Supplementary Material

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Modulated structure and phase transitions of $Sr_{10}Ga_6O_{19}$ *

Hannes Krüger[†‡] Biljana Lazić[§] Erik Arroyabe[‡] Volker Kahlenberg[‡]

Abstract

The crystal structure of $Sr_{10}Ga_6O_{19}$ was investigated by *in-situ* single-crystal X-ray diffraction in the temperature range from 298 to 673 K. At ambient conditions the compound shows a (3+1)-dimensional modulated structure in superspace group $C2/c(0\beta0)s0$ (a = 34.9145(13), b = 7.9369(2), c = 15.9150(7) Å and β = 103.551(3)°) with a modulation wavevector of $\mathbf{q} = 0.4288(2)\mathbf{b}^*$. Whereas the presented structural model uses first-order harmonic modulation functions only, some features of the modulations are discussed utilising an electron density derived by the maximum entropy method. Furthermore, two phase-transitions were identified: between 453 and 503 K the incommensurate superstructure is replaced by a doubling of the a and b lattice constant, and between 503 and 673 K a phase with the basic cell is formed, identical to α-$Sr_{10}Ga_6O_{19}$. Depending on the cooling conditions crystals showing a combined diffraction pattern of both superstructures can be obtained.

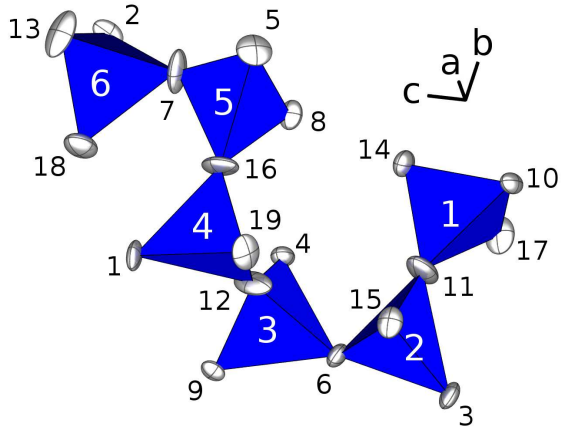
The relation of these results to α-$Sr_{10}Ga_6O_{19}$ [Kahlenberg (2001). *J. Solid State Chem.* **160**, 421] are discussed.

1 Introduction

This document contains supplementary material to the above referenced publication. The structural data can be taken from the accompanying cif file.

Fig. 1 gives an overview over the [Ga_6O_{19}] unit, and the locations of individual gallium and oxygen atoms.

Figure 1: One hexagallate unit [Ga_6O_{19}] with atom labels.



2 Movie

A movie of the structural variations of one hexagallate unit is available as supplementary material, or via youtube: http://www.youtube.com/watch?v=KkiepOPIuqE The movie was produced with DRAWxtl,[1] POV-Ray and MEncoder.

3 Interatomic distances

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[†]Email: Hannes.Krueger@gmail.com

[‡]Institute of Mineralogy and Petrography, University of Innsbruck

[§]Institute of Geology, University of Bern

Table 1: Interatomic distances, with their average, minimum and maximum values. Symmetry codes used: (i) x,1-y,-1/2+z; (ii) x,1-y,1/2+z; (iii) x,-y,1/2+z; (iv) -x,1-y,1-z; (v) x,1+y,z; (vi) -x,1-y,-z; (vii) 1/2-x,1/2-y,1-z; (viii) x,-1+y,z; (ix) 1/2-x,-1/2+y,1/2-z; (x) 1/2-x,1/2+y,1/2-z; (xi) -x,y,1/2-z; (xii) -x,-y,1-z; (xiii) x,-y,-1/2+z; (xiv) x,y,-1+z; (xv) x,1+y,-1+z

Atom	d_{ave} [Å]	d_{min} [Å]	d_{max} [Å]
Sr1–O1	2.580(13)	2.487(13)	2.669(13)
Sr1–O2	2.686(11)	2.583(11)	2.792(11)
Sr1–O7	2.720(16)	2.661(17)	2.755(15)
Sr1–O8	2.912(13)	2.855(13)	2.965(13)
Sr1–O9	2.513(9)	2.449(9)	2.585(9)
Sr1–O10^{i}	2.583(12)	2.568(12)	2.604(11)
Sr1–O11^{ii}	3.17(2)	2.899(19)	3.45(2)
Sr1–O15^{iii}	2.872(15)	2.727(14)	3.026(14)
Sr2–O2^{i}	2.355(14)	2.318(14)	2.388(14)
Sr2–O4	2.713(13)	2.555(13)	2.877(13)
Sr2–O8	2.625(13)	2.565(13)	2.681(13)
Sr2–O11	2.704(15)	2.496(15)	2.928(16)
Sr2–O12	2.586(14)	2.527(15)	2.675(13)
Sr2–O14	2.645(12)	2.563(12)	2.731(12)
Sr2–O16	3.013(13)	2.664(13)	3.339(13)
Sr3–O4	2.534(12)	2.494(12)	2.564(12)
Sr3–O8	2.437(11)	2.414(10)	2.474(11)
Sr3–O9	2.455(11)	2.433(11)	2.477(11)
Sr3–O10^{i}	2.512(10)	2.460(10)	2.570(10)
Sr3–O14	2.486(11)	2.441(11)	2.540(11)
Sr3–O17^{iv}	2.354(10)	2.315(10)	2.387(10)
Sr4–O3^{iv}	2.594(13)	2.571(13)	2.619(13)
Sr4–O4	2.714(10)	2.687(10)	2.739(10)
Sr4–O6^{v}	2.872(12)	2.592(12)	3.150(11)
Sr4–O6^{vi}	2.501(11)	2.472(10)	2.529(11)
Sr4–O11	2.74(2)	2.577(19)	2.91(2)
Sr4–O14^{vi}	3.075(12)	2.642(12)	3.515(12)
Sr4–O17^{iv}	2.629(14)	2.425(14)	2.837(14)
Sr5–O1	2.505(12)	2.458(12)	2.567(11)
Sr5–O2	2.509(14)	2.430(14)	2.590(14)
Sr5–O13^{vii}	2.384(14)	2.288(14)	2.480(15)
Sr5–O15^{iii}	2.530(11)	2.503(11)	2.559(11)
Sr5–O18^{viii}	2.527(16)	2.467(17)	2.622(16)
Sr5–O19^{iii}	2.456(12)	2.374(12)	2.532(12)
Sr6–O1^{v}	3.199(14)	2.895(14)	3.493(14)
Sr6–O4	2.776(10)	2.699(10)	2.874(10)
Sr6–O7	3.188(16)	2.571(15)	3.803(15)
Sr6–O8	3.330(13)	2.948(13)	3.718(13)
Sr6–O10^{i}	2.427(12)	2.387(12)	2.483(12)
Sr6–O12	3.238(14)	2.673(13)	3.829(13)

continued...

Table 1: Interatomic distances – continued

Atom	d_{ave} [Å]	d_{min} [Å]	d_{max} [Å]
Sr6–O15^{ii}	2.516(14)	2.412(13)	2.630(14)
Sr6–O16	2.882(16)	2.637(16)	3.107(16)
Sr6–O18	2.867(15)	2.383(14)	3.354(14)
Sr7–O1	2.608(13)	2.533(12)	2.685(13)
Sr7–O5	2.867(16)	2.595(15)	3.156(16)
Sr7–O5^{ix}	2.597(17)	2.466(17)	2.715(17)
Sr7–O7	2.865(16)	2.377(16)	3.347(15)
Sr7–O13	3.24(2)	2.621(18)	3.88(2)
Sr7–O13^{vii}	2.65(2)	2.530(19)	2.83(2)
Sr7–O16^{ix}	2.849(16)	2.449(16)	3.261(16)
Sr7–O19^{x}	3.030(15)	2.554(15)	3.474(15)
Sr8–O6	3.182(11)	2.796(11)	3.560(11)
Sr8–O8	2.490(13)	2.416(13)	2.572(13)
Sr8–O12^{viii}	2.603(14)	2.433(13)	2.800(13)
Sr8–O14	2.516(12)	2.430(12)	2.609(12)
Sr8–O15	2.651(13)	2.636(14)	2.669(12)
Sr8–O18^{i}	2.51(2)	2.450(19)	2.607(18)
Sr8–O19	2.986(13)	2.701(13)	3.275(13)
Sr9–O3^{iv}	2.401(12)	2.368(12)	2.431(13)
Sr9–O3^{i}	2.401(12)	2.368(12)	2.431(13)
Sr9–O4	2.921(13)	2.495(13)	3.368(13)
Sr9–O4^{xi}	2.930(13)	2.495(13)	3.368(13)
Sr9–O10^{iv}	3.214(11)	2.837(11)	3.590(10)
Sr9–O10^{i}	3.207(11)	2.837(11)	3.590(10)
Sr9–O17^{iv}	2.607(14)	2.527(13)	2.716(14)
Sr9–O17^{i}	2.605(14)	2.527(13)	2.716(14)
Sr10–O3^{xii}	2.521(12)	2.426(12)	2.619(13)
Sr10–O3^{xiii}	2.523(12)	2.426(12)	2.619(13)
Sr10–O9	2.448(11)	2.412(11)	2.483(11)
Sr10–O9^{xi}	2.448(11)	2.412(11)	2.483(11)
Sr10–O17^{iv}	3.345(14)	2.965(14)	3.731(14)
Sr10–O17^{i}	3.352(14)	2.965(14)	3.731(14)
Sr11–O1^{x}	3.250(14)	2.873(13)	3.635(14)
Sr11–O5	2.361(16)	2.318(16)	2.410(17)
Sr11–O7^{ix}	2.991(16)	2.806(16)	3.178(16)
Sr11–O13^{ix}	3.13(2)	2.73(2)	3.58(2)
Sr11–O13^{i}	2.85(2)	2.37(2)	3.32(2)
Sr11–O16^{ix}	2.761(13)	2.552(13)	2.932(13)
Sr11–O18^{ix}	3.02(2)	2.693(18)	3.389(19)
Sr11–O18^{i}	3.013(16)	2.490(14)	3.543(14)
Sr11–O19	2.454(15)	2.425(15)	2.494(14)
Ga1–O10^{xiv}	1.819(12)	1.807(12)	1.829(12)
Ga1–O11	1.866(16)	1.822(16)	1.901(16)
Ga1–O14	1.831(10)	1.808(10)	1.870(11)
Ga1–O17^{xiv}	1.831(10)	1.810(10)	1.857(10)
Ga2–O3^{xv}	1.812(11)	1.787(11)	1.854(11)

continued...

Table 1: Interatomic distances – continued

Atom	d_{ave} [Å]	d_{min} [Å]	d_{max} [Å]
Ga2–O6^{v}	1.896(11)	1.858(11)	1.925(11)
Ga2–O11	1.821(16)	1.794(16)	1.854(16)
Ga2–O15^{v}	1.816(12)	1.794(12)	1.844(12)
Ga3–O4	1.840(12)	1.825(12)	1.852(12)
Ga3–O6^{v}	1.858(10)	1.831(10)	1.881(10)
Ga3–O9^{v}	1.812(11)	1.792(11)	1.834(11)
Ga3–O12	1.892(12)	1.867(13)	1.921(11)
Ga4–O1^{v}	1.817(12)	1.803(12)	1.833(12)
Ga4–O12	1.884(11)	1.836(11)	1.917(11)
Ga4–O16	1.874(14)	1.850(15)	1.891(14)
Ga4–O19^{v}	1.806(14)	1.782(14)	1.826(14)
Ga5–O5	1.773(14)	1.744(15)	1.798(14)
Ga5–O7	1.836(13)	1.779(13)	1.891(12)
Ga5–O8	1.822(10)	1.806(10)	1.842(10)
Ga5–O16	1.879(14)	1.857(15)	1.915(14)
Ga6–O2	1.804(14)	1.789(14)	1.821(14)
Ga6–O7	1.860(12)	1.795(12)	1.936(13)
Ga6–O13	1.794(13)	1.689(13)	1.894(13)
Ga6–O18	1.824(17)	1.776(17)	1.877(16)

