Solving the phase boundary between two solid phases via the common tangent procedure

David C. de Busturia

Department of Chemistry. Imperial College London

Saturday 9th June, 2018

Outline

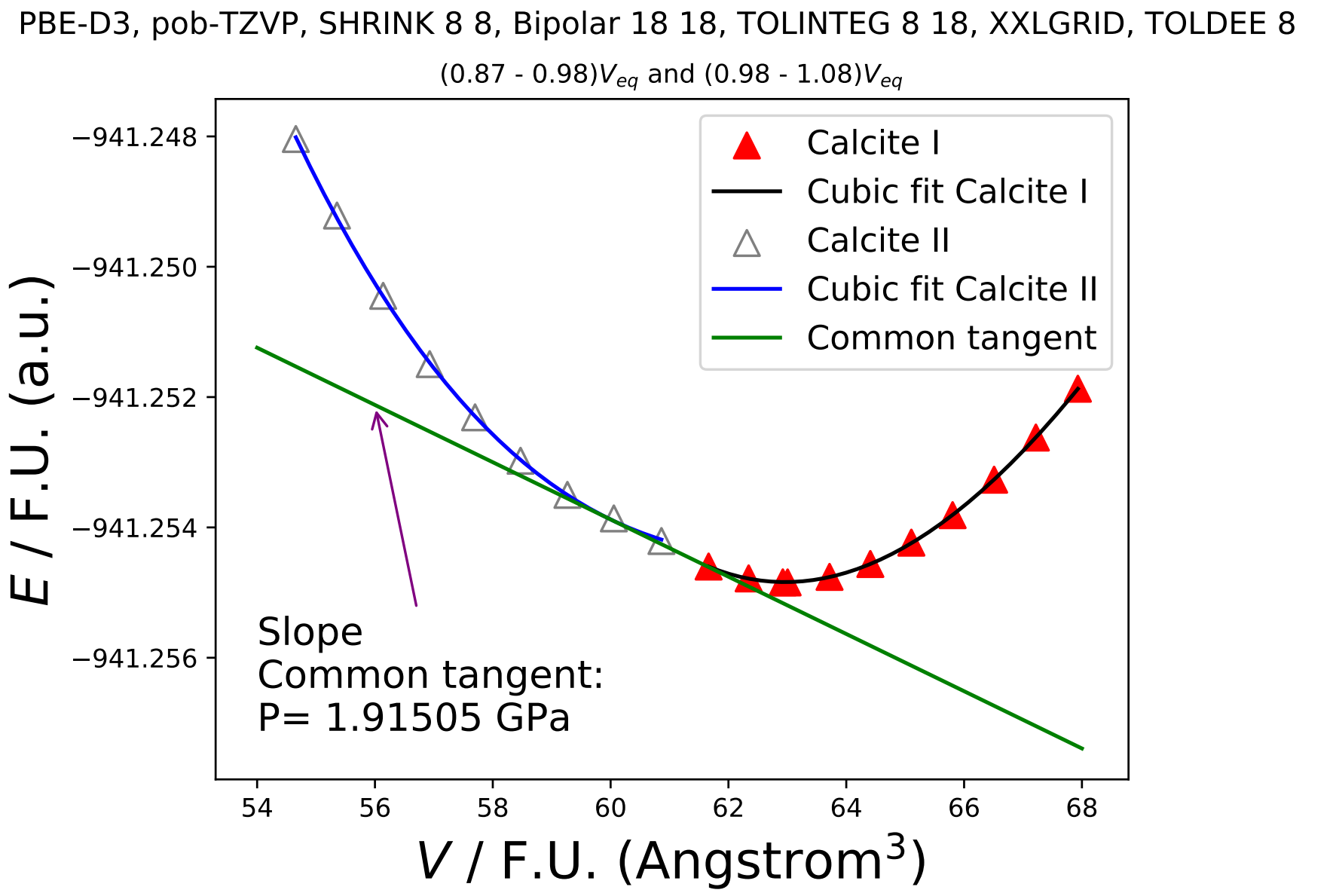
$E(V)$, $E(V) + E_{ZP}$, $F(V;T)$ and pressure of transition. Thermal evolution

