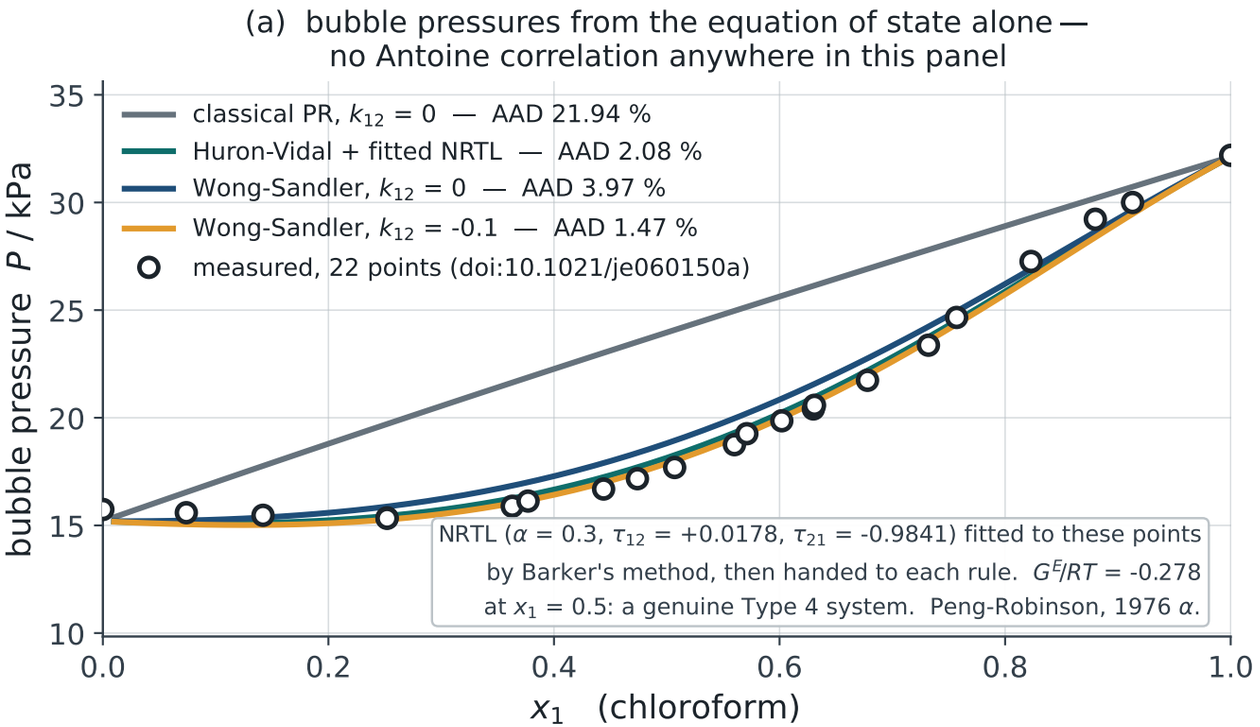
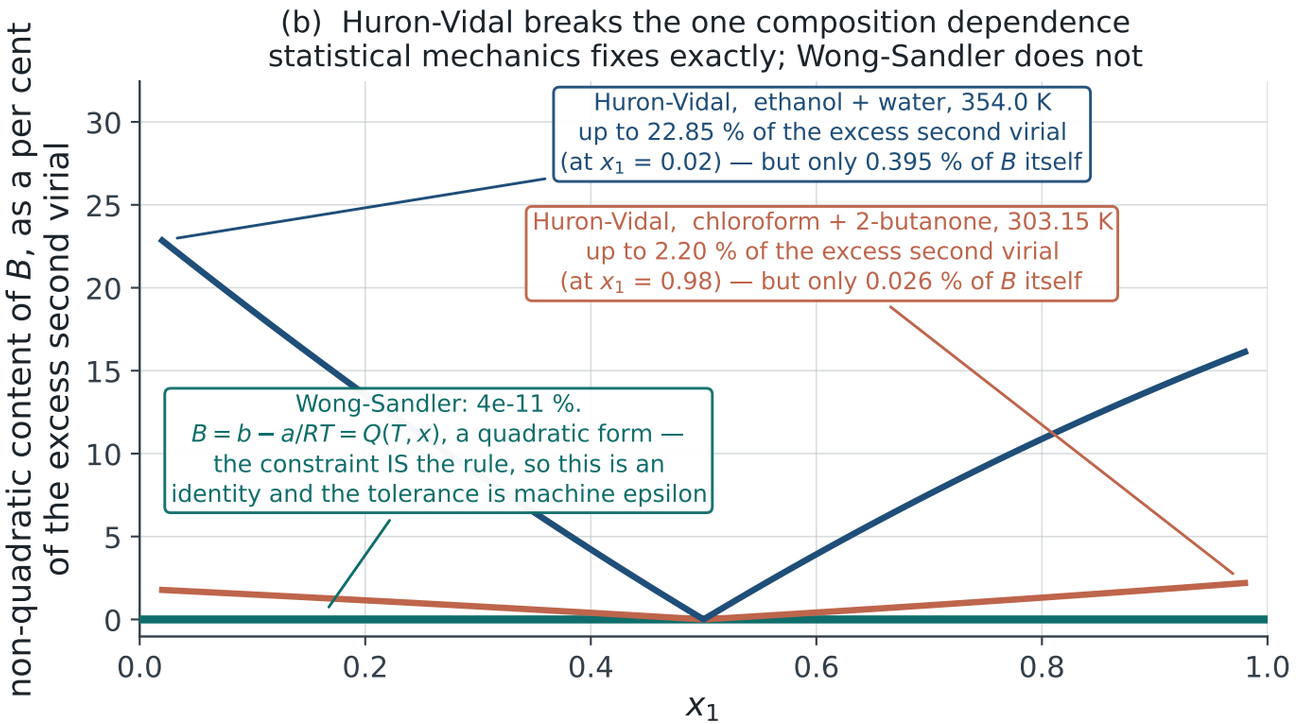
Two ways to put an activity model inside a cubic — and the low-density identity that separates them





chloroform (1) + 2-butanone (2) at 303.15 K, 22 points, doi:10.1021/je060150a. NRTL fitted to P and x_1 only (Barker), then used ONLY as the G^E input to the mixing rule; the bubble points are solved from Peng-Robinson alone by successive substitution (gemix.bubble_P), warm-started from the rule's own activity model. T_c, P_c, ω from vlekit.data.LIBRARY.

AAD over the 22 points: classical PR, k12 = 0 21.94 %, Huron-Vidal + fitted NRTL 2.08 %, Wong-Sandler, k12 = 0 3.97 %, Wong-Sandler, k12 = -0.1 1.47 %. The pure-component vapour pressures the equation of state predicts are themselves off by -0.2 % (chloroform) and -3.5 % (2-butanone) against the measured end points, so a couple of per cent is the floor here, not a failure.

In panel (b) the reference quadratic is built from the rule's own B_{11}, B_{22} and from B_{12} read off the rule at $x_1 = 1/2$, so it agrees with the rule at three compositions by construction and every departure elsewhere is genuine non-quadratic content. Both denominators are shown because only one of them is informative. The residual is exactly zero at x_1 = 0, 1/2 and 1 and grows towards the dilute ends, where the excess second virial itself is going to zero, so the sweep is quoted over x_1 = 0.02-0.98 and the composition of the peak is stated with it.