4 Displacive modulation functions

4.1 Strontium atoms

Figure 2: Displacements of strontium atoms 1–3

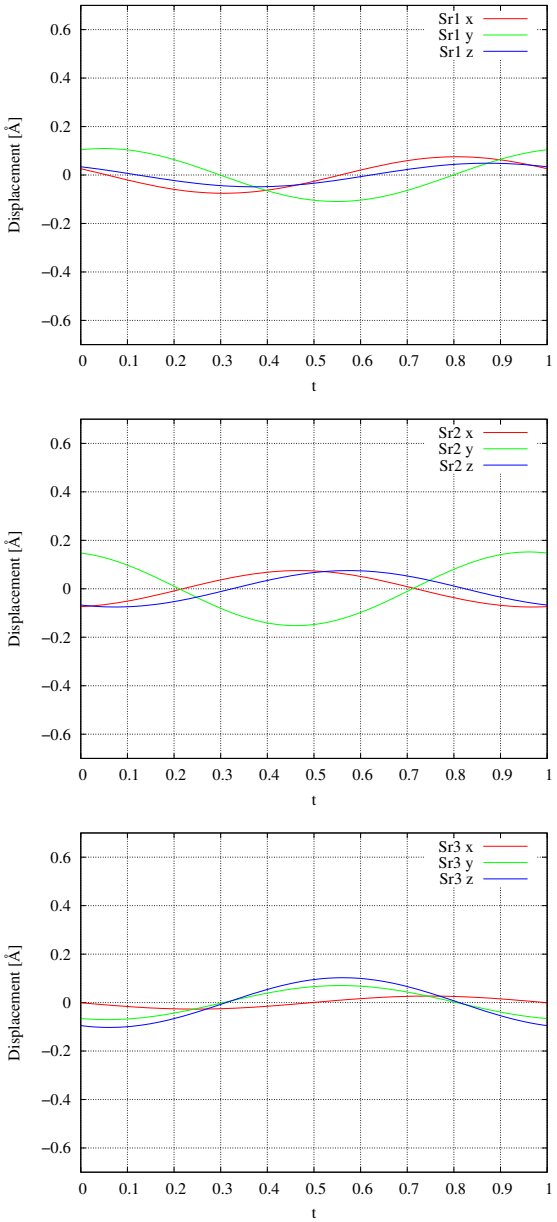


Figure 3: Displacements of strontium atoms 4–6

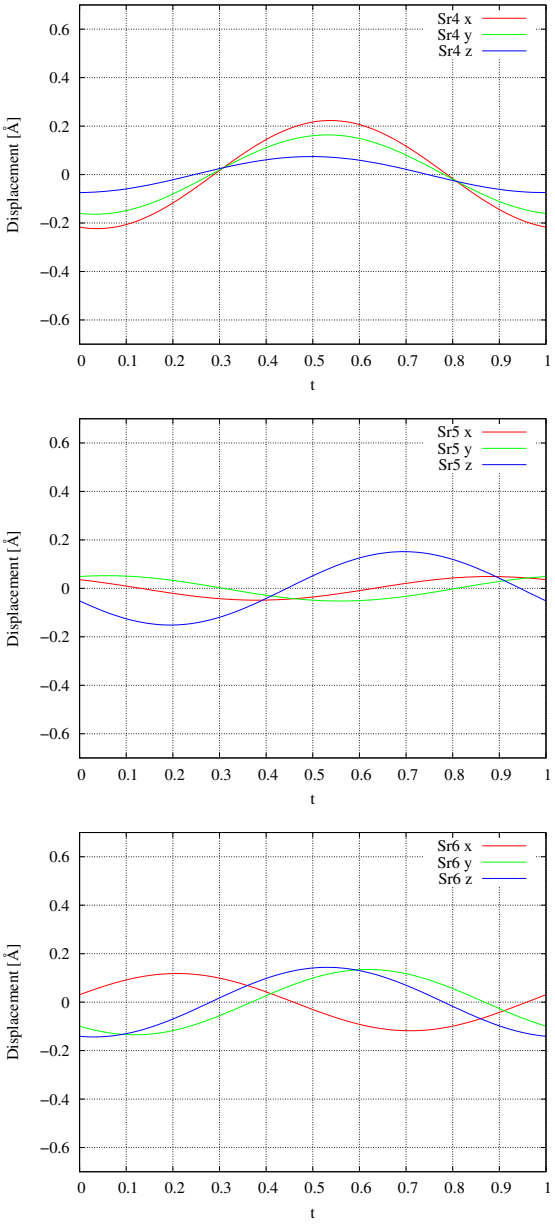


Figure 4: Displacements of strontium atoms 7–9

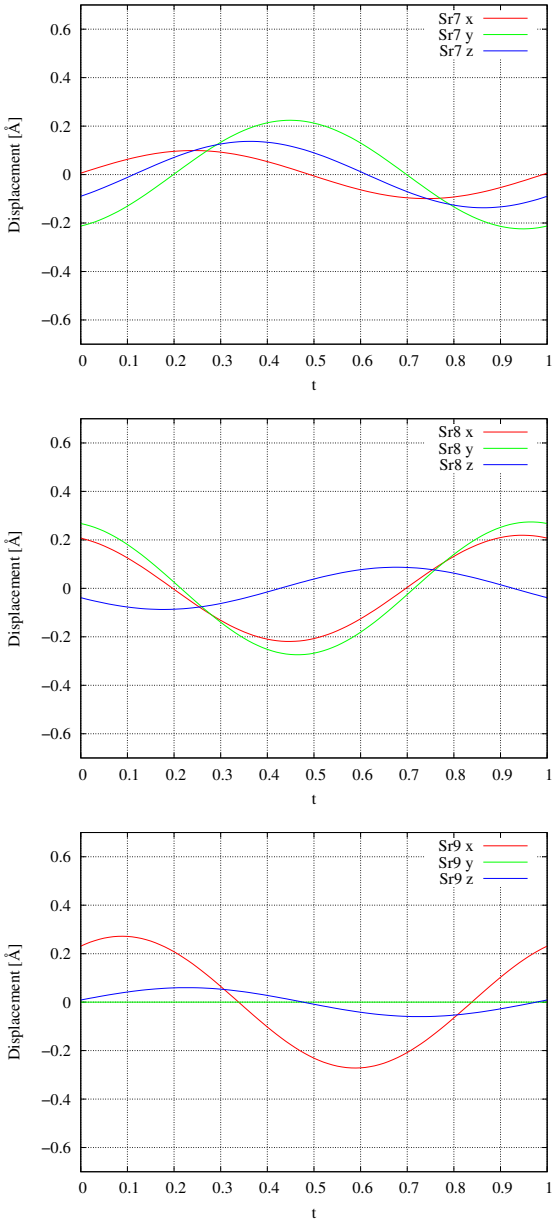
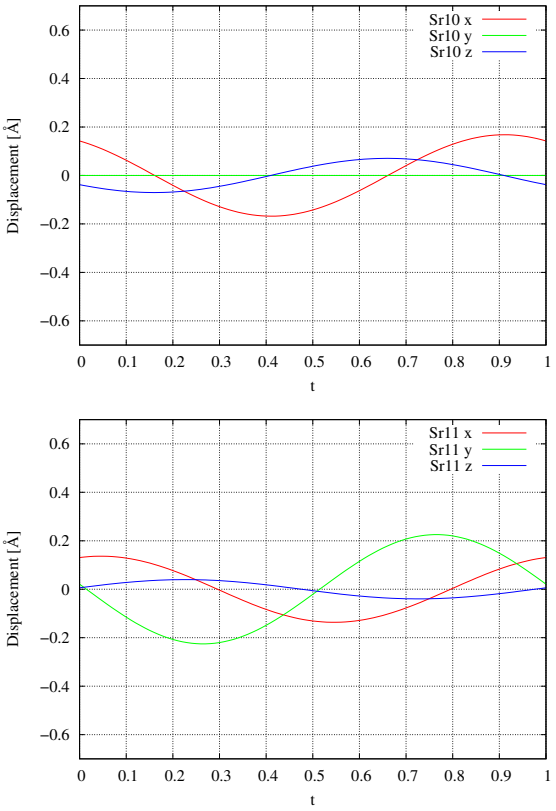


Figure 5: Displacements of strontium atoms 10–11



4.2 Gallium atoms

Figure 6: Displacements of gallium atoms 1–3

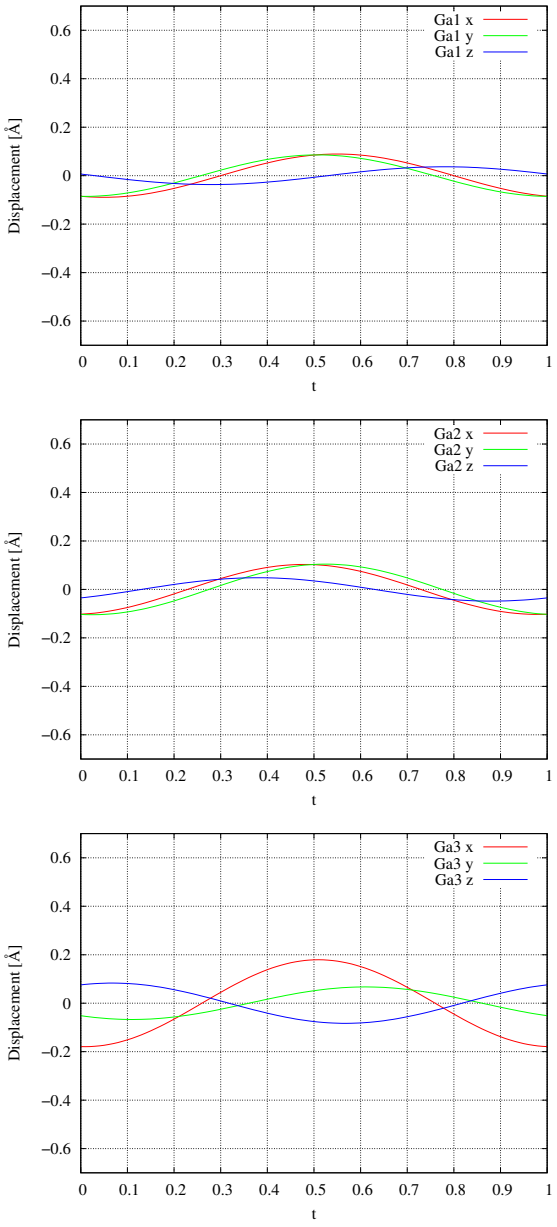
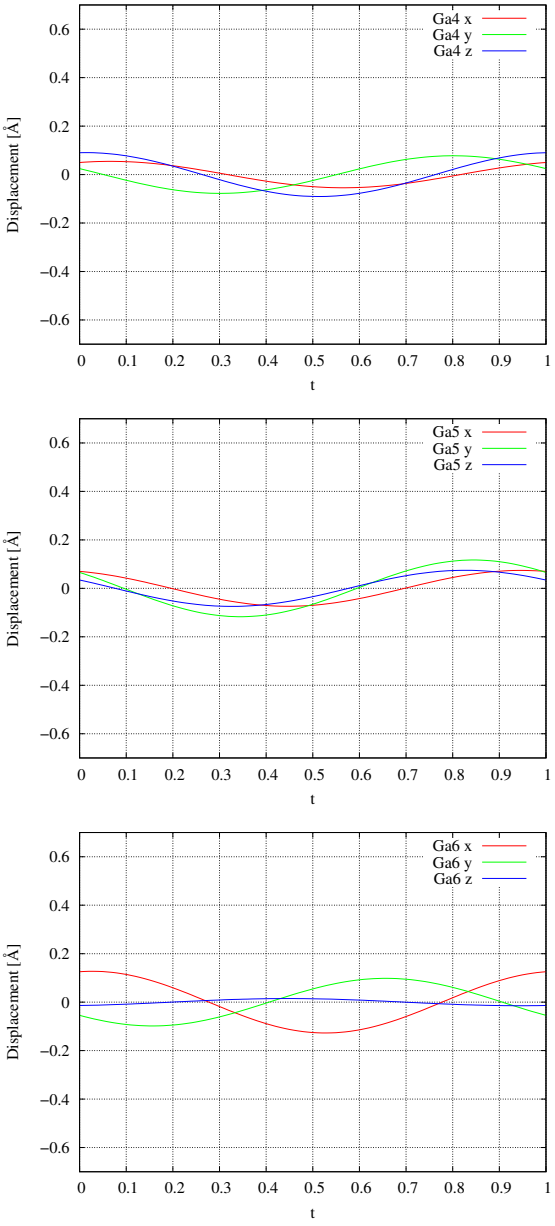