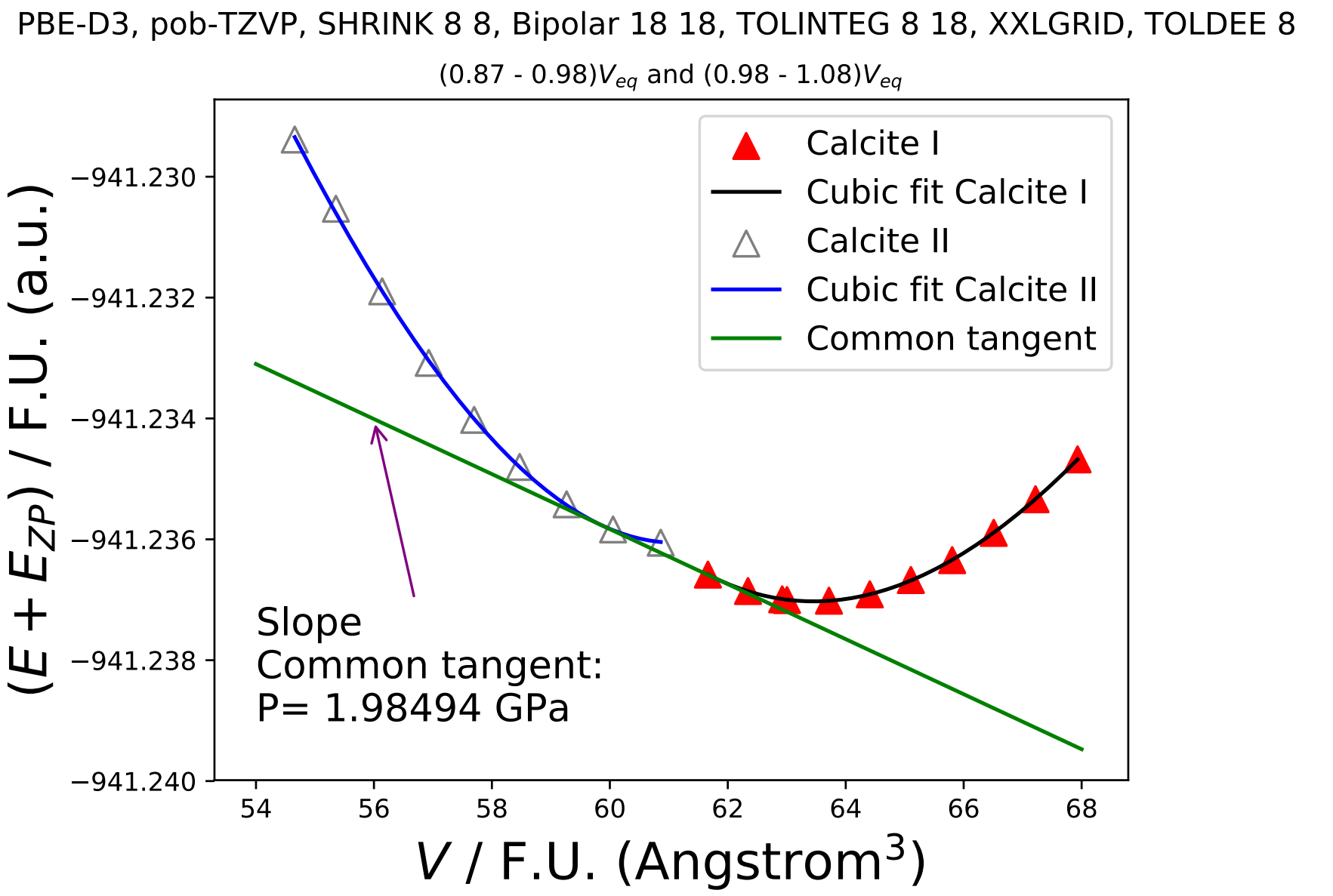
Phase Boundary

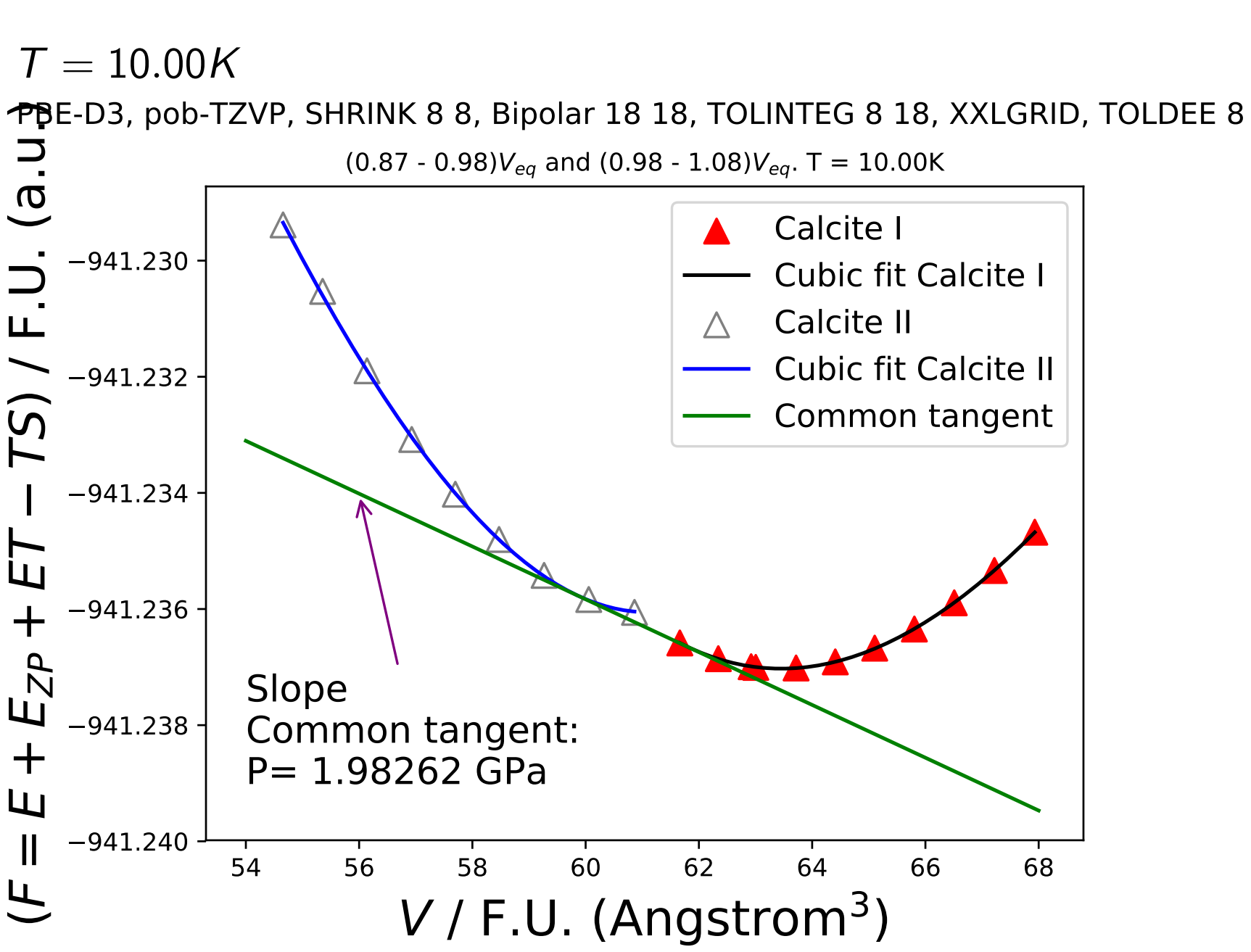
Outline I

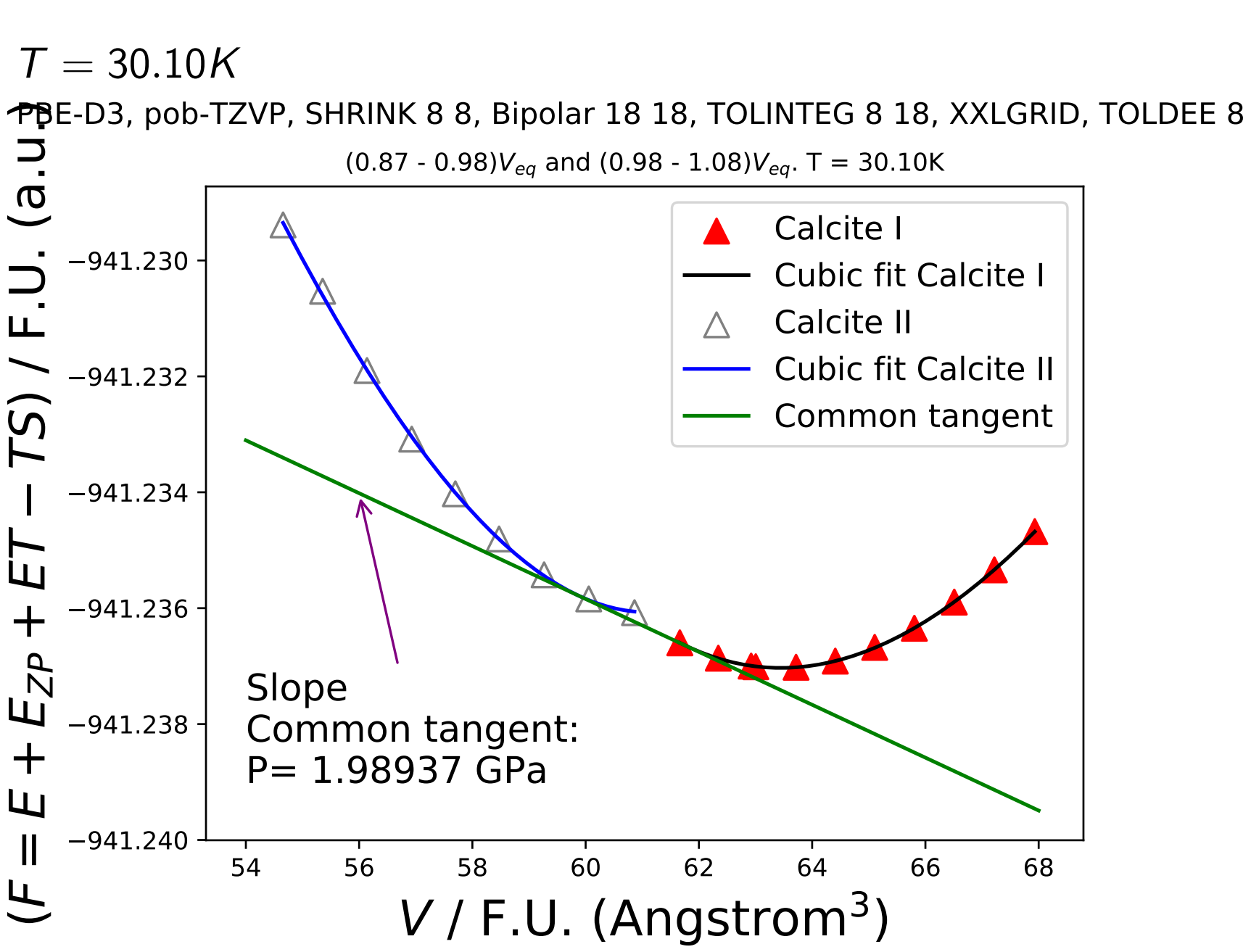
$E(V)$, $E(V) + E_{ZP}$, $F(V;T)$ and pressure of transition. Thermal evolution

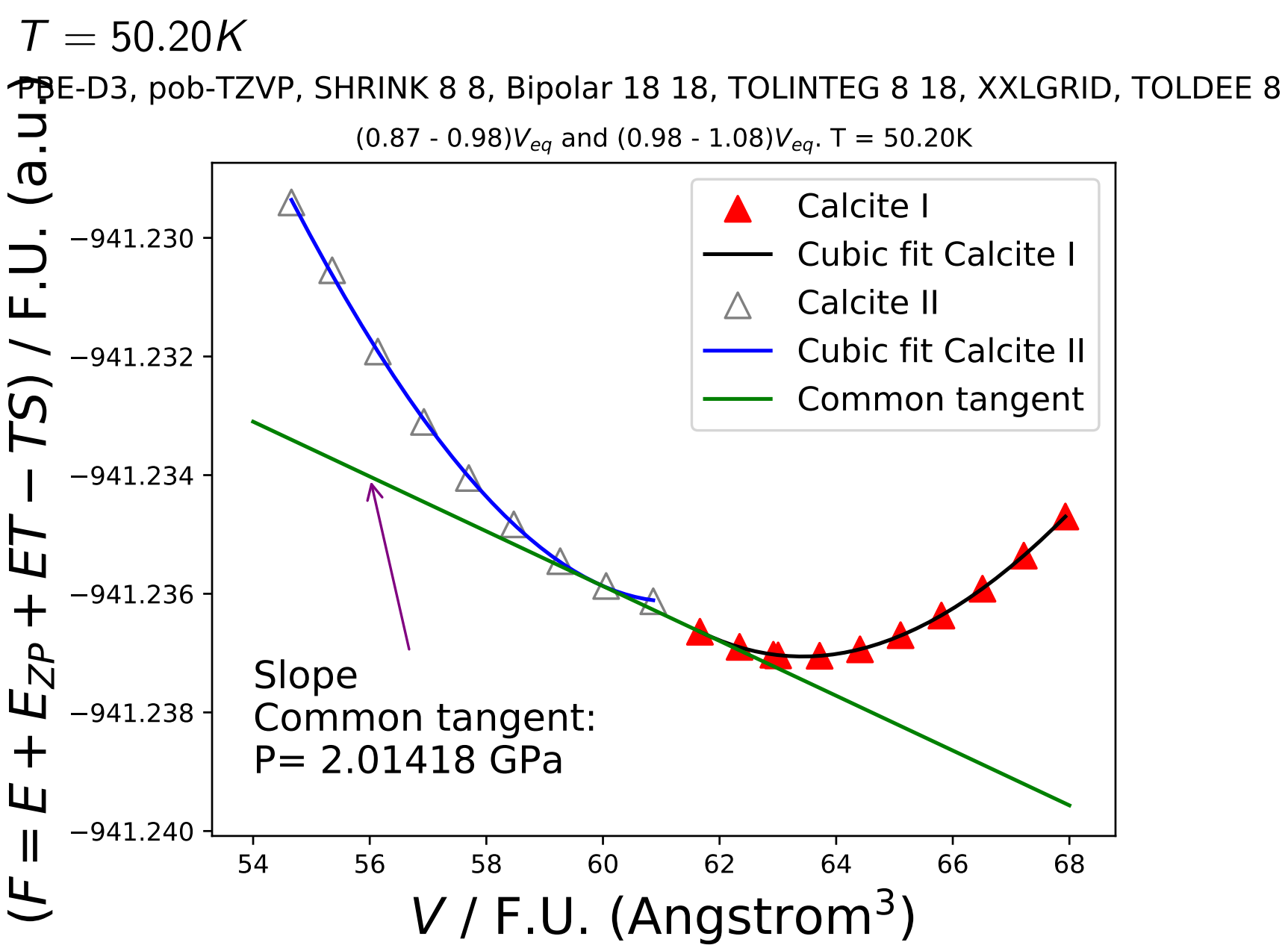
Phase Boundary

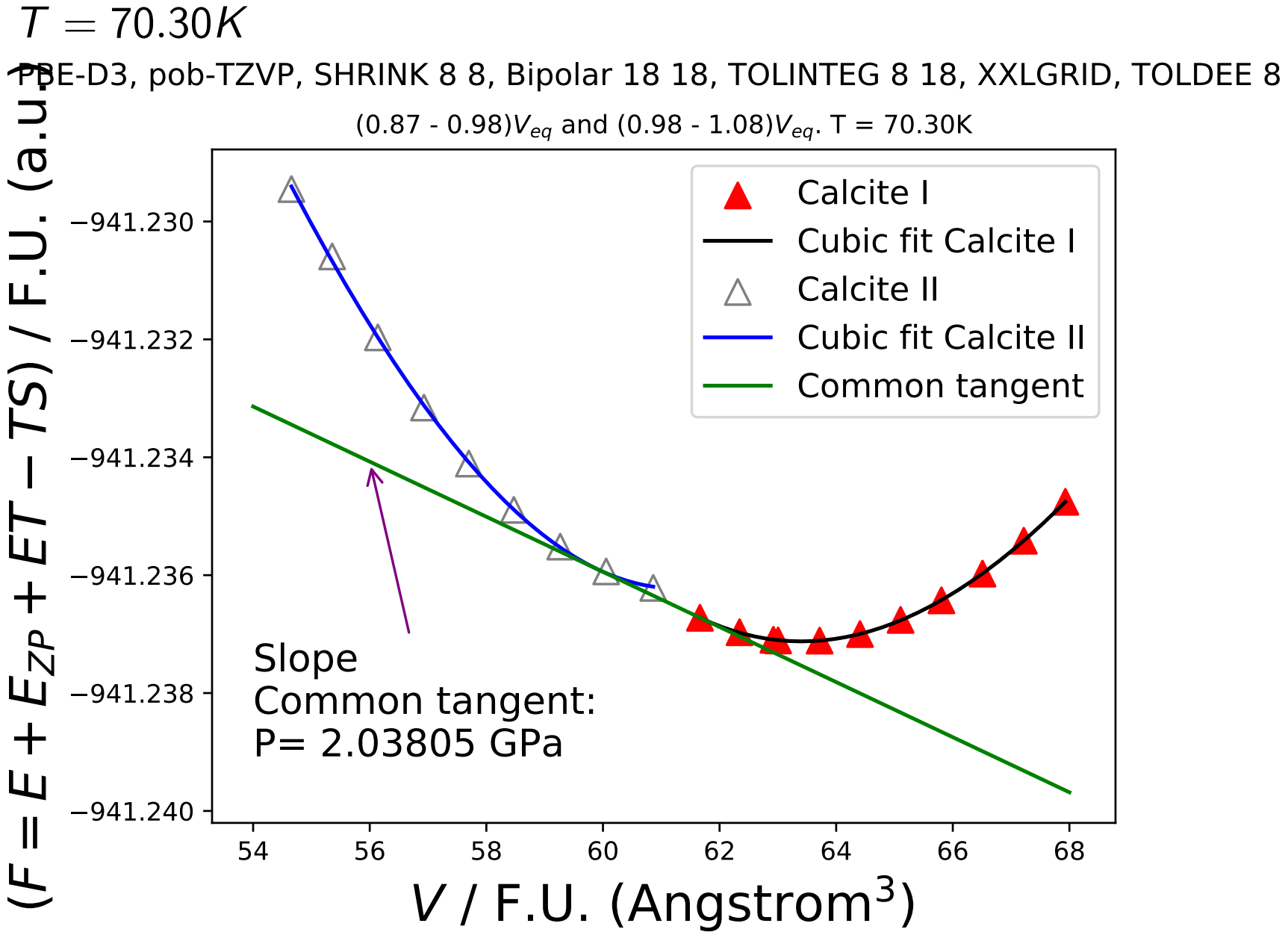

PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}
Calcite I
Cubic fit Calcite I
Calcite II
Cubic fit Calcite II
Common tangent
Slope
Common tangent:
P= 1.91505 GPa
−941.248
−941.250
−941.252
−941.254
−941.256
54
56
58
60
62
64
66
68
E / F.U. (a.u.)
V / F.U. (Angstrom^3)

