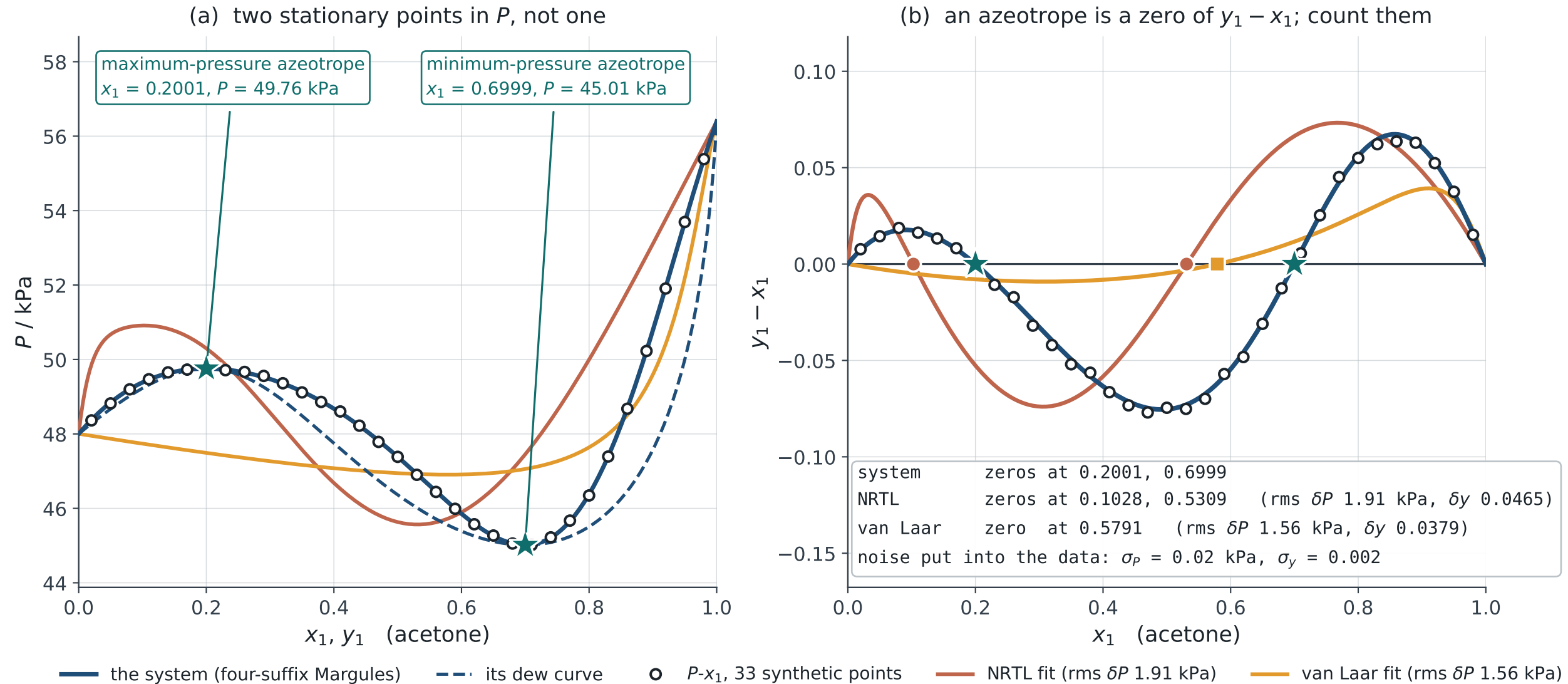


Neither two-parameter fit reproduces the double azeotrope — and one of them cannot, whatever its parameters



ILLUSTRATIVE SYSTEM: four-suffix Margules $A = -0.42$, $B = -0.93$, $C = -0.32$ for acetone (1) / chloroform (2) at 313.15 K, constructed to place two azeotropes inside the range. Not fitted to measured VLE; the Antoine constants are vlekitt's.

Honest small print, every number computed in this script.

van Laar cannot give two interior azeotropes for any same-sign A , B : that is algebra, and the scan here finds at most 1 interior zero.

NRTL can — 1564 of 25921 pairs on a 161×161 grid over $\tau \in [-8, 8]$ give two — but the best of those 1564 still leaves rms $\delta P = 1.96$ kPa.

The three-suffix Margules, also two-parameter, keeps two zeros (0.1669, 0.6628) yet misplaces both, at rms $\delta P = 0.51$ kPa. Refitting the generating form recovers (0.1999, 0.6999) at rms $\delta P = 0.017$ kPa.

It is the shape of G^E that decides, not the number of parameters.