Figure 7: Displacements of gallium atoms 4–6



4.3 Oxygen atoms

Figure 8: Displacements of oxygen atoms 1–3

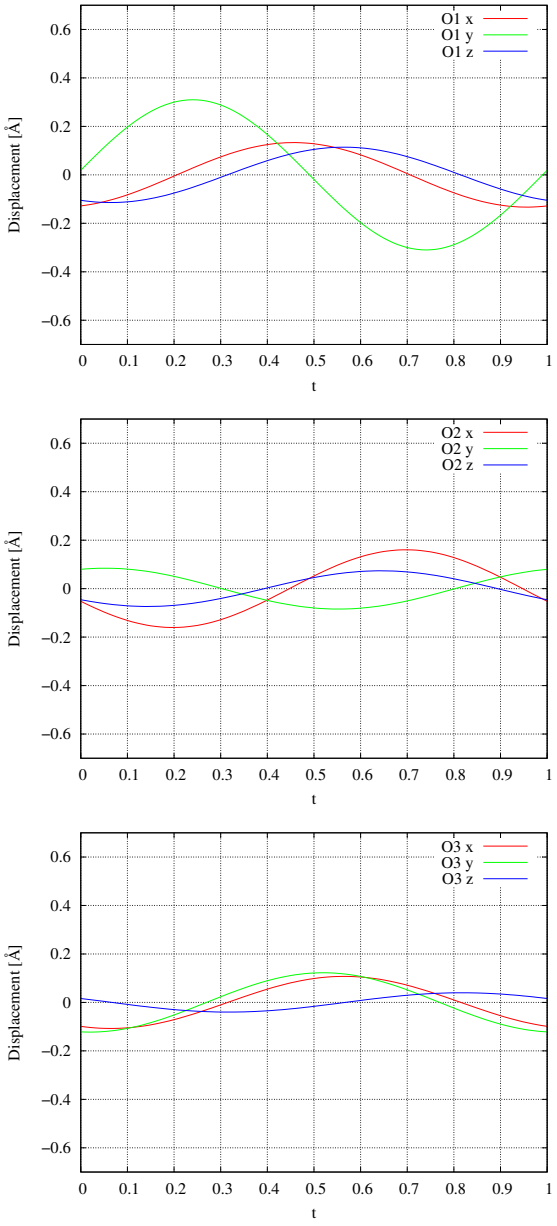


Figure 9: Displacements of oxygen atoms 4–6

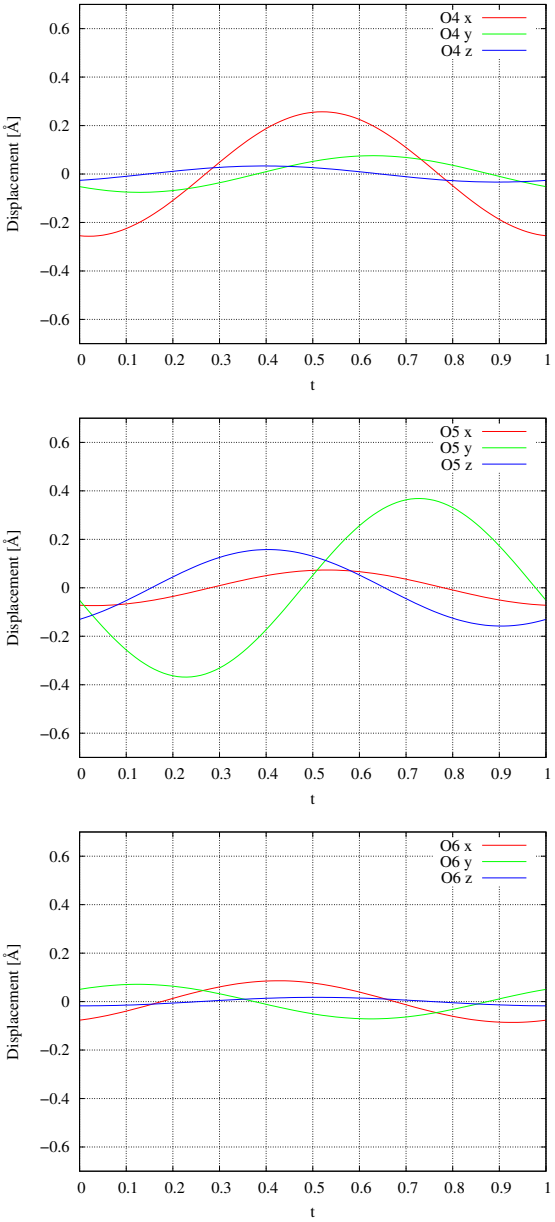
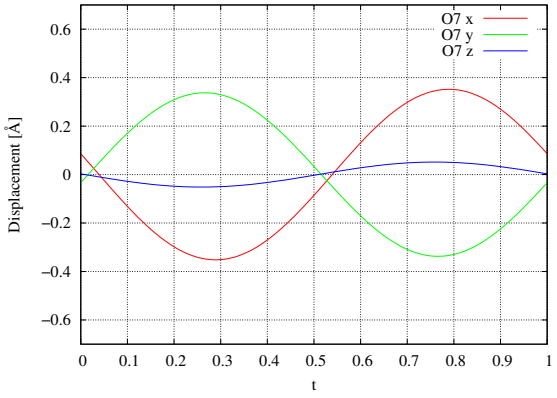
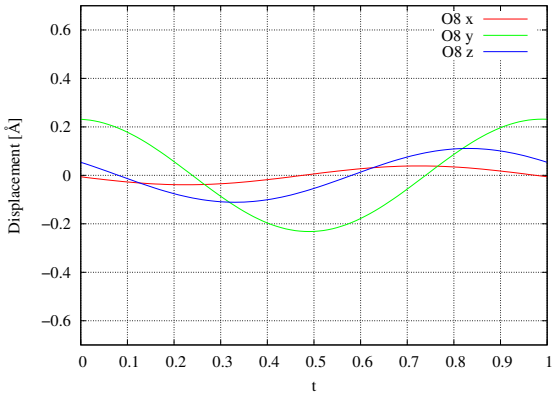


Figure 10: Displacements of oxygen atoms 7–9





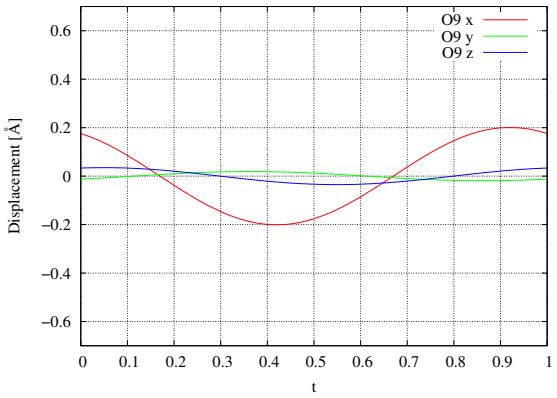
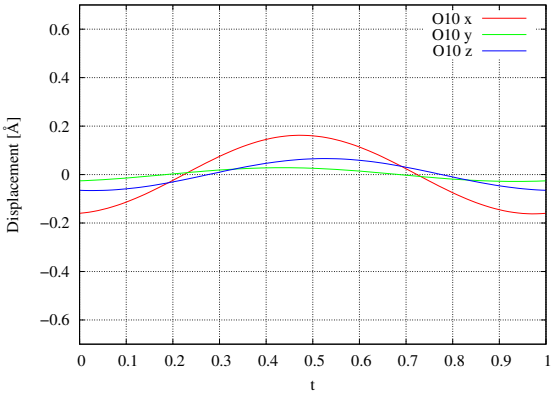
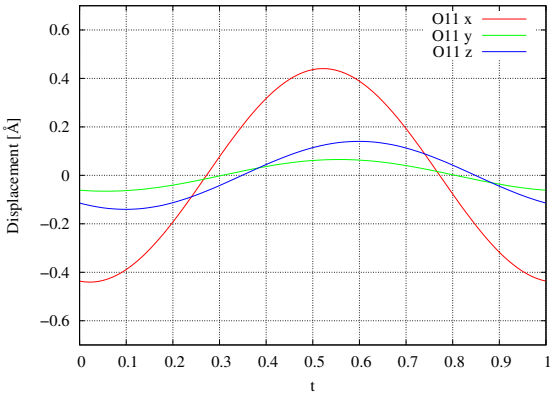


Figure 11: Displacements of oxygen atoms 10–12





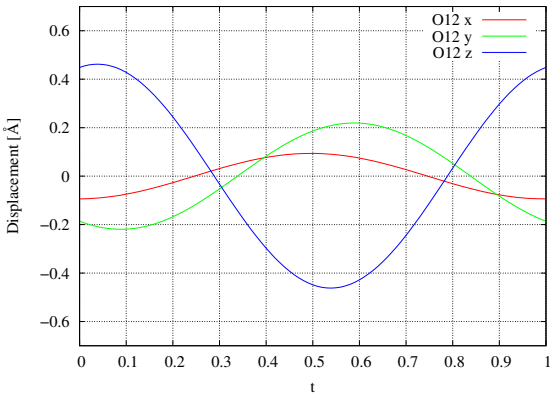
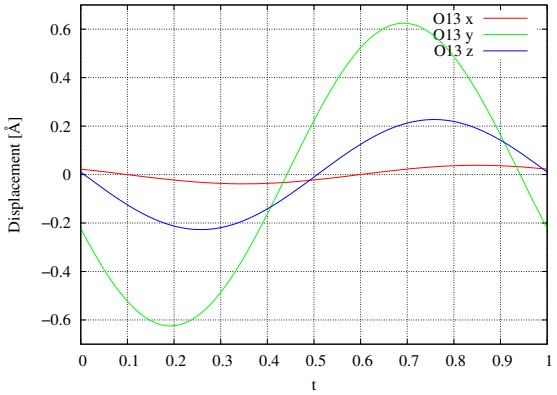
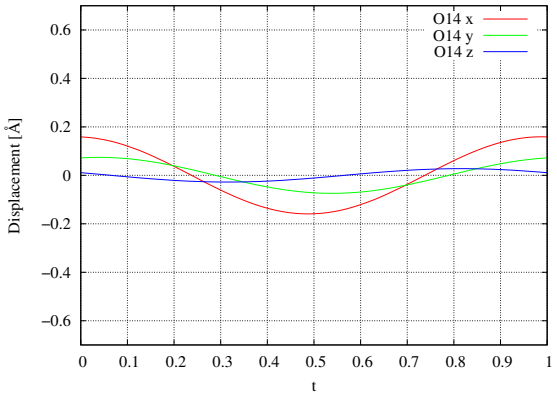


Figure 12: Displacements of oxygen atoms 13–15





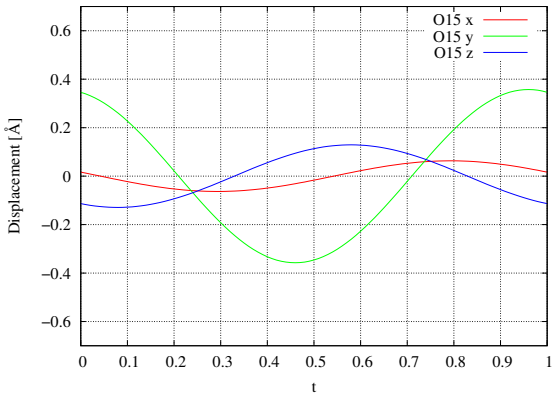
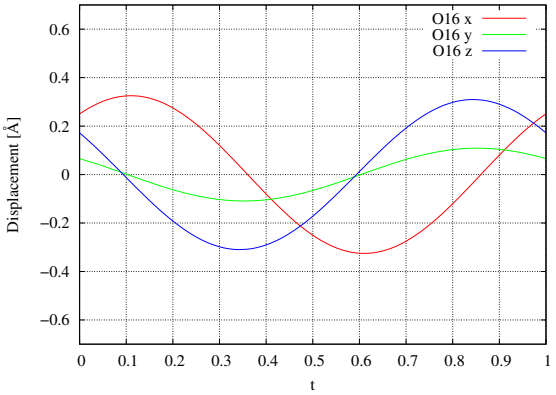
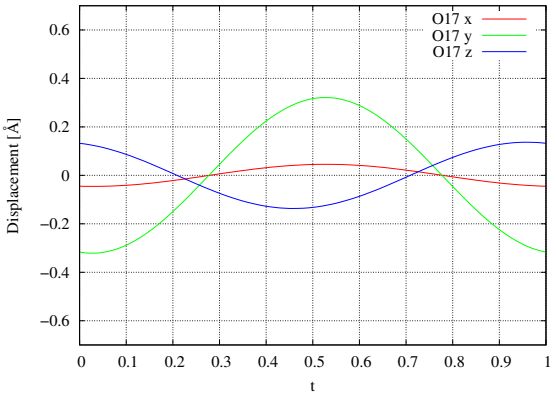


Figure 13: Displacements of oxygen atoms 16–18





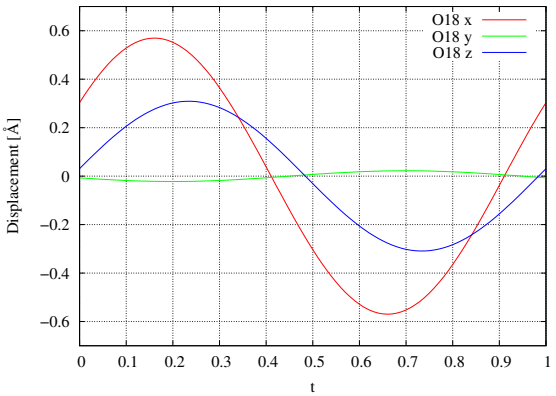
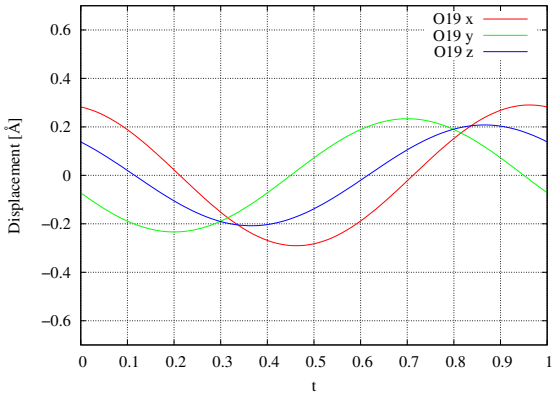