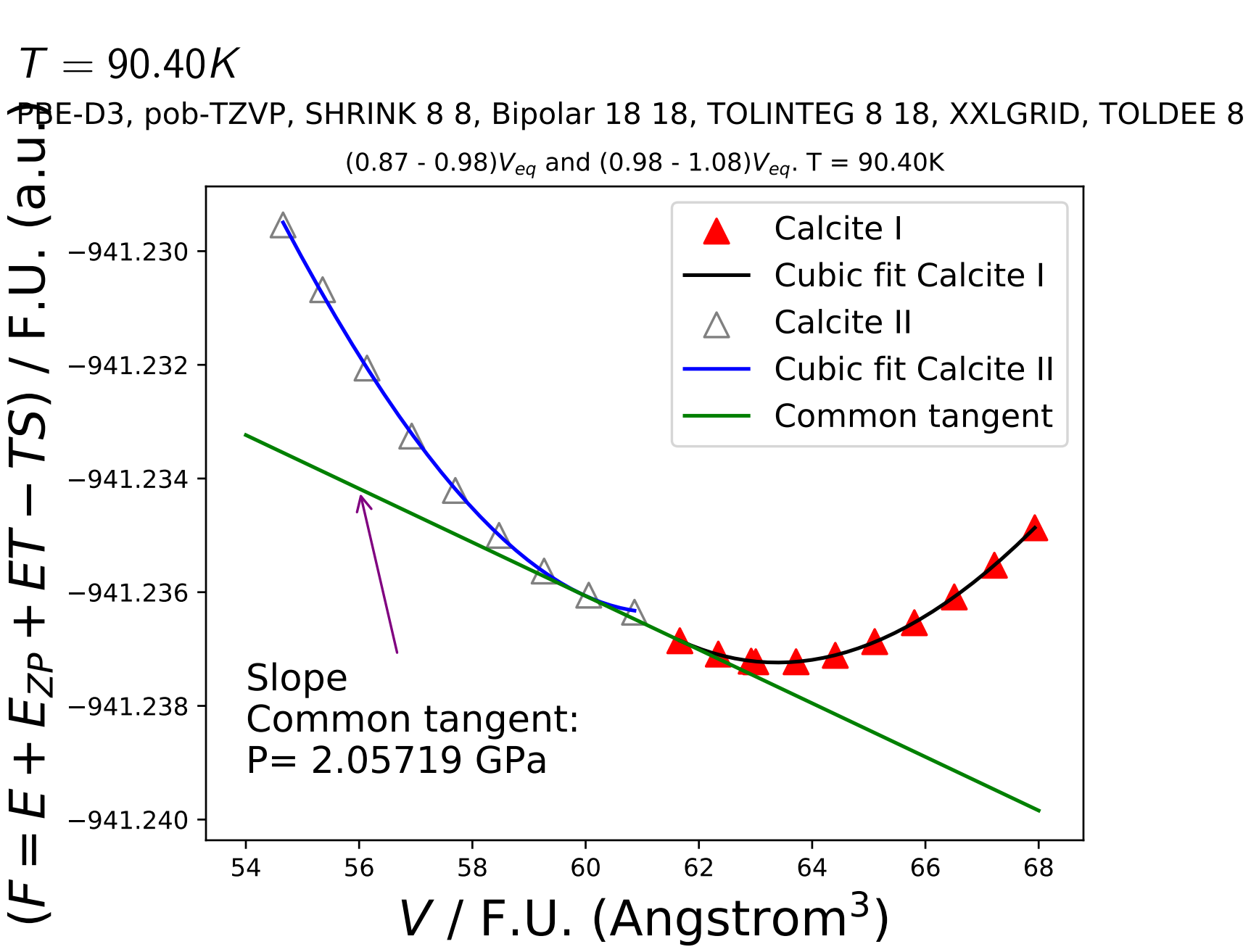

PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}
Calcite I
Cubic fit Calcite I
Calcite II
Cubic fit Calcite II
Common tangent
Slope
Common tangent:
P= 1.98494 GPa
$(E + E_{ZP})$ / F.U. (a.u.)
−941.230
−941.232
−941.234
−941.236
−941.238
−941.240
54
56
58
60
62
64
66
68
V / F.U. (Angstrom^3)

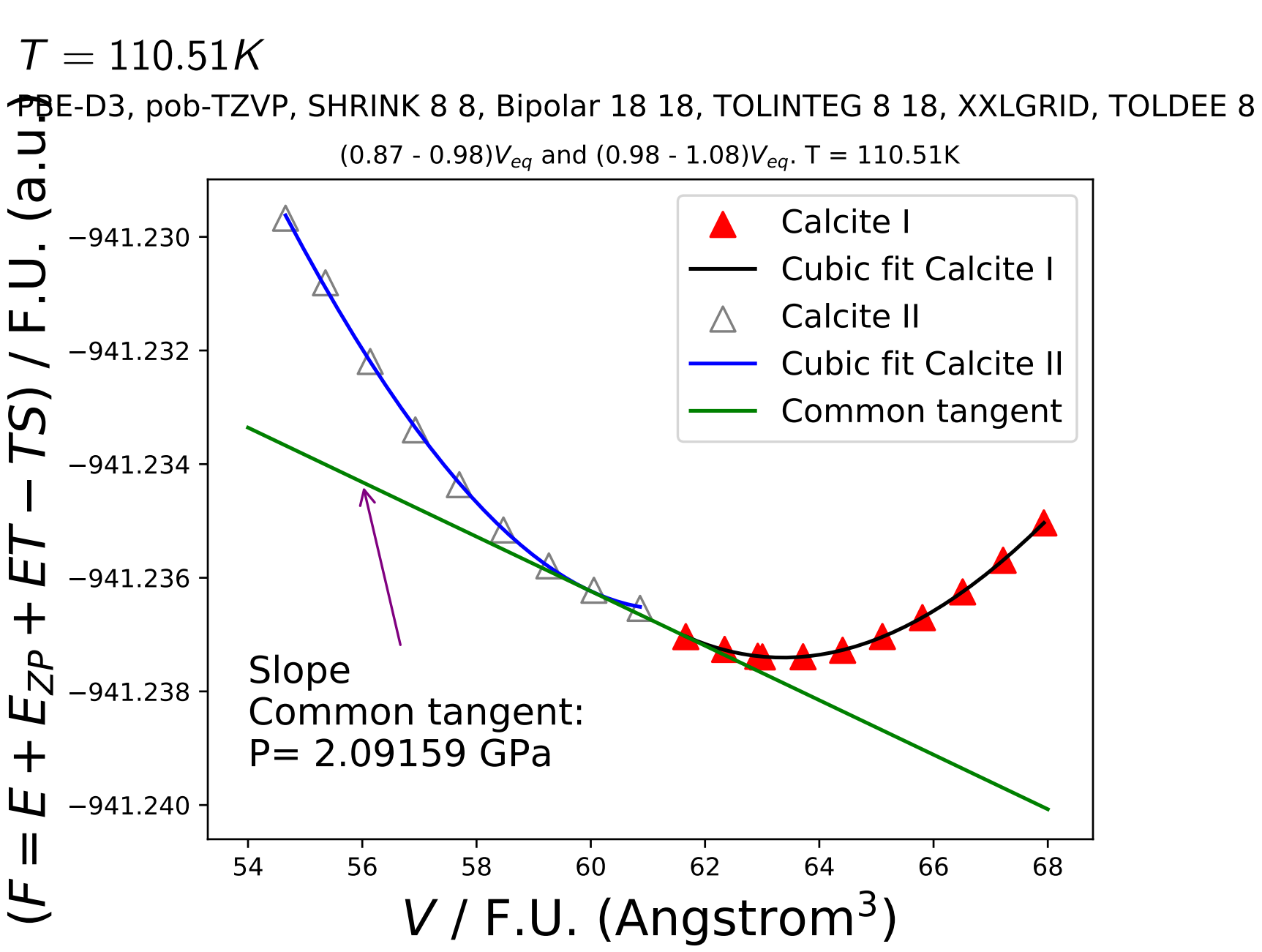

$T = 10.00K$
PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}. T = 10.00K
$(F = E + E_{ZP} + ET - TS)$ / F.U. (a.u.)
−941.230
−941.232
−941.234
−941.236
−941.238
−941.240
54
56
58
60
62
64
66
68
V / F.U. (Angstrom^3)
Calcite I
Cubic fit Calcite I
Calcite II
Cubic fit Calcite II
Common tangent
Slope
Common tangent:
P= 1.98262 GPa

