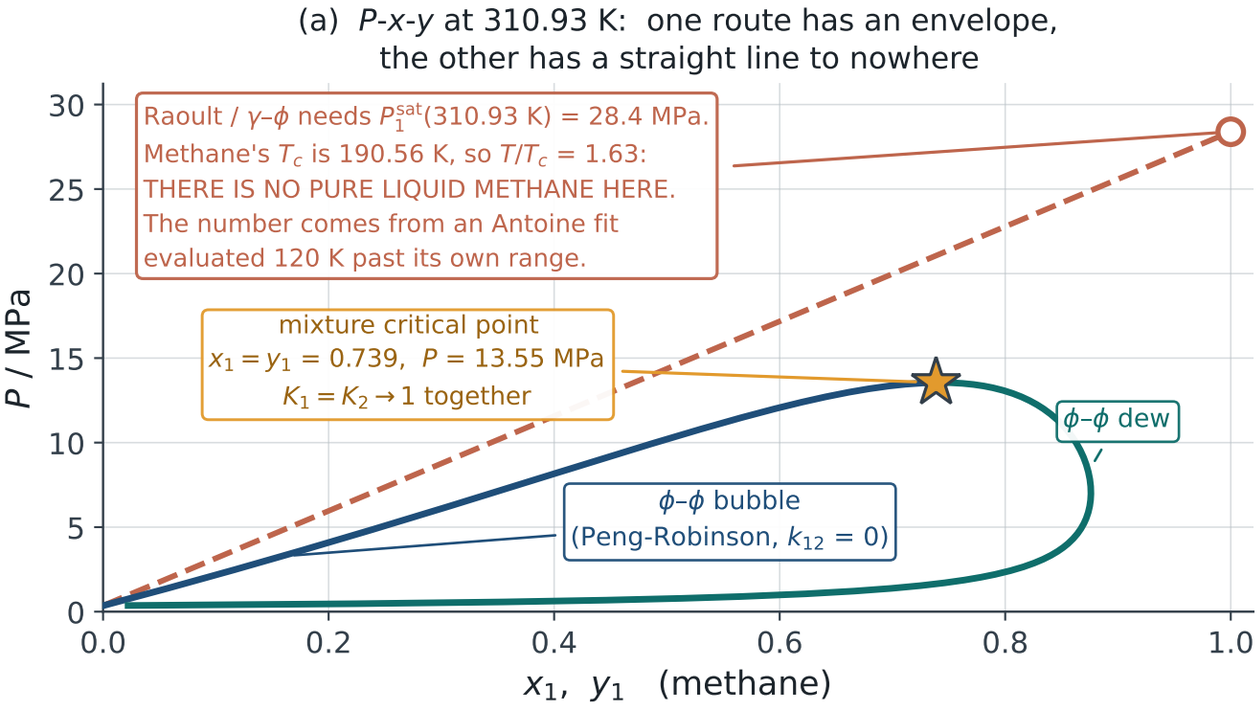
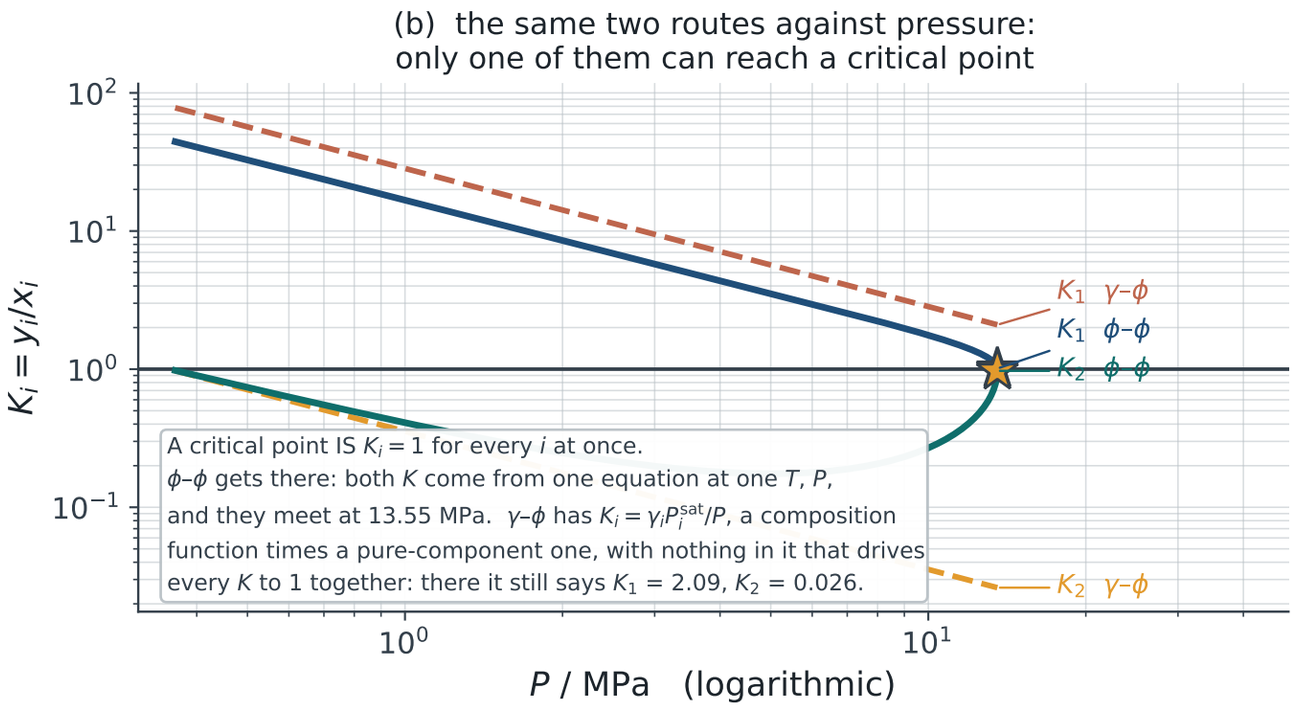
Where the activity-coefficient route stops working: γ–ϕ needs a pure-liquid reference fugacity, and sometimes there is not one





methane (1) + n-butane (2) at 310.93 K. BOTH CURVES ARE CALCULATIONS; no measurement is claimed and none is needed for the point. Peng-Robinson, 1976 alpha function, k_{12} = 0, with T_c, P_c and ω from Poling, Prausnitz & O'Connell as stored in vlekit.data.LIBRARY; the Raoult line uses the Antoine constants from the same table.

The bubble branch is marched with each point warm-starting the next and stops where $y_1 - x_1$ collapses, which is the numerical signature of the mixture critical point: 249 converged points, last at x_1 = 0.7387, P = 13.551 MPa. Raoult's law overstates the bubble pressure by 1 to 55 per cent across the range where the equation of state has an answer at all.

n-butane is subcritical here and does have a reference state: P_2^{sat} = 354.8 kPa from Antoine, 355.0 kPa from the same Peng-Robinson equation (-0.1 per cent) — the disagreement between the two descriptions of the ONE component that has a liquid, for scale.