Figure 14: Displacements of oxygen atom 19



5 U_{eq} parameters in Å^2

Figure 15: U_{eq} parameters of gallium atoms

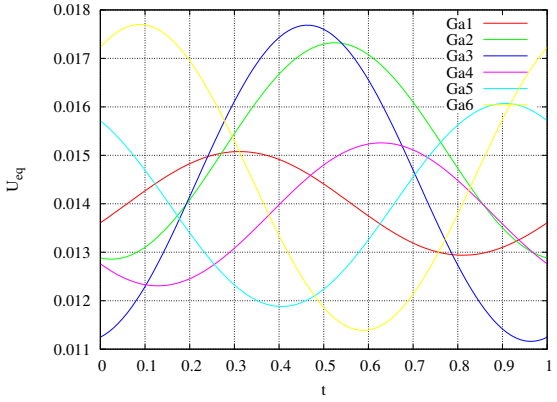


Figure 16: U_{eq} parameters of strontium atoms 1–5

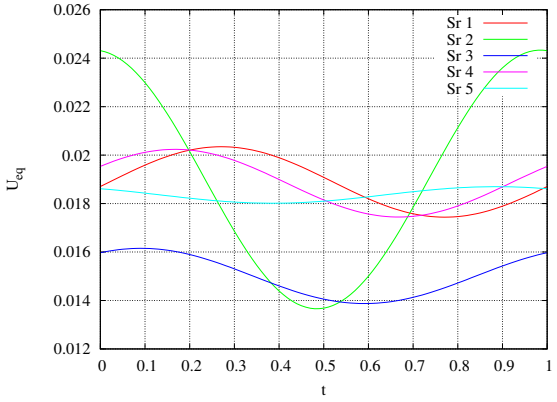


Figure 17: U_{eq} parameters of strontium atoms 6–11

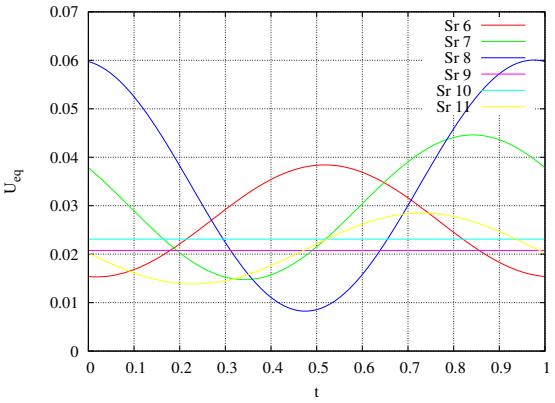


Figure 18: U_{eq} parameters of oxygen atoms 1–7

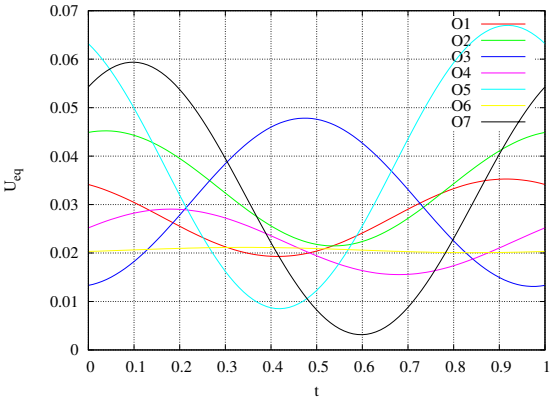


Figure 19: U_{eq} parameters of oxygen atoms 8–13

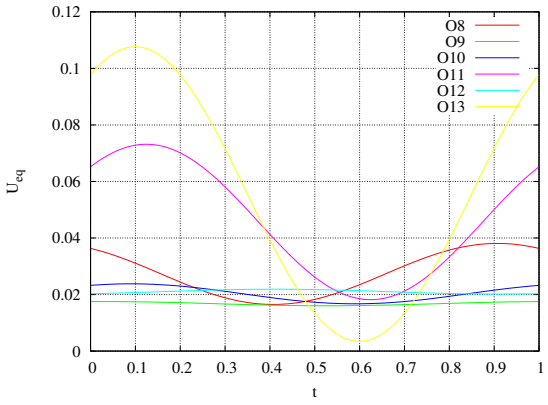
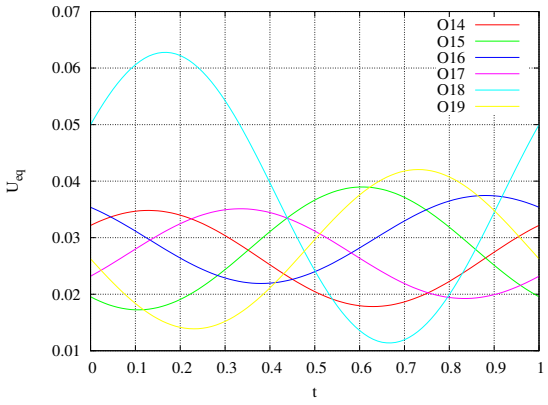


Figure 20: U_{eq} parameters of oxygen atoms 14–19



6 Electron density sections

The electron density sections $x1$–$x4$, $x2$–$x4$ and $x3$–$x4$ for each atom is given twice: the left column shows the densities as derived from ordinary F_{obs} synthesis, the right column shows ρ_{MEM}; results from the Maximum Entropy Method.[2–5] The shown sections were extracted using the *editm81* utility.[6]

The following electron density sections are grouped according to the coordination of the Ga atoms. The contour lines of the oxygen atoms are drawn with 0.5 eÅ^{-3} spacing, lines at the Ga and Sr atoms with 2 eÅ^{-3}.

The width of the plots along the x-axis is 2 Å. The two remaining dimensions are summed in a range of 1.5 Å.