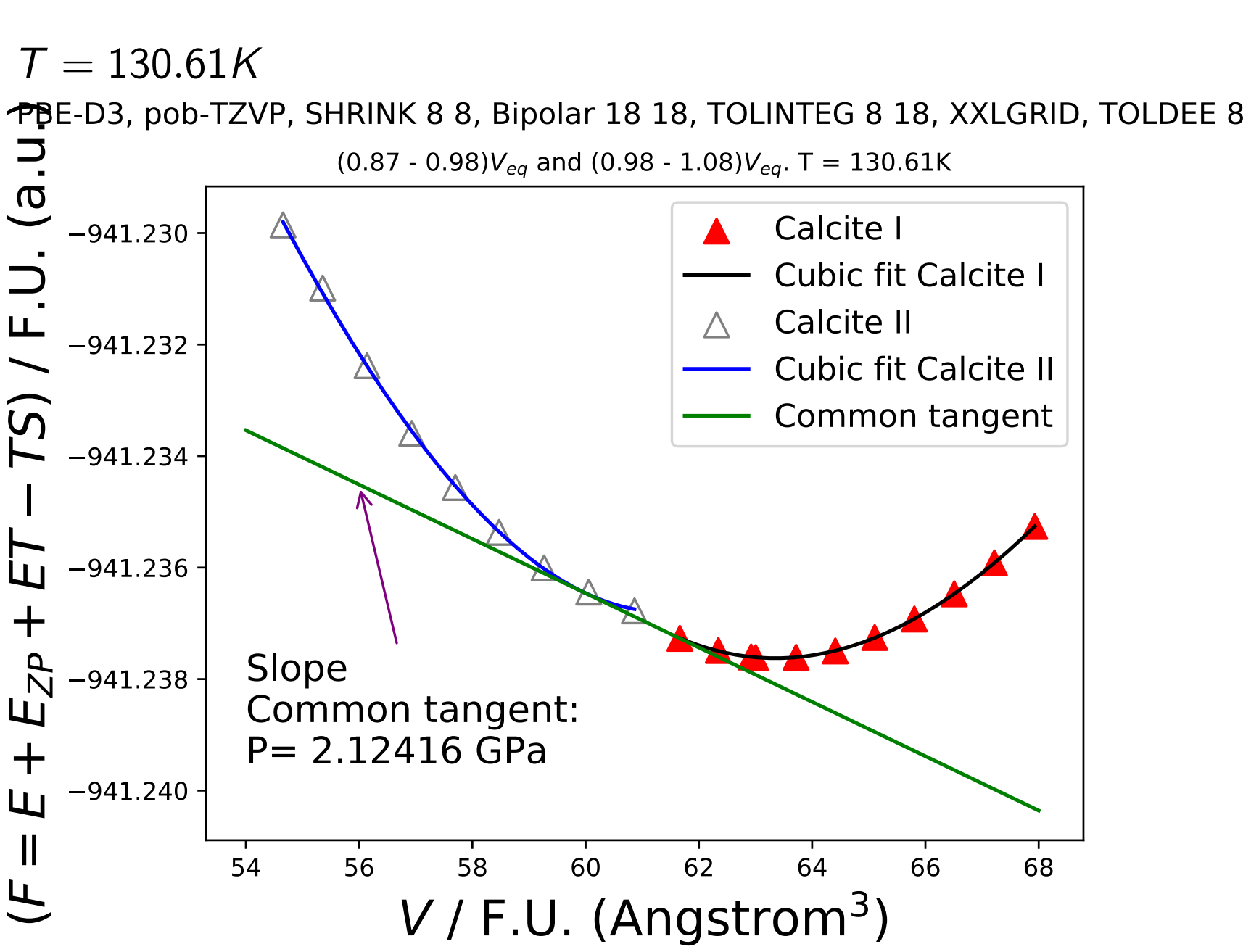

$T = 30.10K$
PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}. T = 30.10K
Calcite I
Cubic fit Calcite I
Calcite II
Cubic fit Calcite II
Common tangent
Slope
Common tangent:
P= 1.98937 GPa
$(F = E + E_{ZP} + ET - TS)$ / F.U. (a.u.)
V / F.U. (Angstrom^3)
−941.230
−941.232
−941.234
−941.236
−941.238
−941.240
54
56
58
60
62
64
66
68

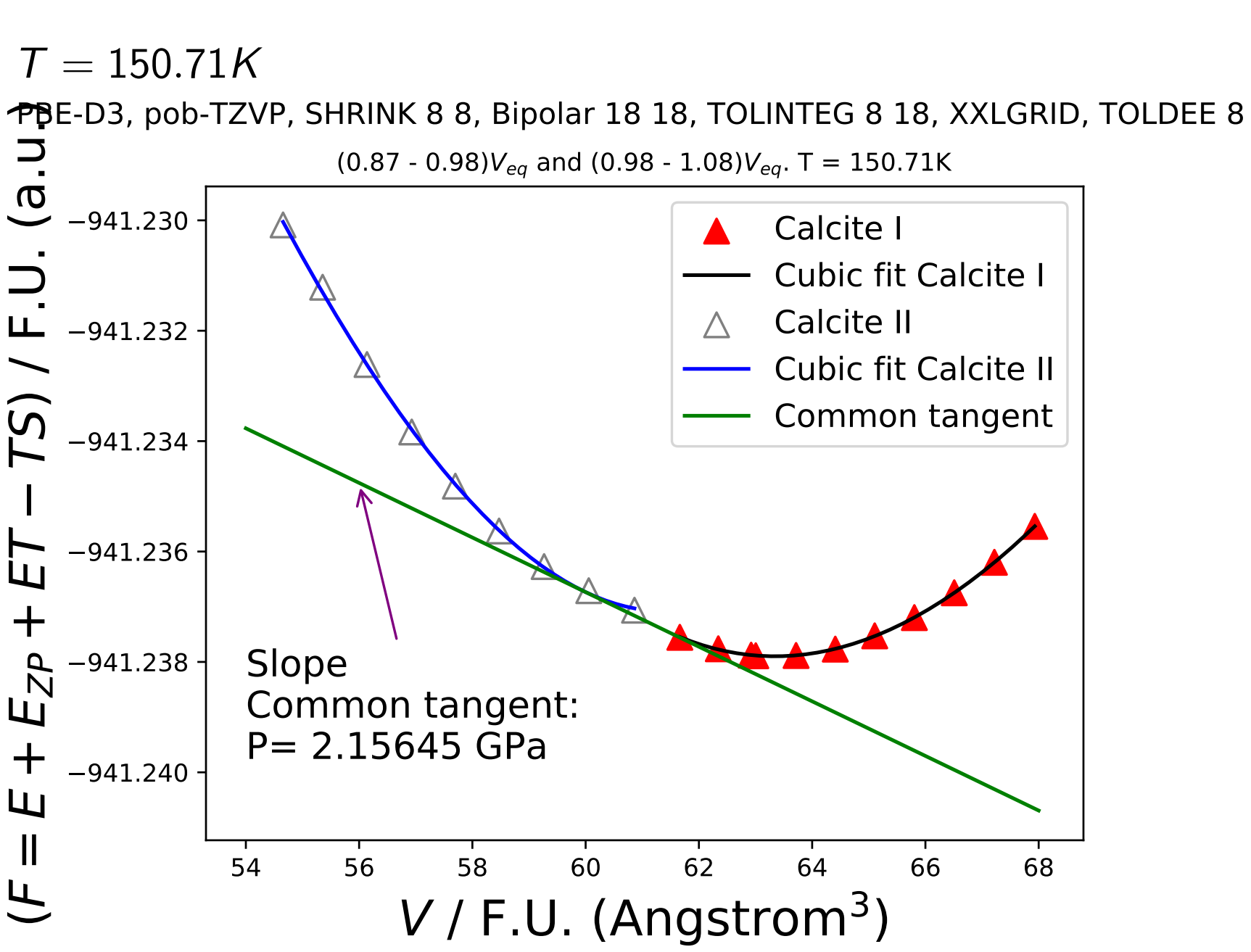

$T = 50.20K$
PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}. T = 50.20K
Calcite I
Cubic fit Calcite I
Calcite II
Cubic fit Calcite II
Common tangent
Slope
Common tangent:
P= 2.01418 GPa
−941.230
−941.232
−941.234
−941.236
−941.238
−941.240
54
56
58
60
62
64
66
68
$(F = E + E_{ZP} + ET - TS)$ / F.U. (a.u.)
V / F.U. (Angstrom^3)


$T = 70.30K$
PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}. T = 70.30K
Calcite I
Cubic fit Calcite I
Calcite II
Cubic fit Calcite II
Common tangent
Slope
Common tangent:
P= 2.03805 GPa
$(F = E + E_{ZP} + ET - TS)$ / F.U. (a.u.)
V / F.U. (Angstrom^3)
−941.230
−941.232
−941.234
−941.236
−941.238
−941.240
54
56
58
60
62
64
66
68


$T = 90.40K$
PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}. T = 90.40K
Calcite I
Cubic fit Calcite I
Calcite II
Cubic fit Calcite II
Common tangent
Slope
Common tangent:
P= 2.05719 GPa
$(F = E + E_{ZP} + ET - TS)$ / F.U. (a.u.)
V / F.U. (Angstrom^3)
−941.230
−941.232
−941.234
−941.236
−941.238
−941.240
54
56
58
60
62
64
66
68


$T = 110.51K$
PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}. T = 110.51K
$(F = E + E_{ZP} + ET - TS)$ / F.U. (a.u.)
−941.230
−941.232
−941.234
−941.236
−941.238
−941.240
54
56
58
60
62
64
66
68
V / F.U. (Angstrom^3)
Calcite I
Cubic fit Calcite I
Calcite II
Cubic fit Calcite II
Common tangent
Slope
Common tangent:
P= 2.09159 GPa