Figure 21: F_{obs} Ga6

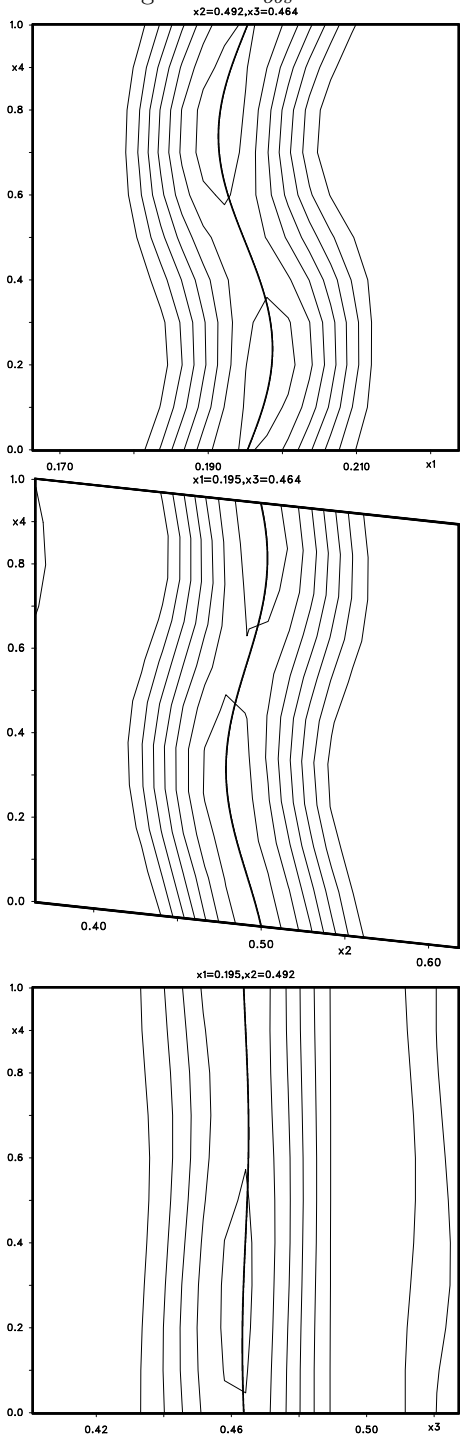


Figure 22: ρ_{MEM} Ga6

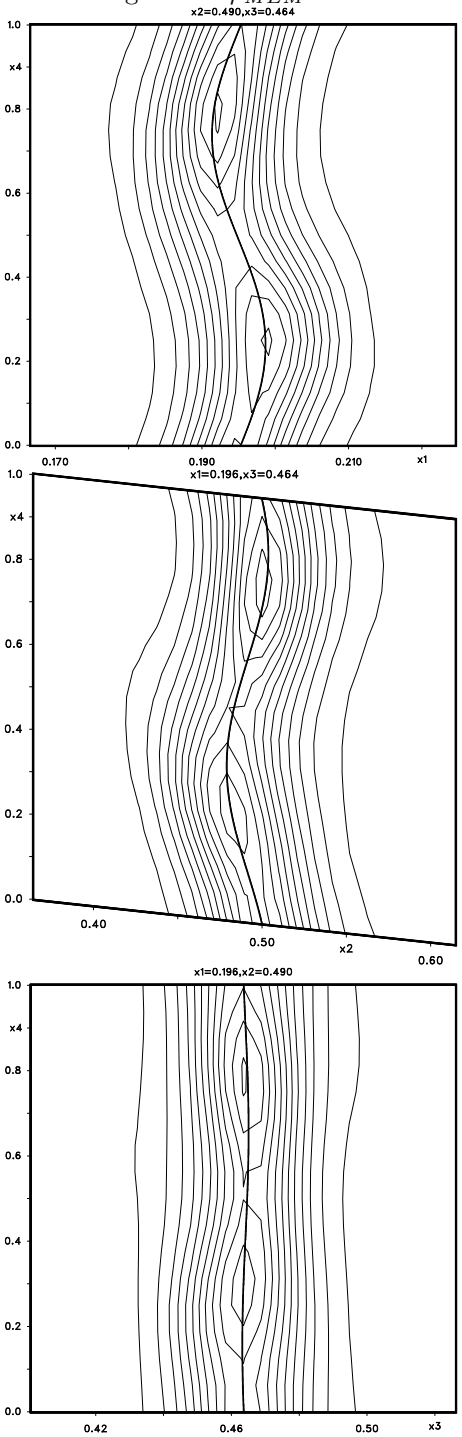


Figure 23: F_{obs} O13

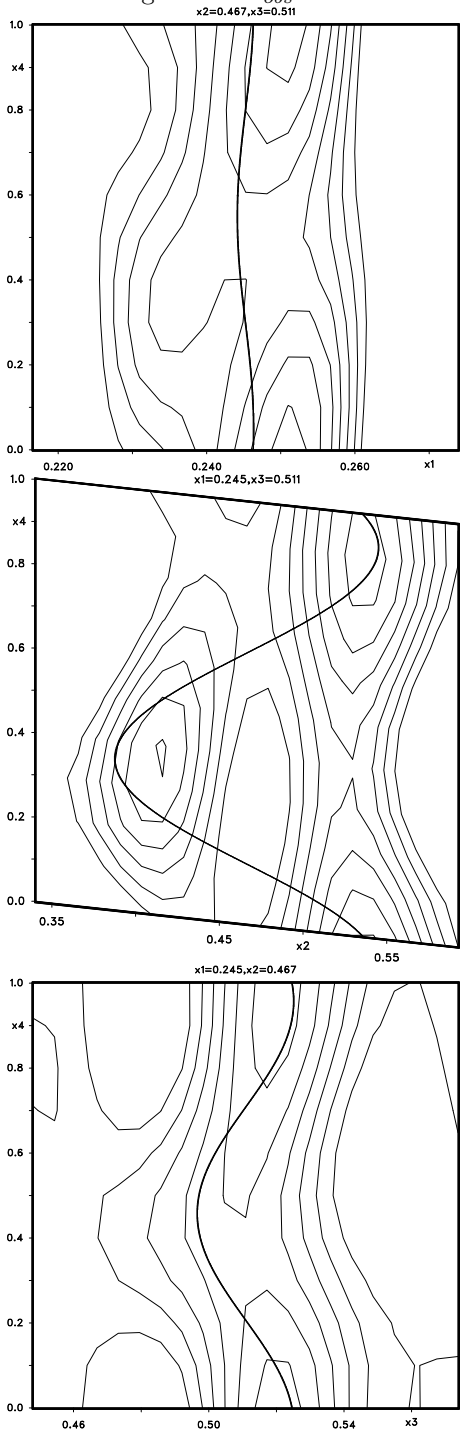


Figure 24: ρ_{MEM} O13

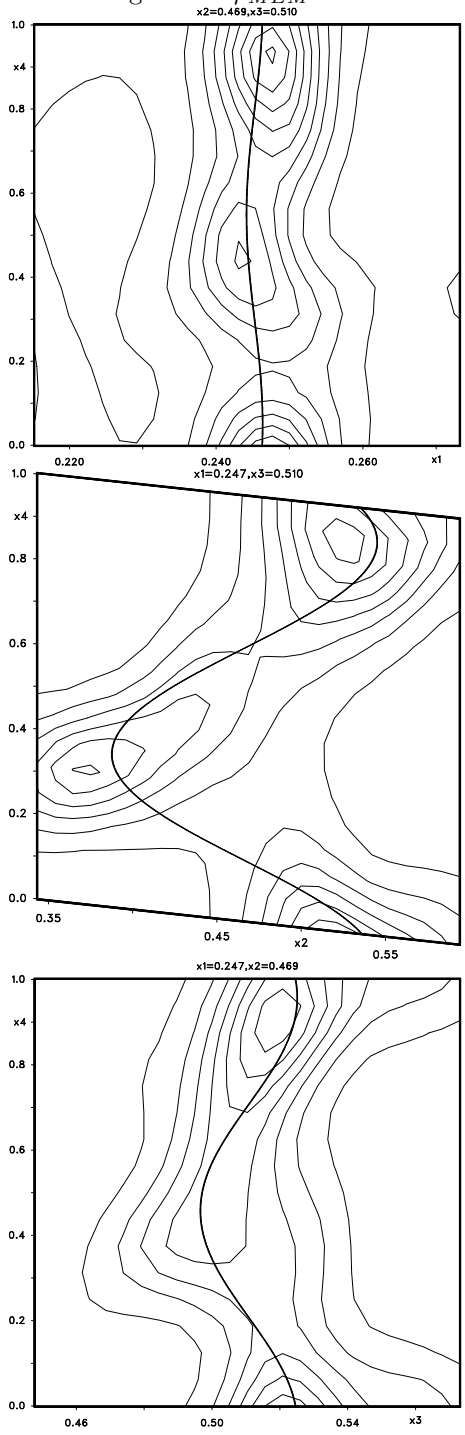


Figure 25: F_{obs} O18

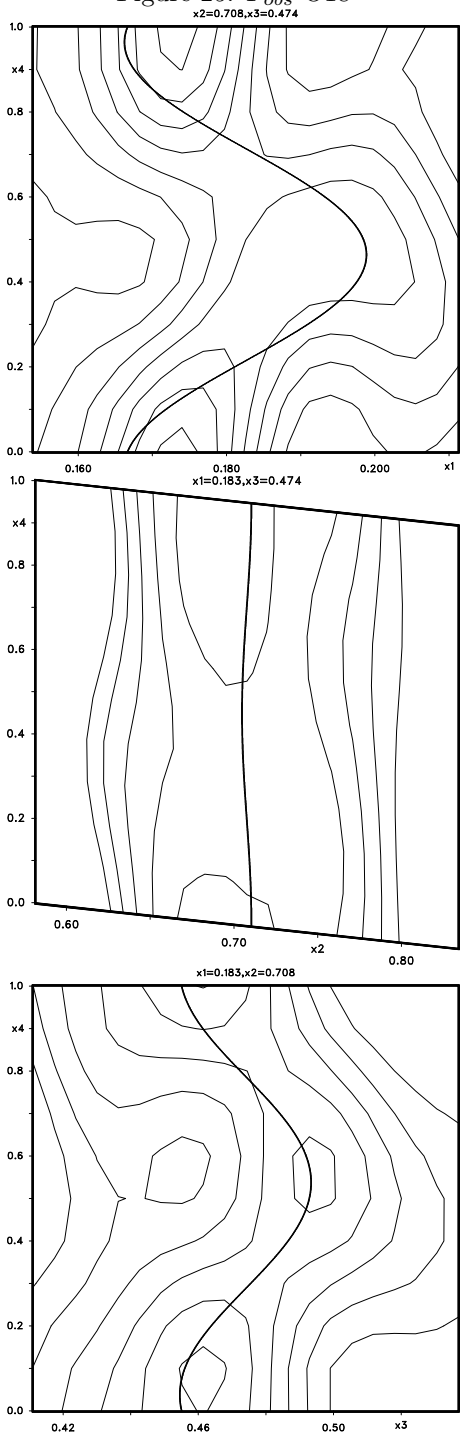


Figure 26: ρ_{MEM} O18

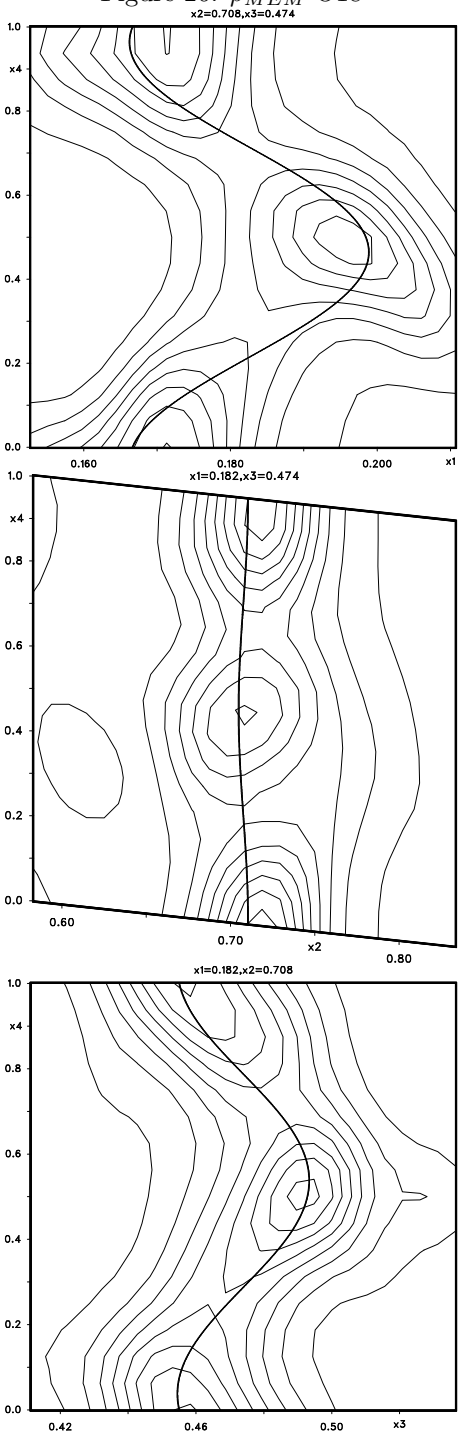


Figure 27: F_{obs} O2

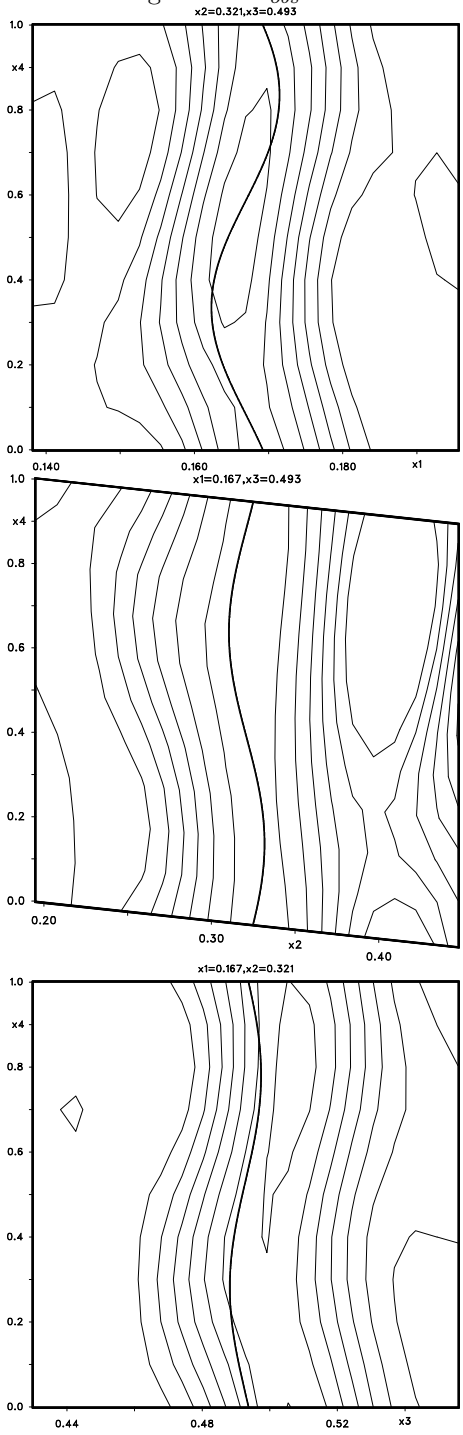


Figure 28: ρ_{MEM} O2

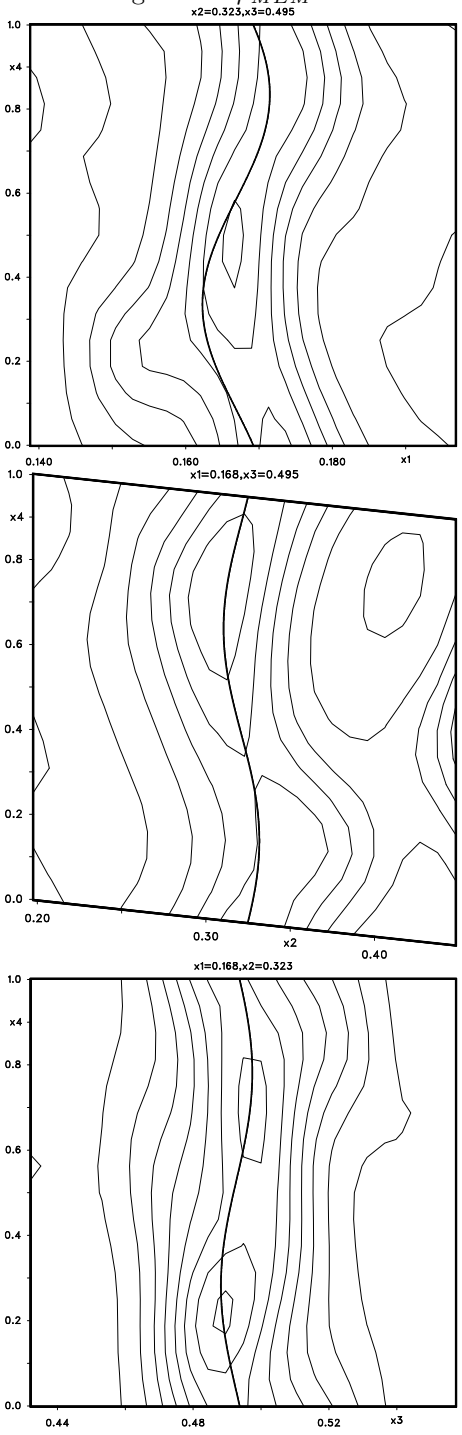


Figure 29: F_{obs} O7

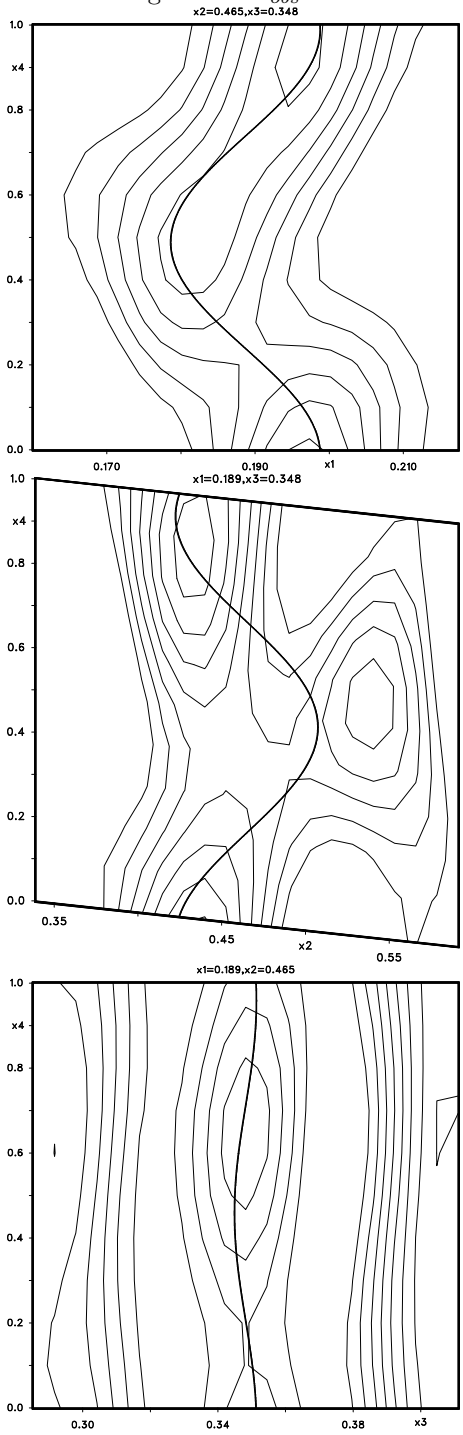


Figure 30: ρ_{MEM} O7

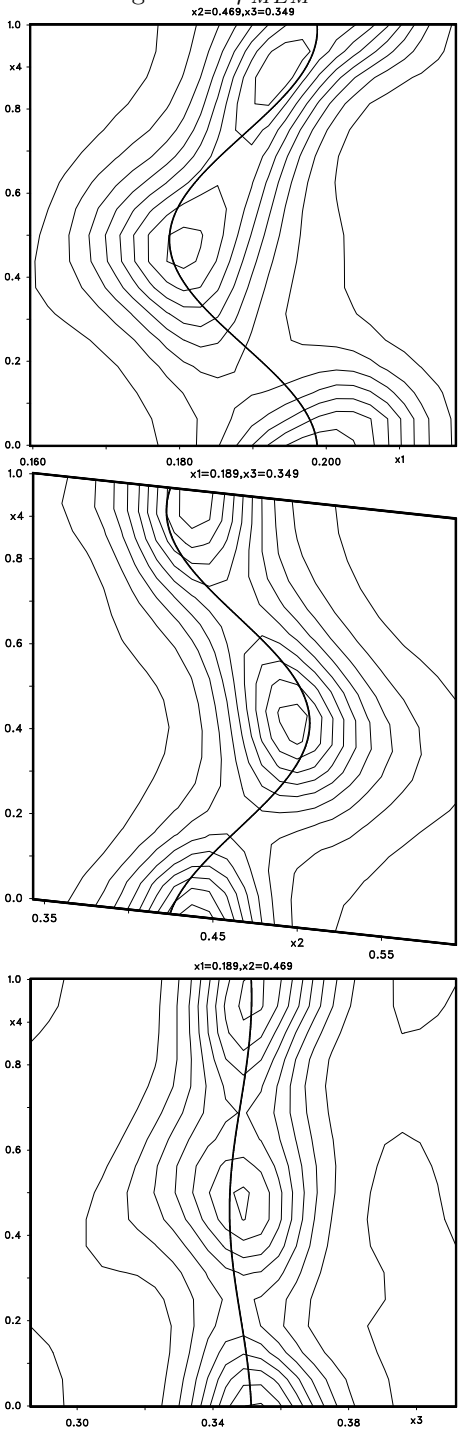


Figure 31: F_{obs} Ga5

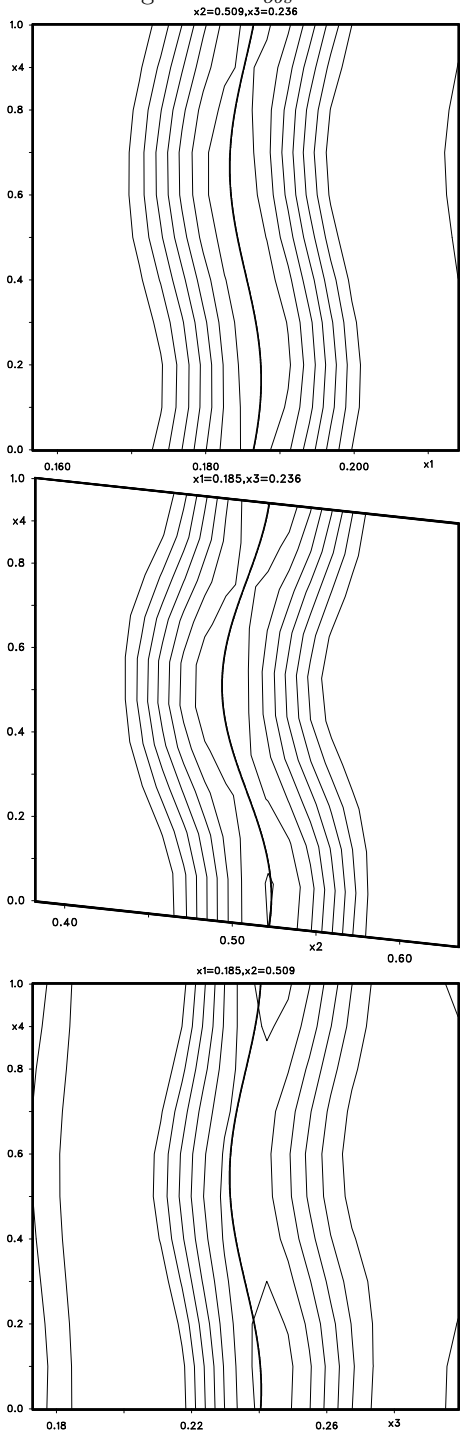


Figure 32: ρ_{MEM} Ga5

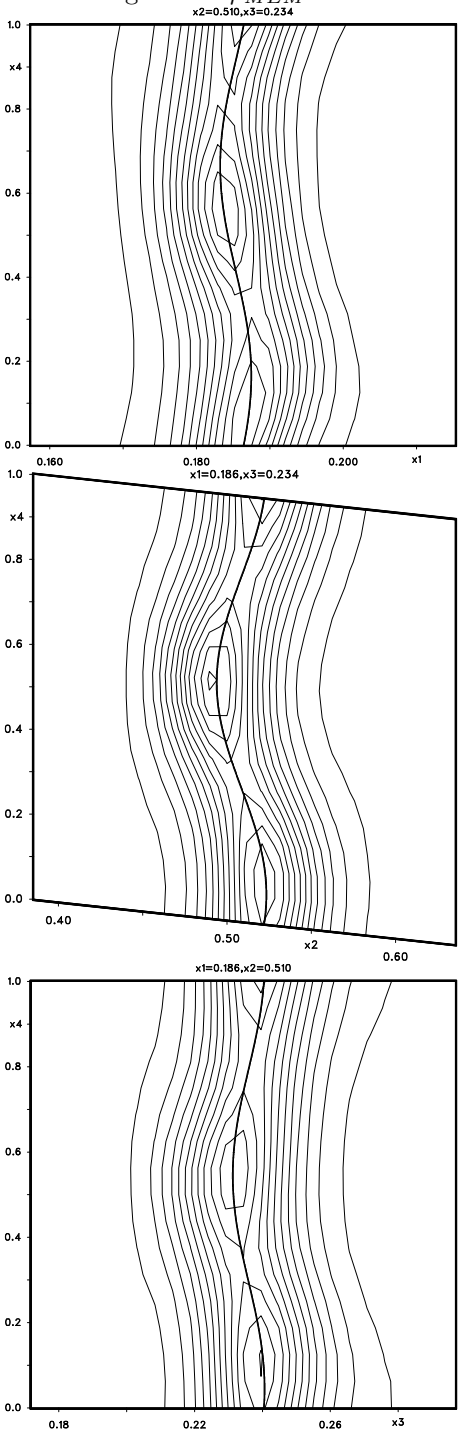


Figure 33: F_{obs} O5

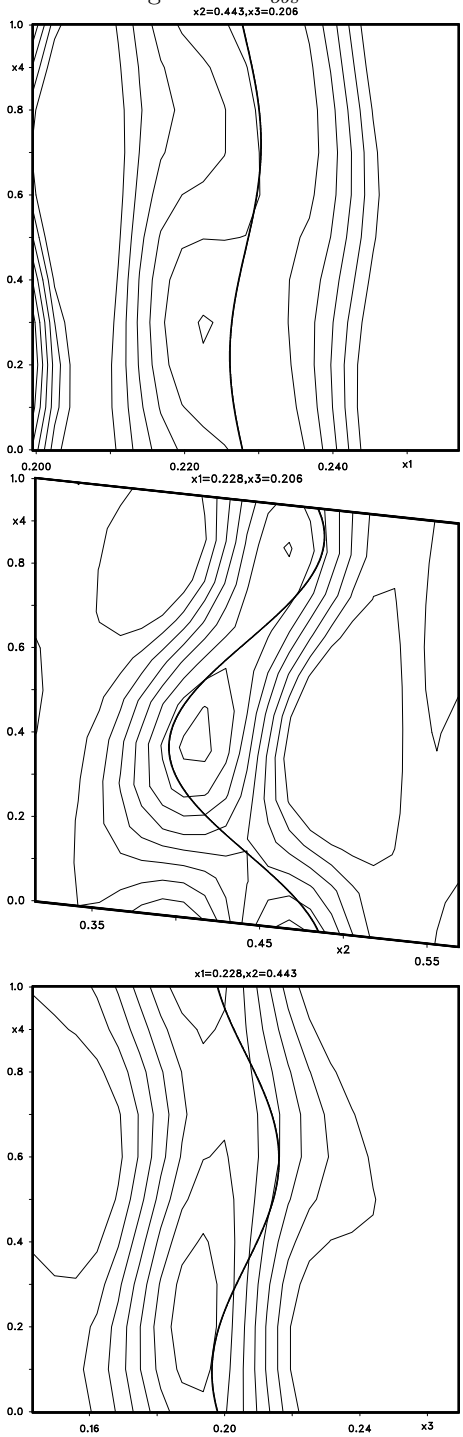


Figure 34: ρ_{MEM} O5

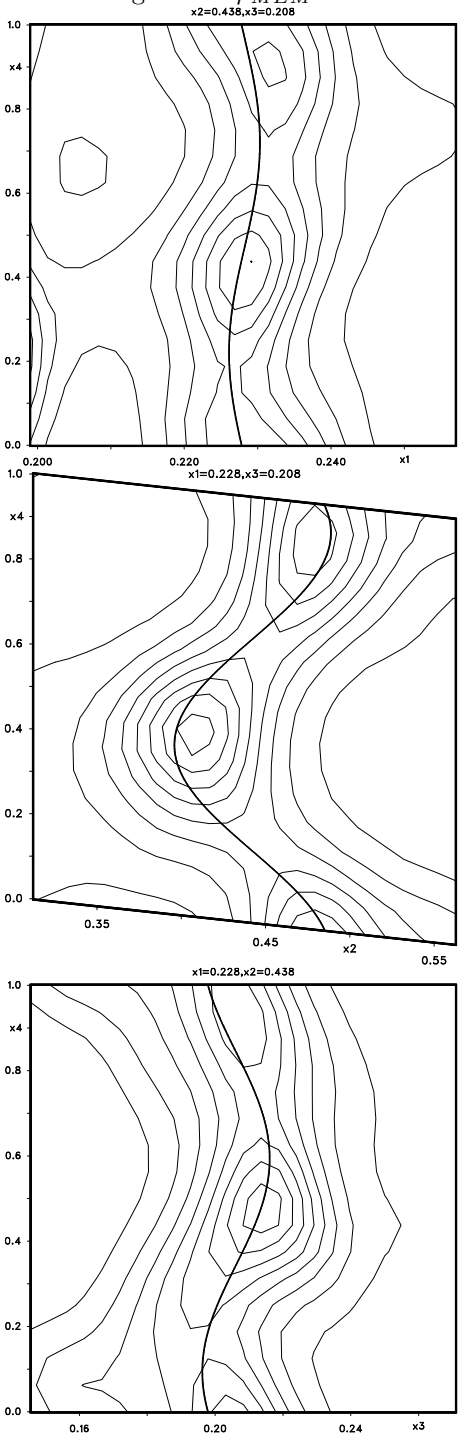


Figure 35: F_{obs} O8

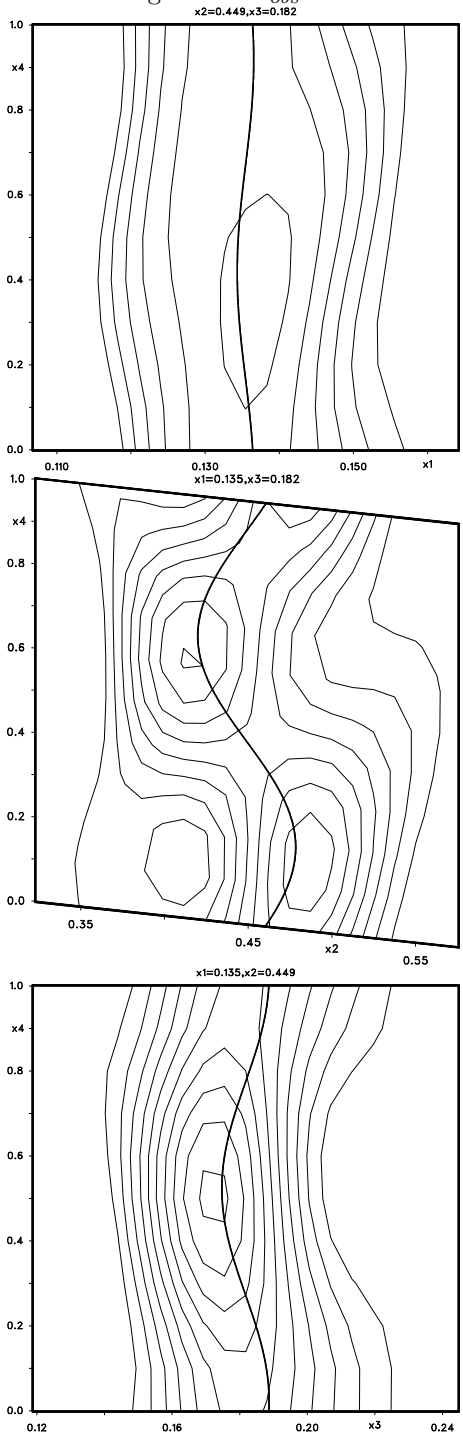


Figure 36: ρ_{MEM} O8