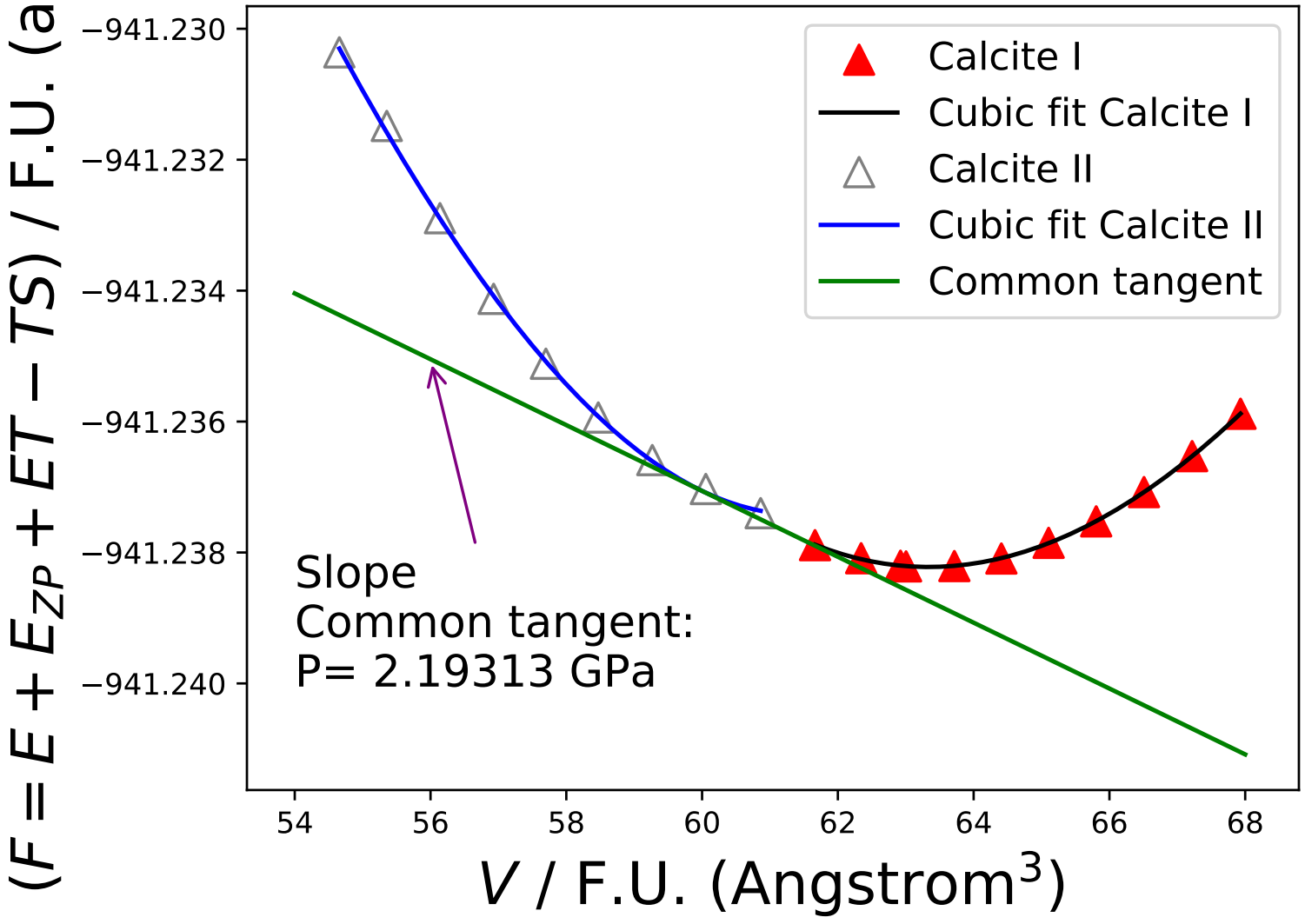

$T = 130.61K$
PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}. T = 130.61K
$(F = E + E_{ZP} + ET - TS)$ / F.U. (a.u.)
−941.230
−941.232
−941.234
−941.236
−941.238
−941.240
54
56
58
60
62
64
66
68
V / F.U. (Angstrom^3)
Calcite I
Cubic fit Calcite I
Calcite II
Cubic fit Calcite II
Common tangent
Slope
Common tangent:
P= 2.12416 GPa


$T = 150.71K$
PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}. T = 150.71K
$(F = E + E_{ZP} + ET - TS)$ / F.U. (a.u.)
−941.230
−941.232
−941.234
−941.236
−941.238
−941.240
54
56
58
60
62
64
66
68
V / F.U. (Angstrom^3)
Calcite I
Cubic fit Calcite I
Calcite II
Cubic fit Calcite II
Common tangent
Slope
Common tangent:
P= 2.15645 GPa

$T = 170.81K$

PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8

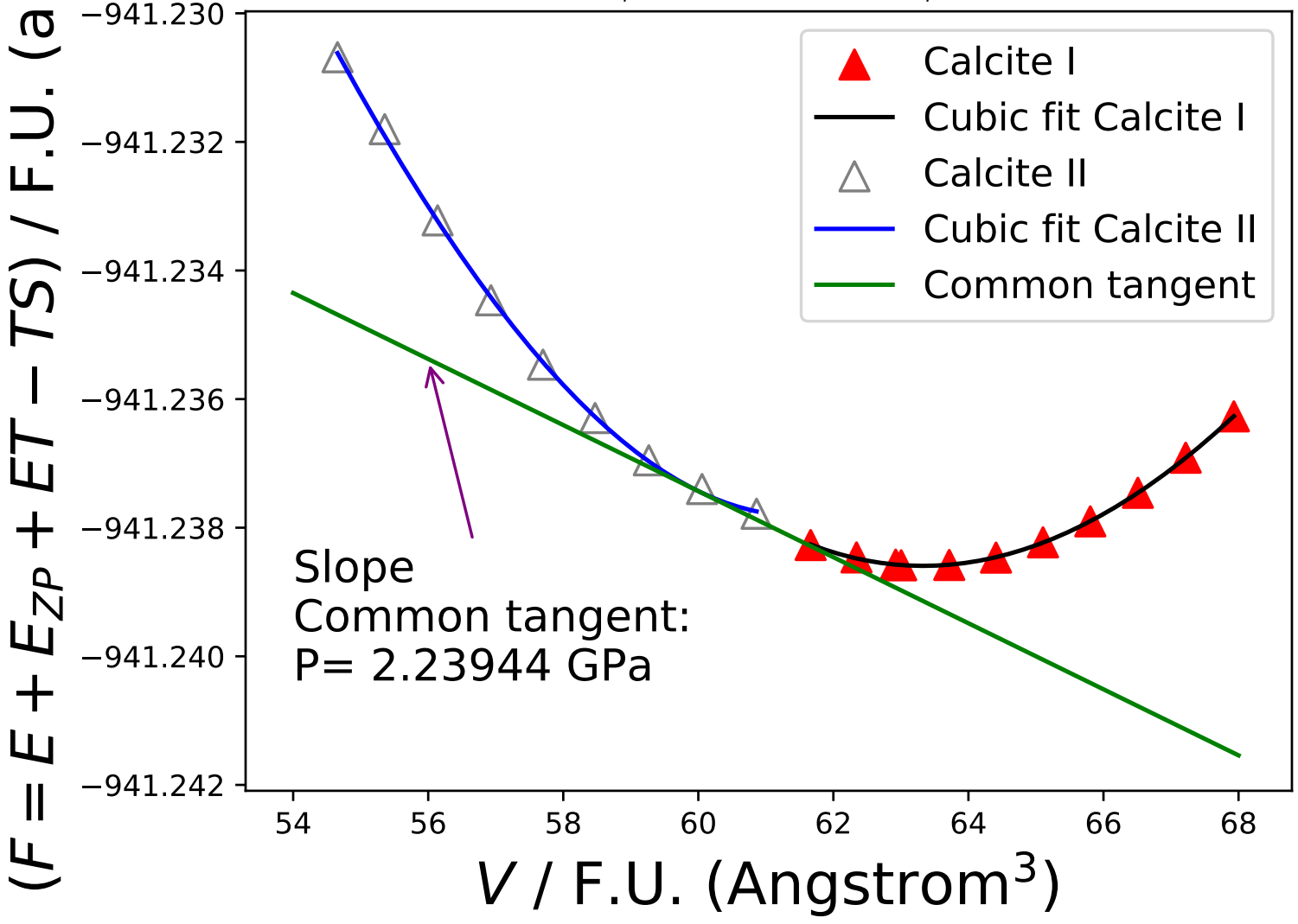
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}. T = 170.81K