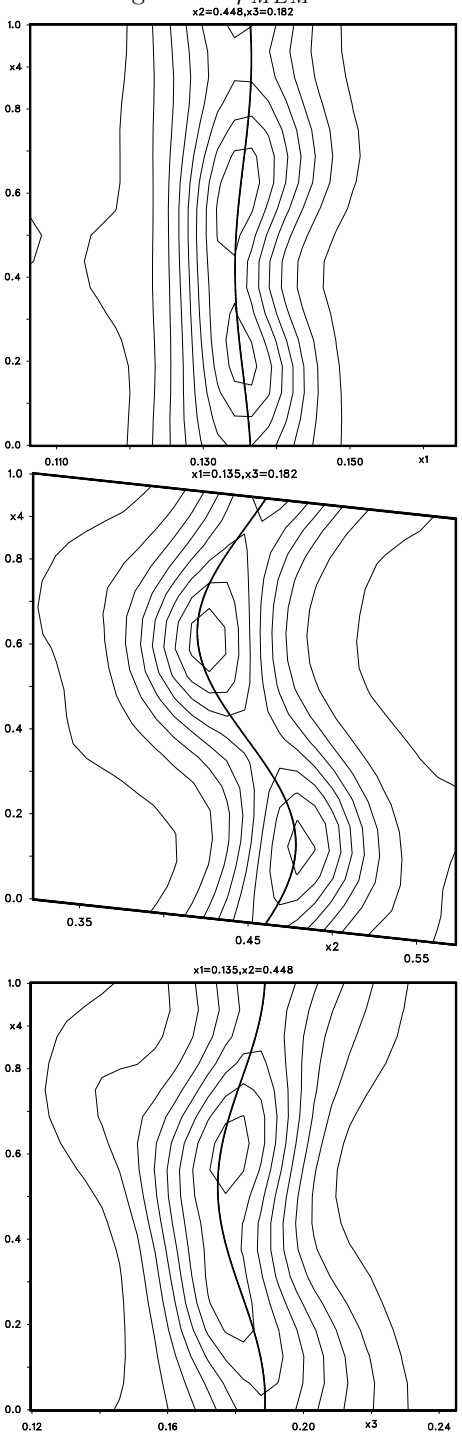


Figure 37: F_{obs} O16

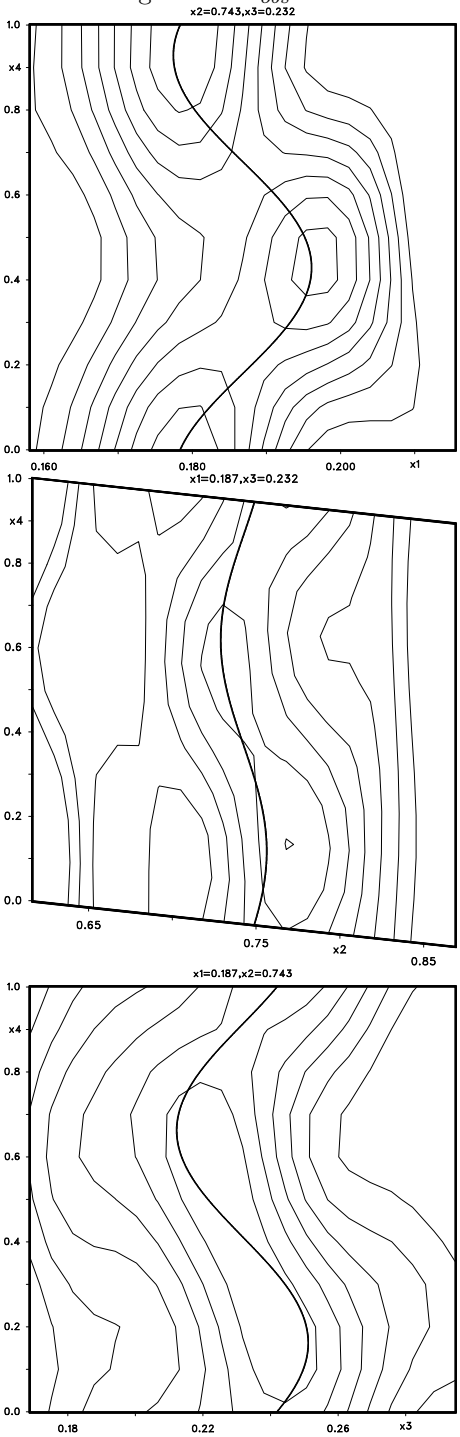


Figure 38: ρ_{MEM} O16

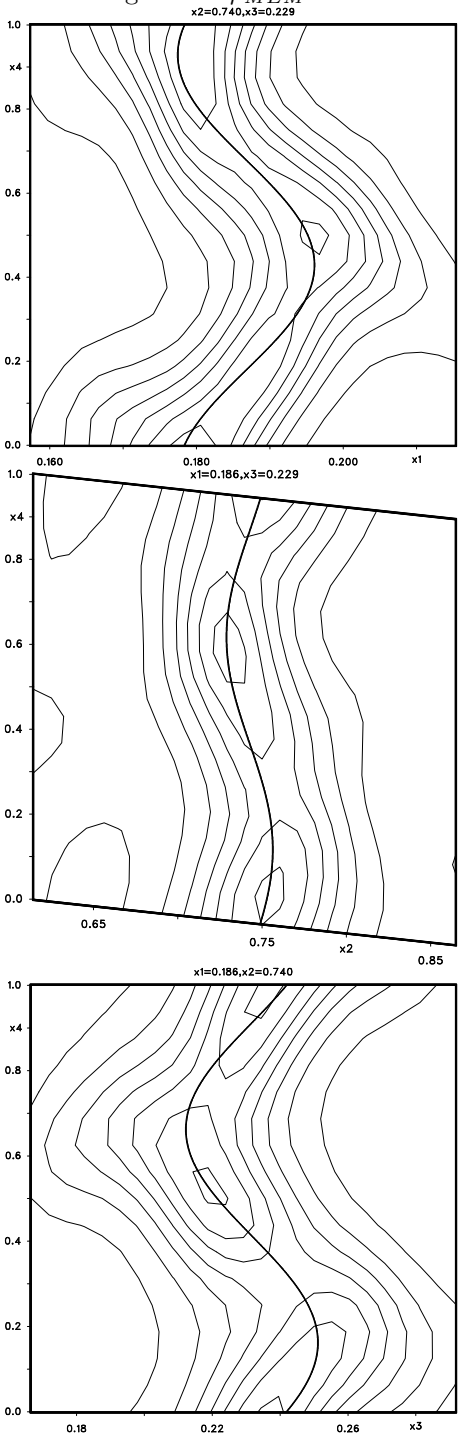


Figure 39: F_{obs} Ga4

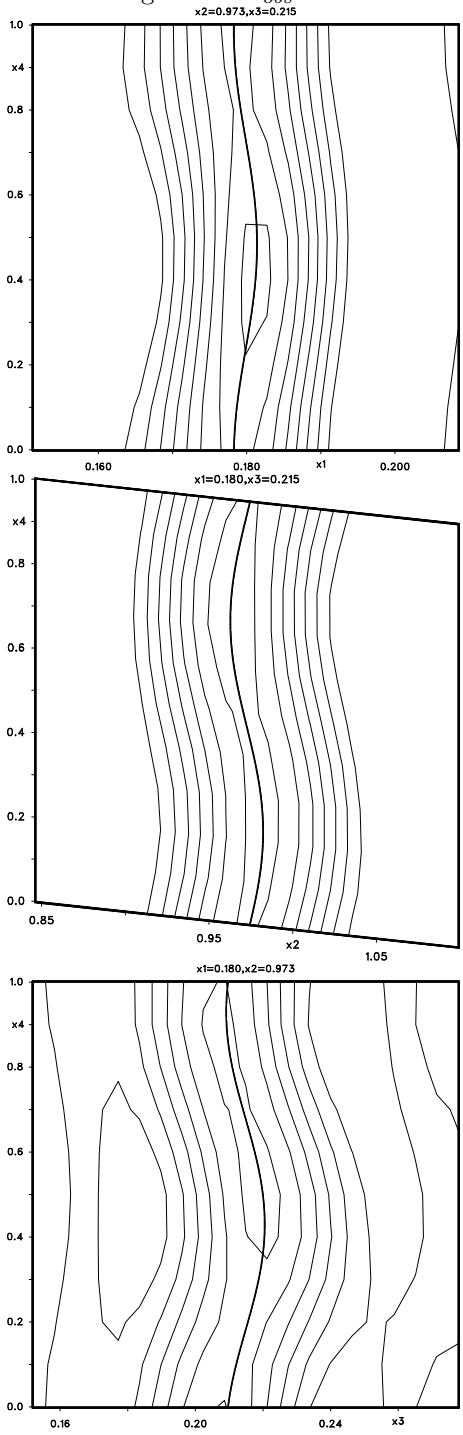


Figure 40: ρ_{MEM} Ga4

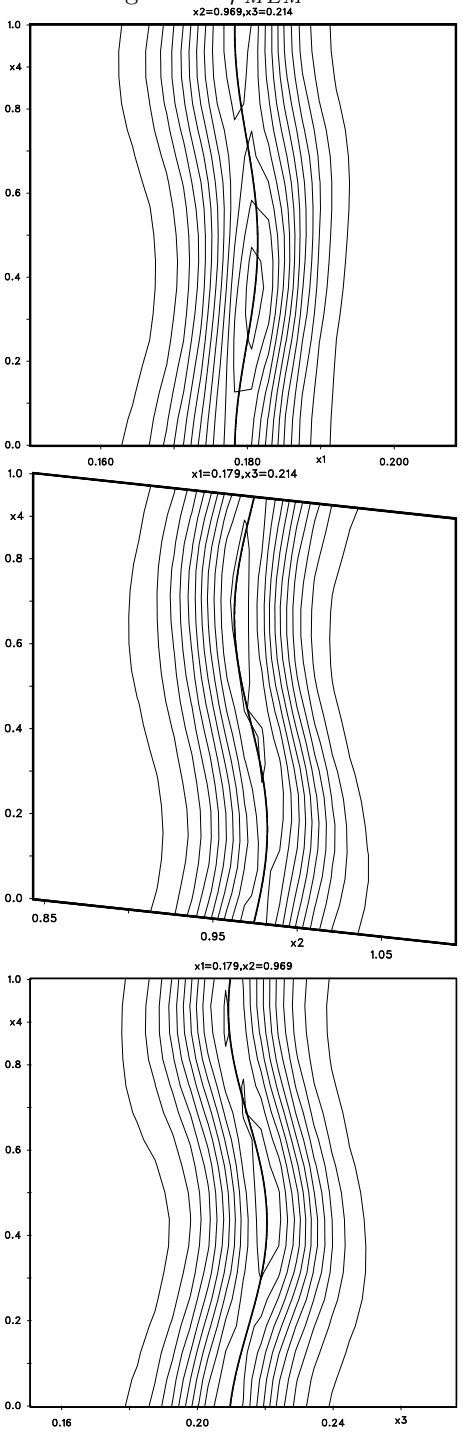


Figure 41: F_{obs} O1

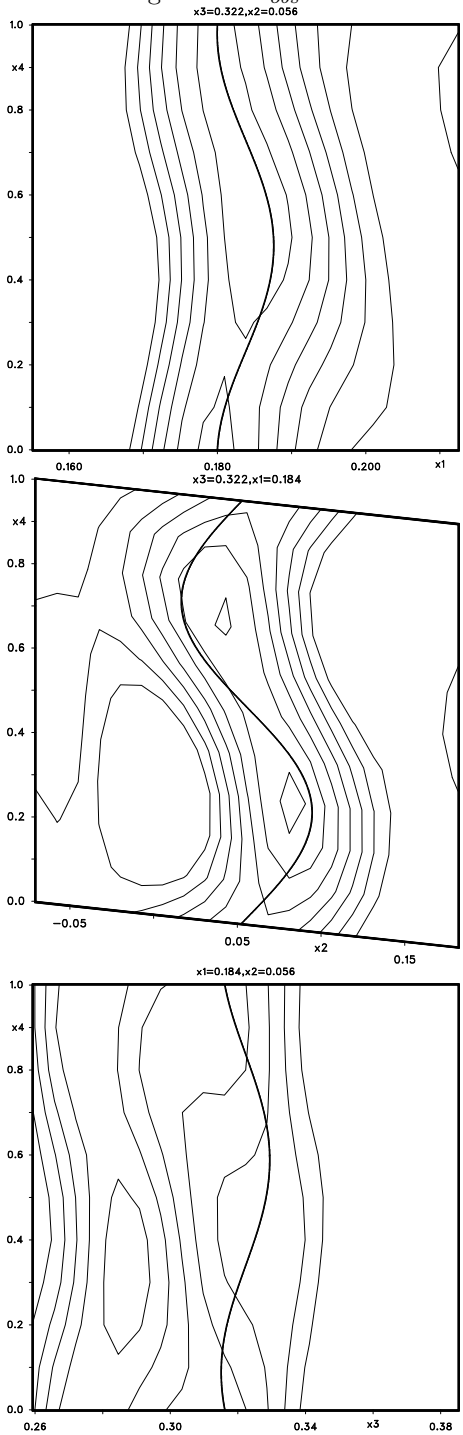


Figure 42: ρ_{MEM} O1

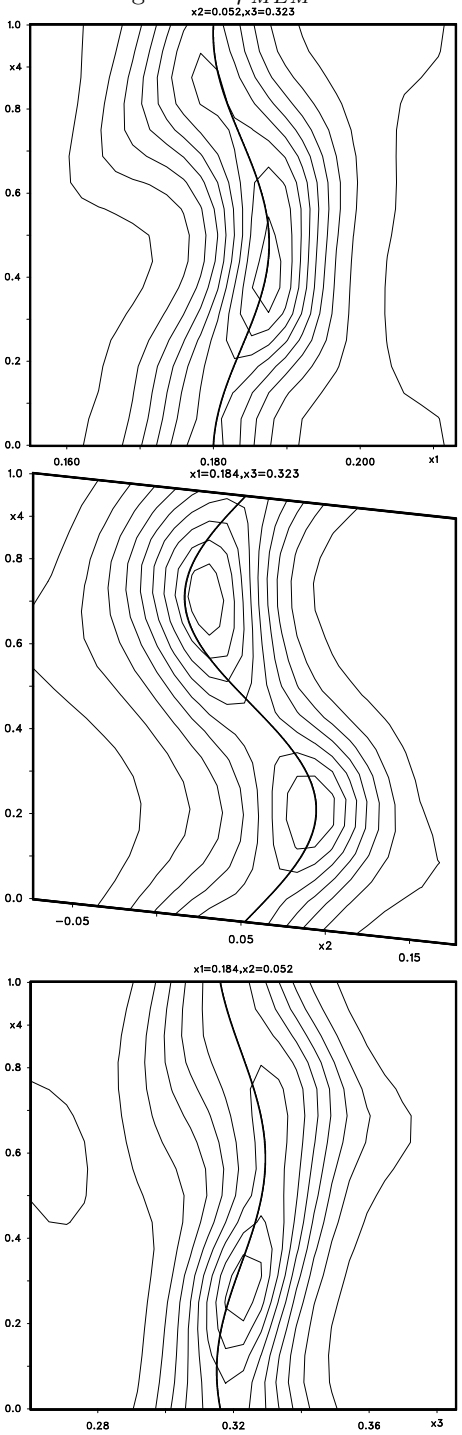


Figure 43: F_{obs} O19

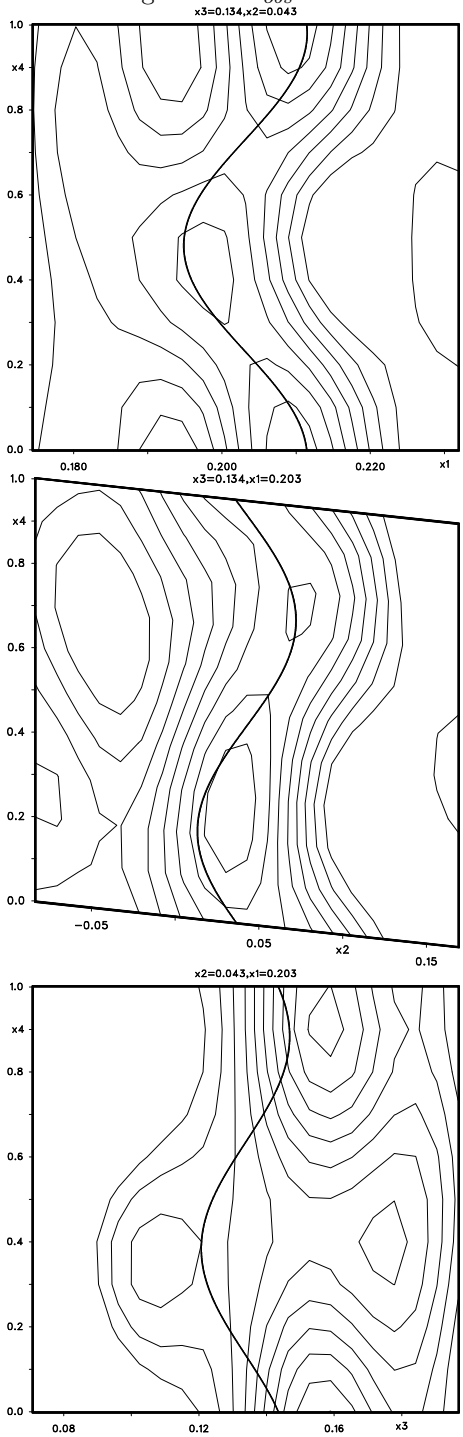