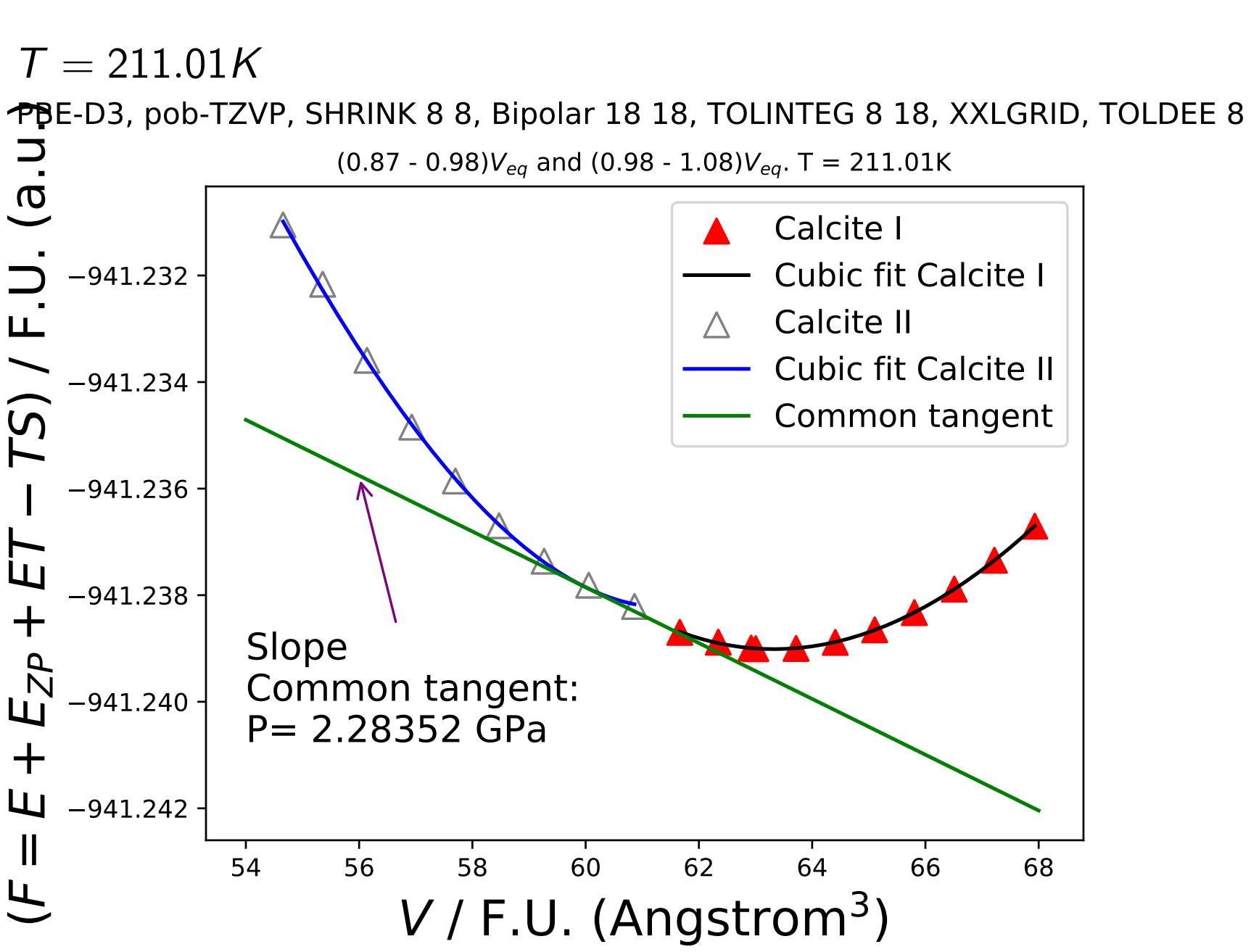


$T = 190.91K$

PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8

(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}. T = 190.91K

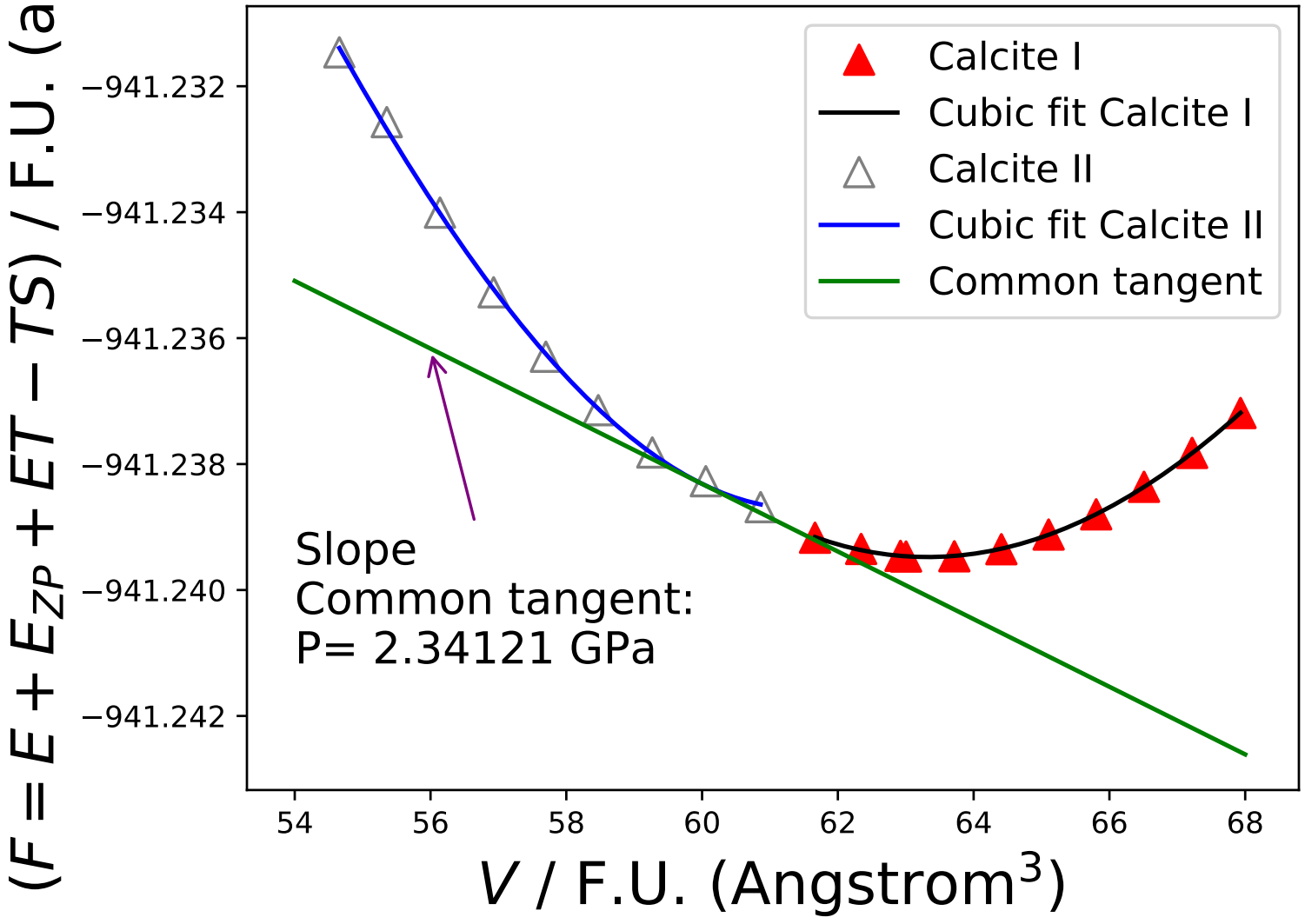



$T = 211.01K$
PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}. T = 211.01K
Calcite I
Cubic fit Calcite I
Calcite II
Cubic fit Calcite II
Common tangent
Slope
Common tangent:
P= 2.28352 GPa
−941.232
−941.234
−941.236
−941.238
−941.240
−941.242
54
56
58
60
62
64
66
68
$(F = E + E_{ZP} + ET - TS)$ / F.U. (a.u.)
V / F.U. (Angstrom^3)

$T = 231.11K$

PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8

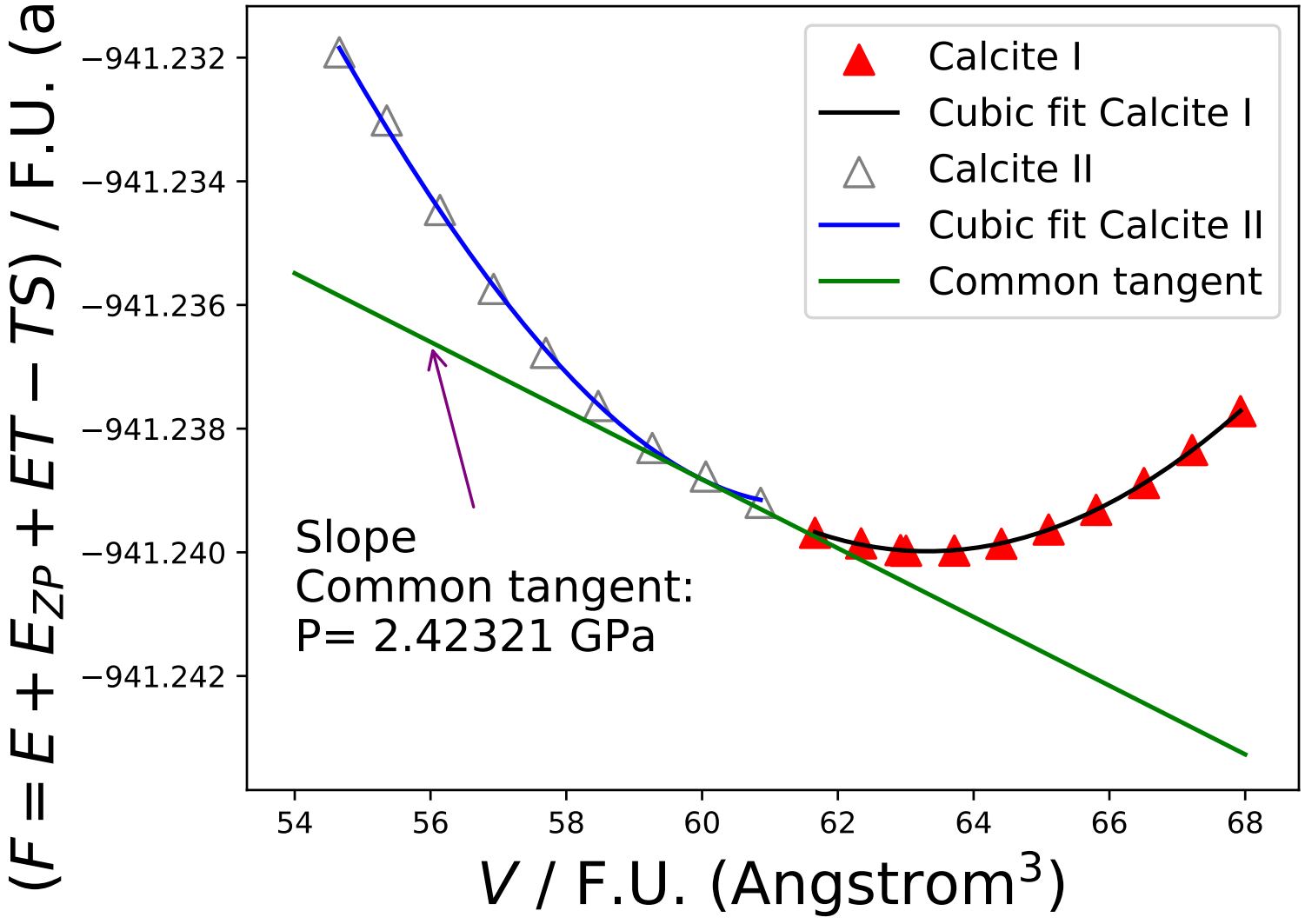
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}. T = 231.11K

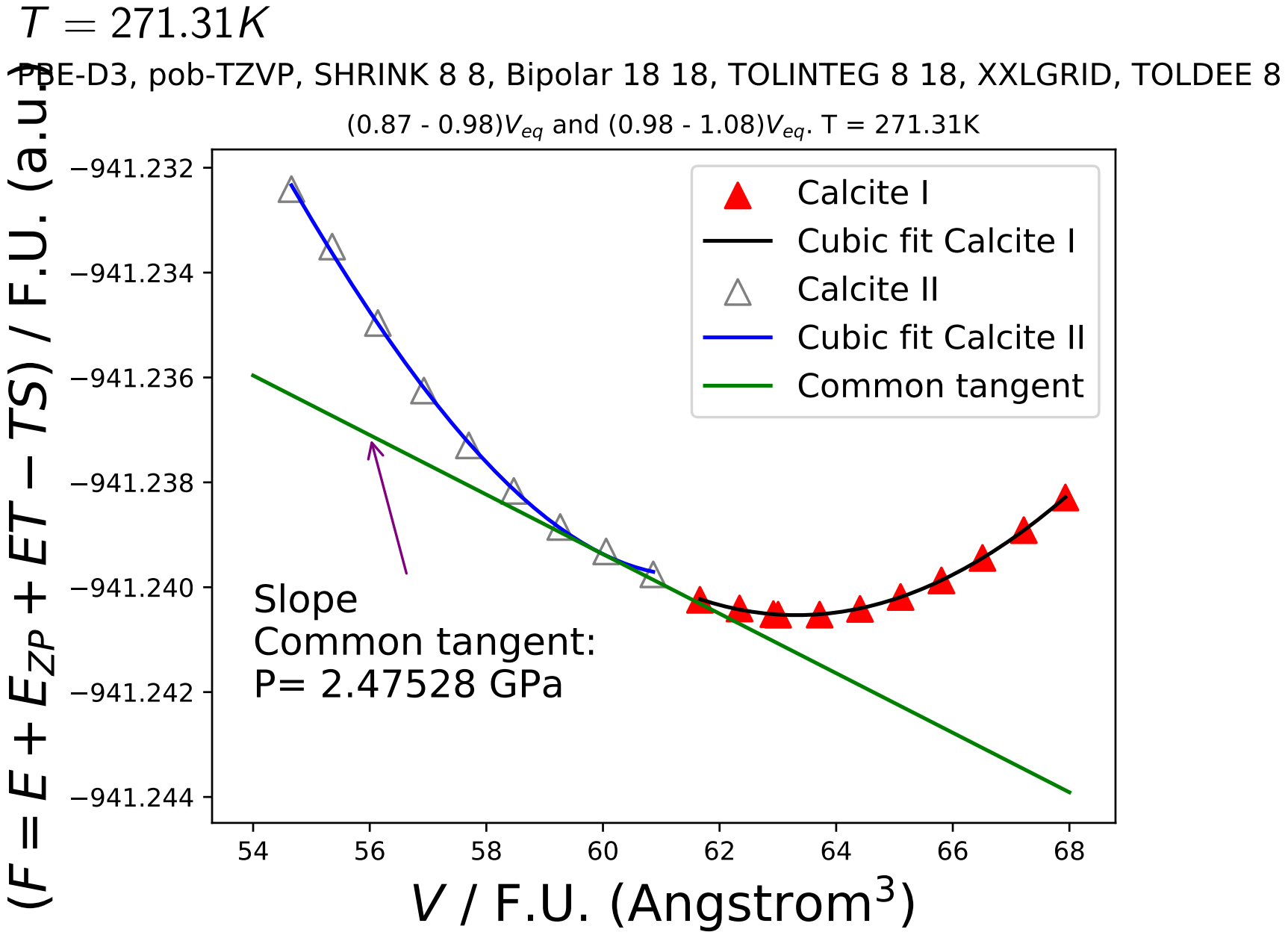


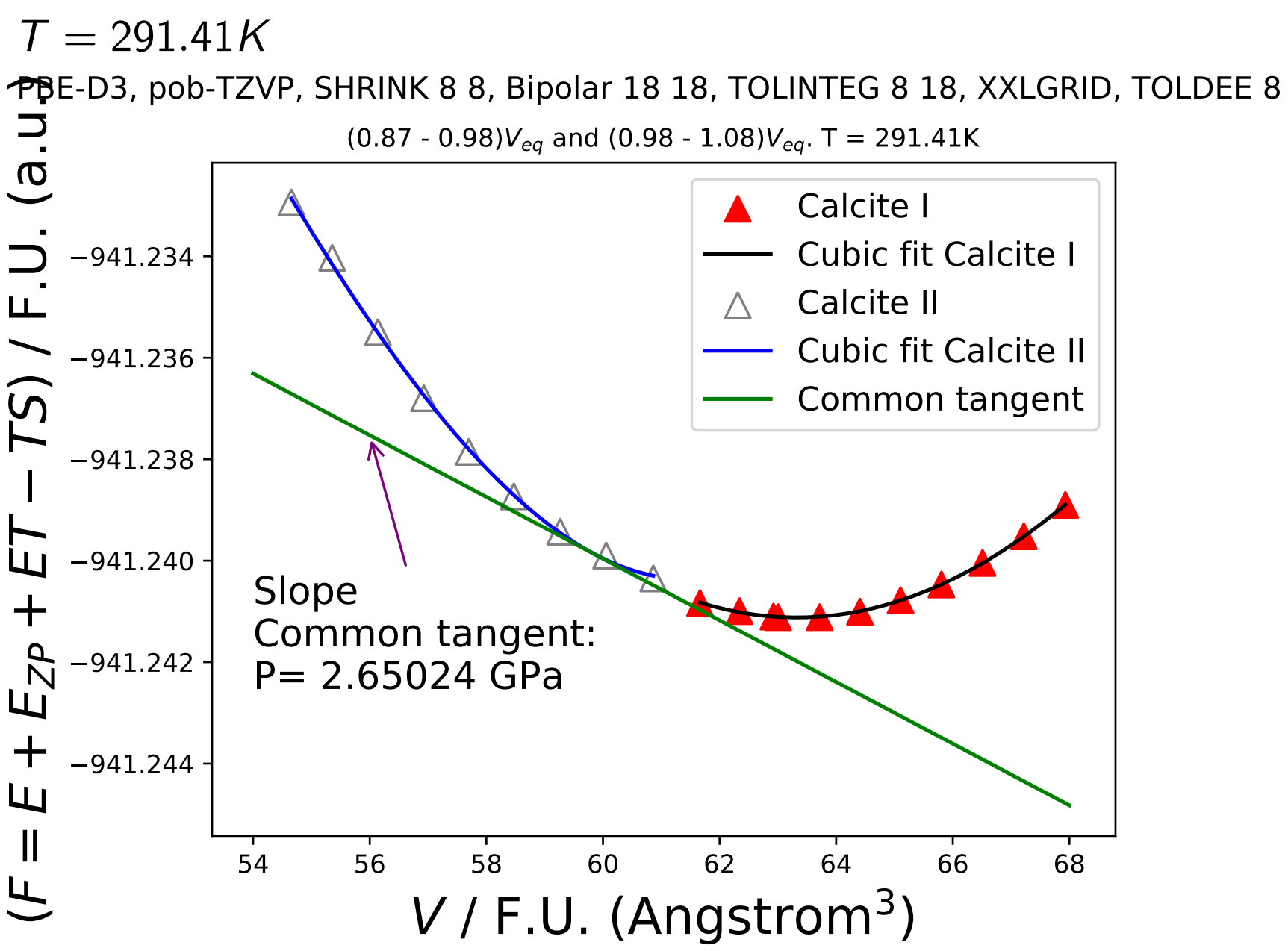
$T = 251.21K$

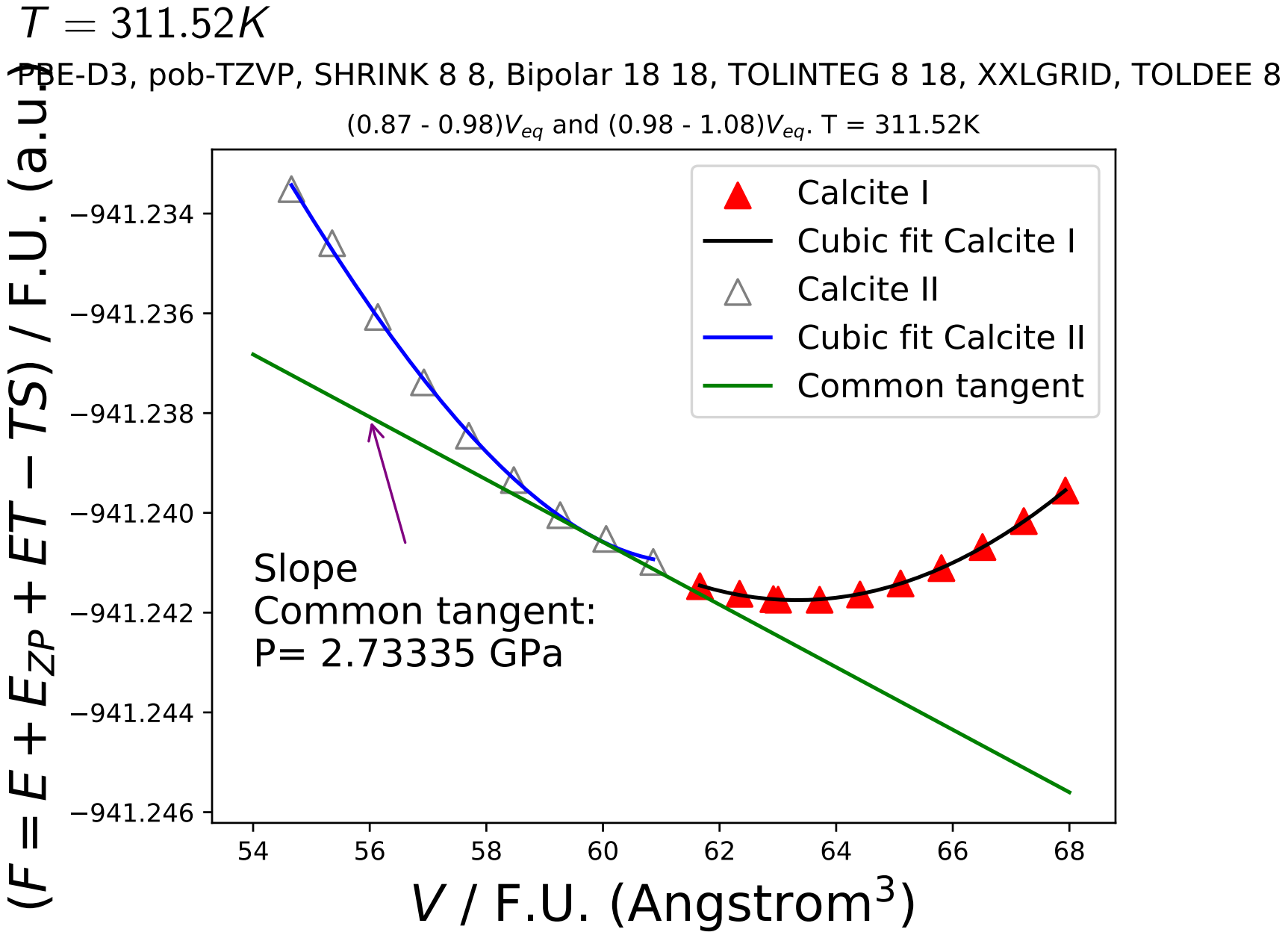
PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8

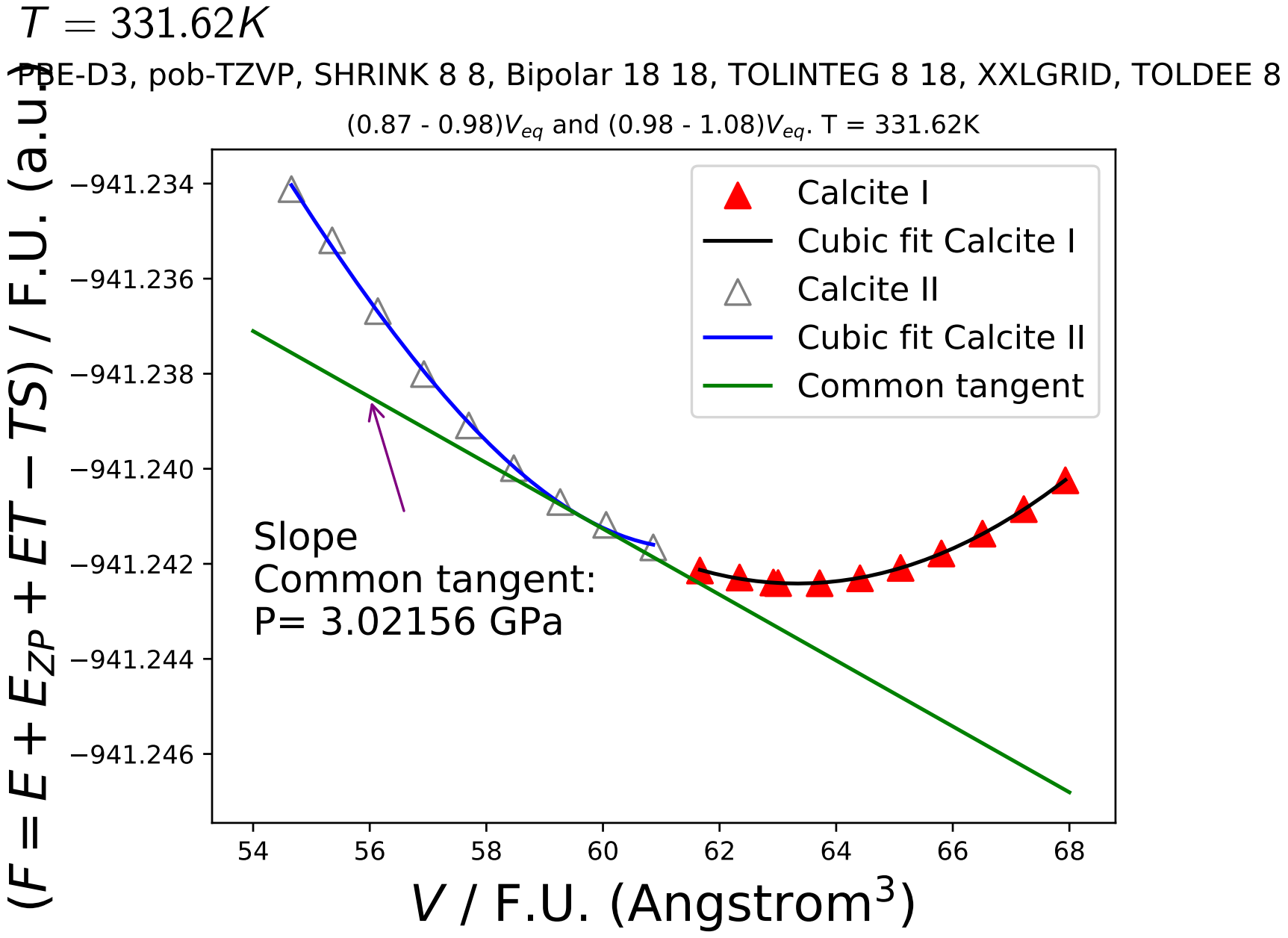
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}. T = 251.21K

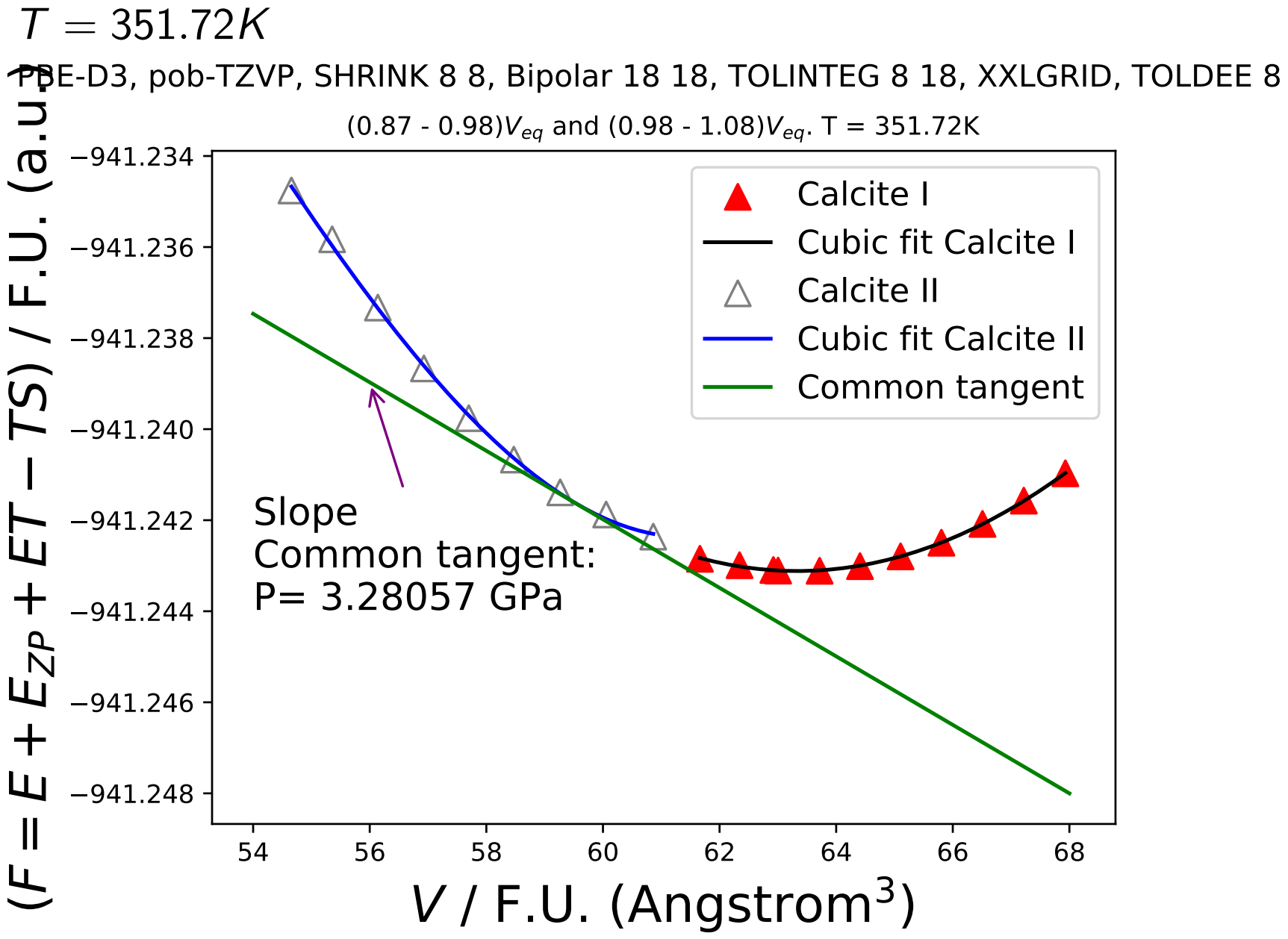



$T = 271.31K$
PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}. T = 271.31K
$(F = E + E_{ZP} + ET - TS)$ / F.U. (a.u.)
−941.232
−941.234
−941.236
−941.238
−941.240
−941.242
−941.244
54
56
58
60
62
64
66
68
V / F.U. (Angstrom^3)
Calcite I
Cubic fit Calcite I
Calcite II
Cubic fit Calcite II
Common tangent
Slope
Common tangent:
P= 2.47528 GPa


$T = 291.41K$
PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}. T = 291.41K
Calcite I
Cubic fit Calcite I
Calcite II
Cubic fit Calcite II
Common tangent
Slope
Common tangent:
P= 2.65024 GPa
$(F = E + E_{ZP} + ET - TS)$ / F.U. (a.u.)
−941.234
−941.236
−941.238
−941.240
−941.242
−941.244
54
56
58
60
62
64
66
68
V / F.U. (Angstrom^3)


$T = 311.52K$
PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}. T = 311.52K
$(F = E + E_{ZP} + ET - TS)$ / F.U. (a.u.)
−941.234
−941.236
−941.238
−941.240
−941.242
−941.244
−941.246
54
56
58
60
62
64
66
68
V / F.U. (Angstrom^3)
Calcite I
Cubic fit Calcite I
Calcite II
Cubic fit Calcite II
Common tangent
Slope
Common tangent:
P= 2.73335 GPa


$T = 331.62K$
PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}. T = 331.62K
$(F = E + E_{ZP} + ET - TS)$ / F.U. (a.u.)
−941.234
−941.236
−941.238
−941.240
−941.242
−941.244
−941.246
54
56
58
60
62
64
66
68
V / F.U. (Angstrom^3)
Calcite I
Cubic fit Calcite I
Calcite II
Cubic fit Calcite II
Common tangent
Slope
Common tangent:
P= 3.02156 GPa


$T = 351.72K$
PBE-D3, pob-TZVP, SHRINK 8 8, Bipolar 18 18, TOLINTEG 8 18, XXLGRID, TOLDEE 8
(0.87 - 0.98)V_{eq} and (0.98 - 1.08)V_{eq}. T = 351.72K
$(F = E + E_{ZP} + ET - TS)$ / F.U. (a.u.)
−941.234
−941.236
−941.238
−941.240
−941.242
−941.244
−941.246
−941.248
54
56
58
60
62
64
66
68
V / F.U. (Angstrom^3)
Calcite I
Cubic fit Calcite I
Calcite II
Cubic fit Calcite II
Common tangent
Slope
Common tangent:
P= 3.28057 GPa

Outline I

$E(V)$, $E(V) + E_{ZP}$, $F(V;T)$ and pressure of transition. Thermal evolution

Phase Boundary

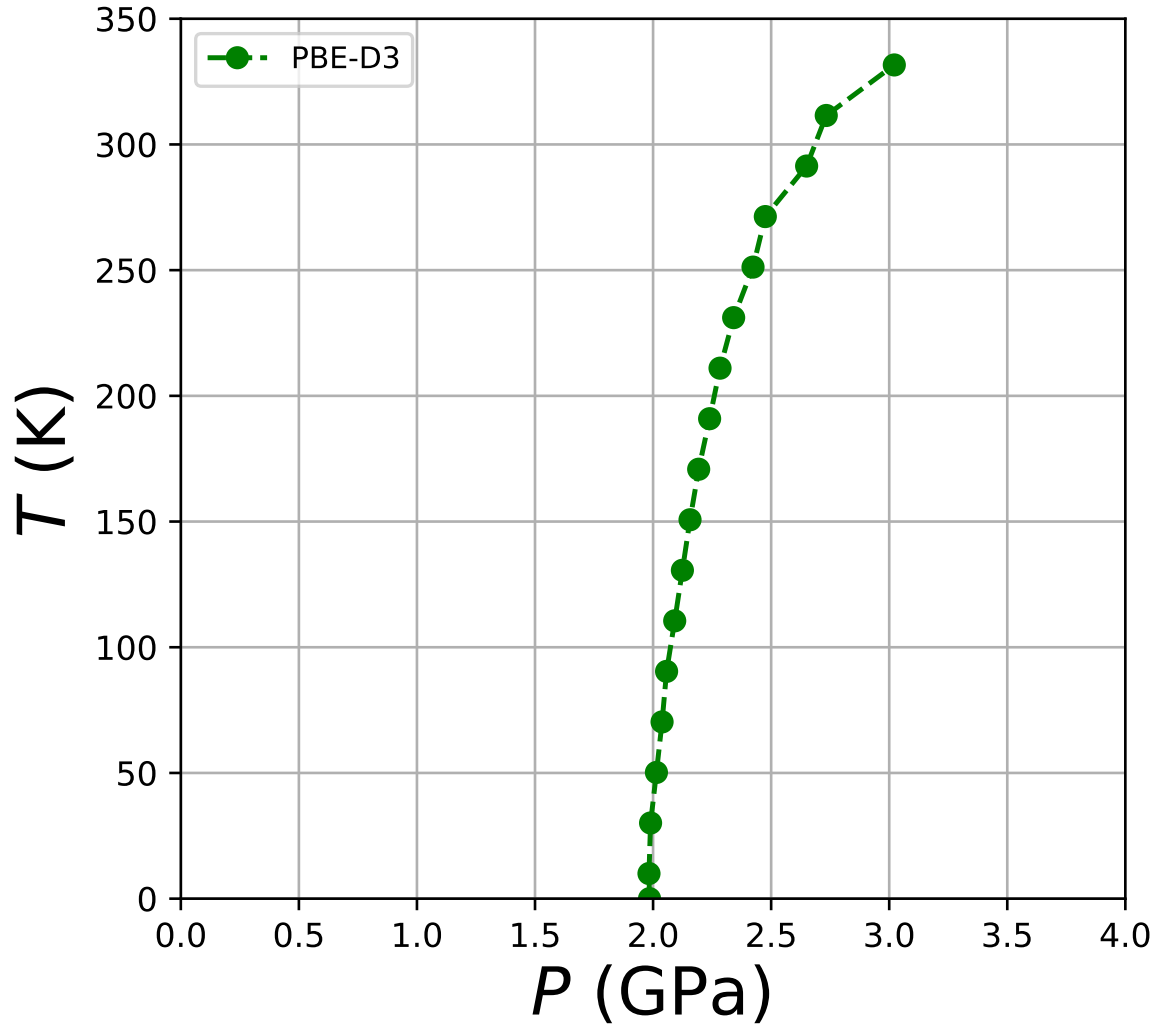


Figure 1: Pressure-temperature phase boundary via common tangent procedure