Figure 44: ρ_{MEM} O19

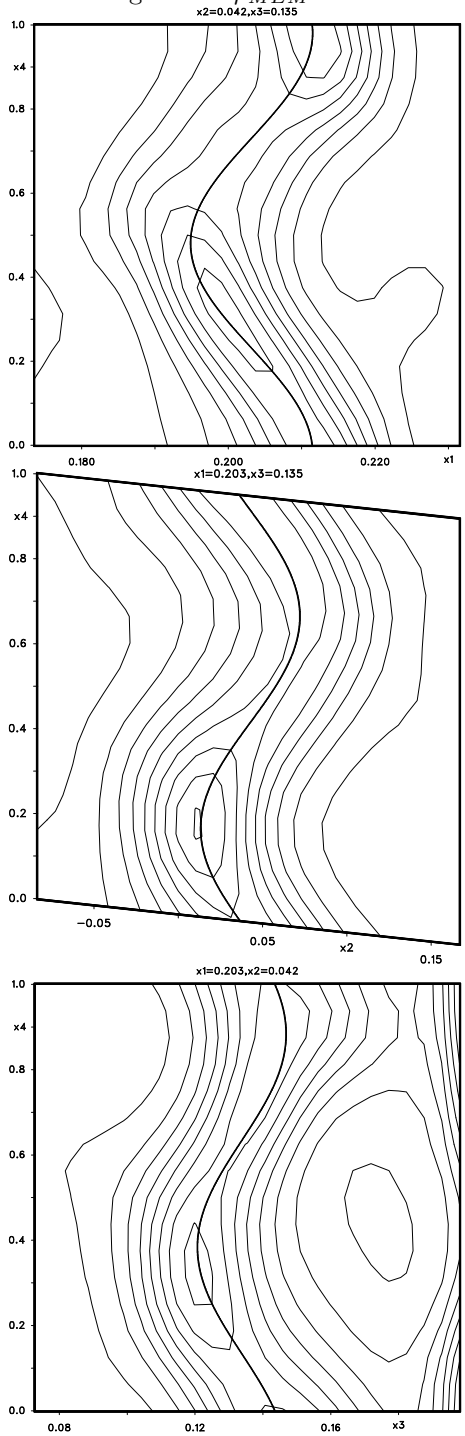


Figure 45: F_{obs} O12

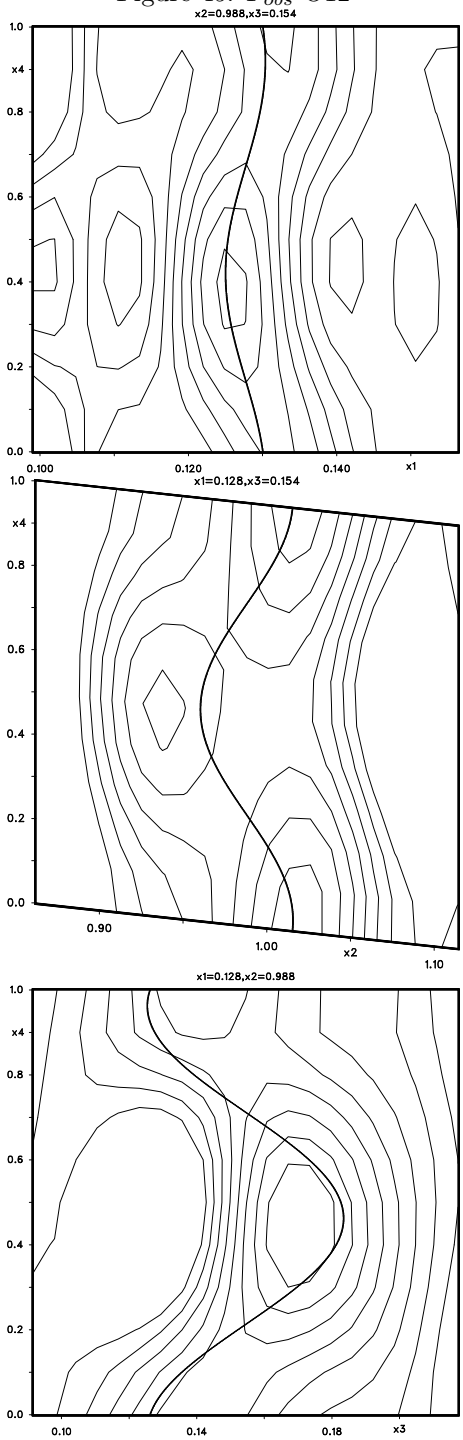


Figure 46: ρ_{MEM} O12

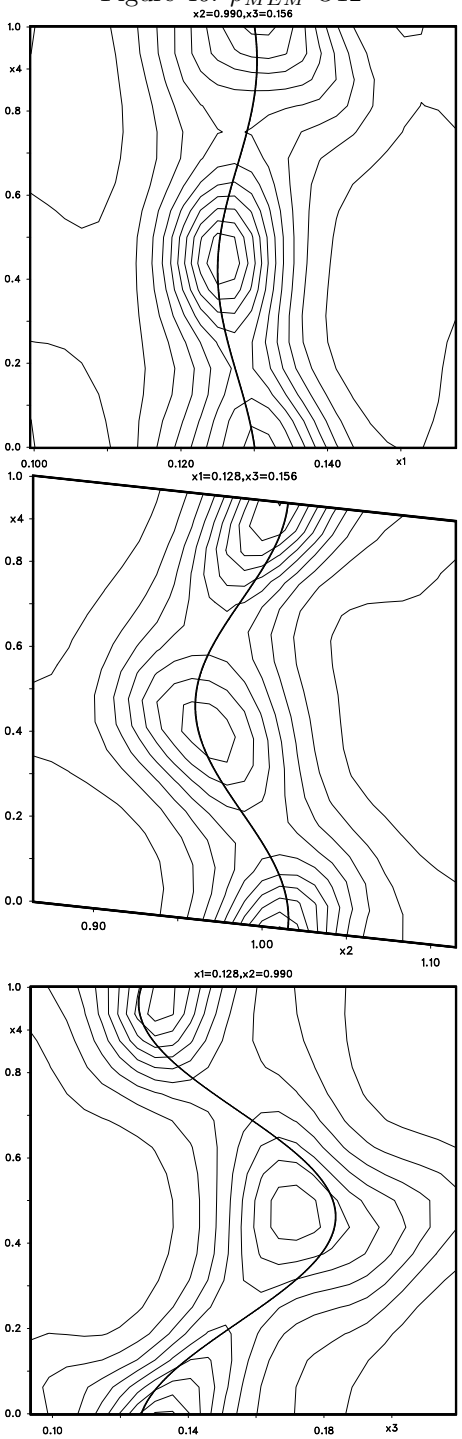


Figure 47: F_{obs} Ga3

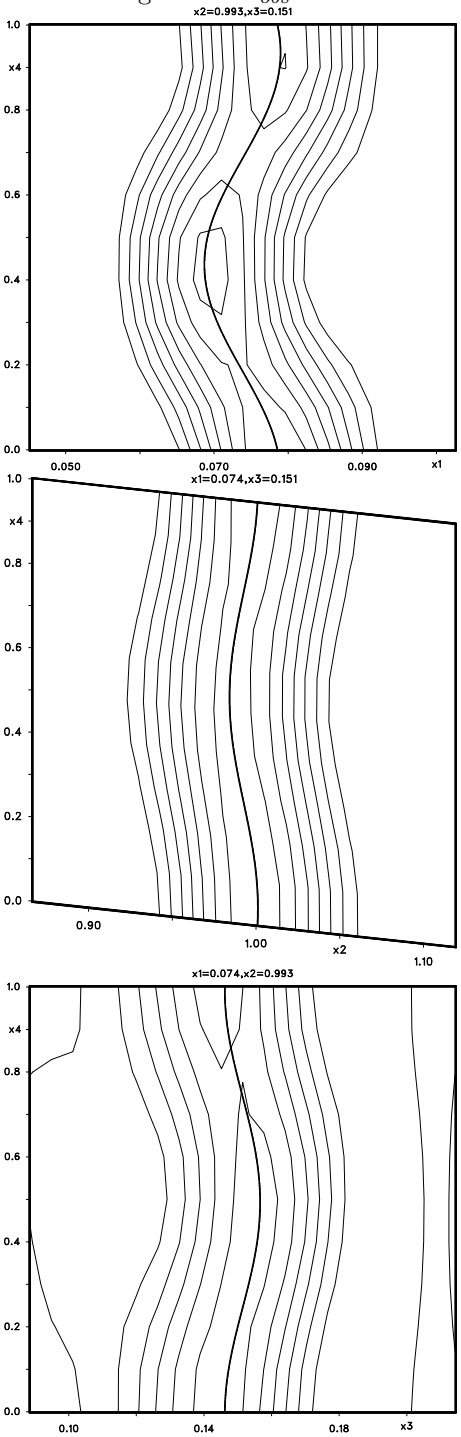


Figure 48: ρ_{MEM} Ga3

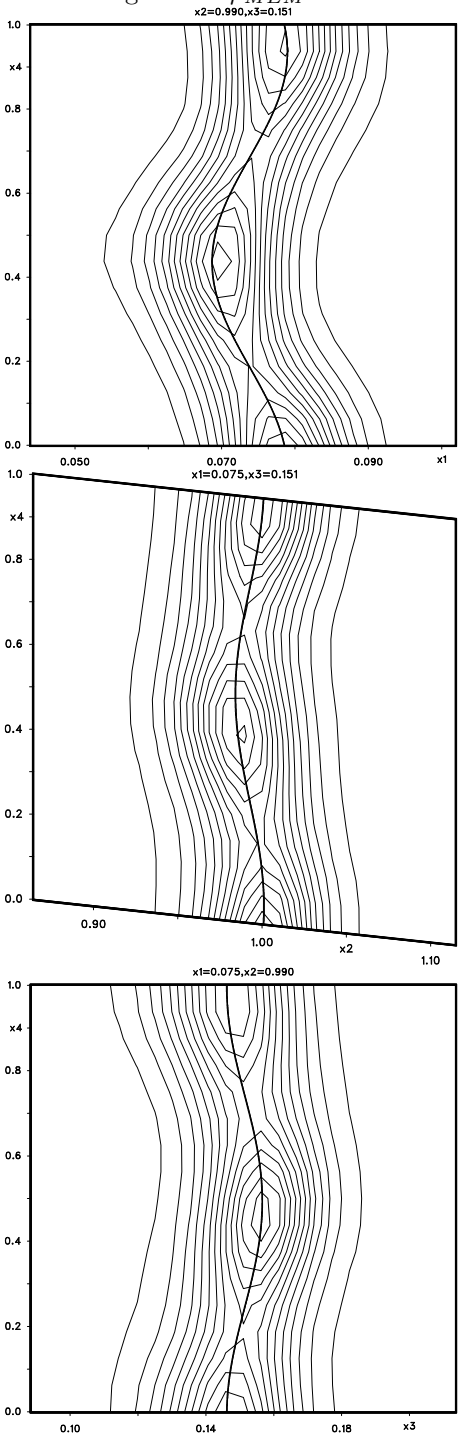


Figure 49: F_{obs} O4

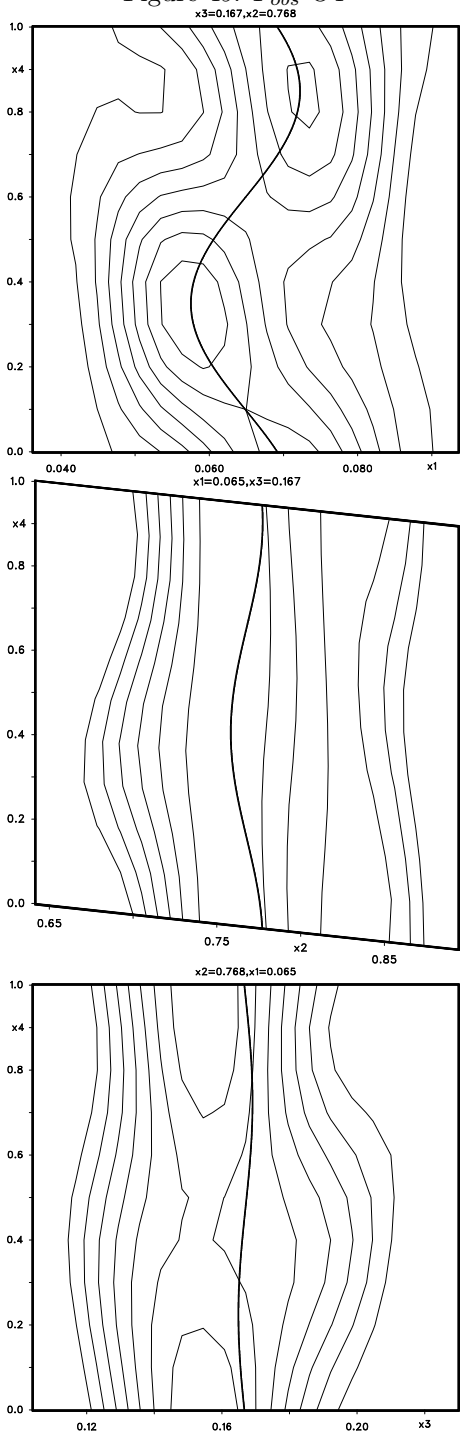


Figure 50: ρ_{MEM} O4

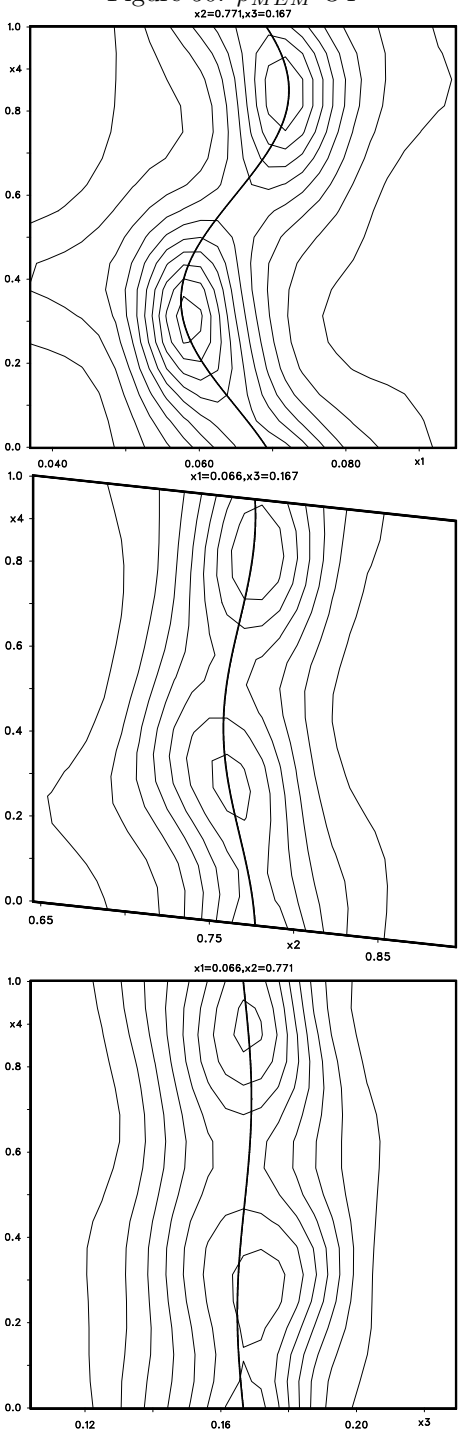


Figure 51: F_{obs} O9

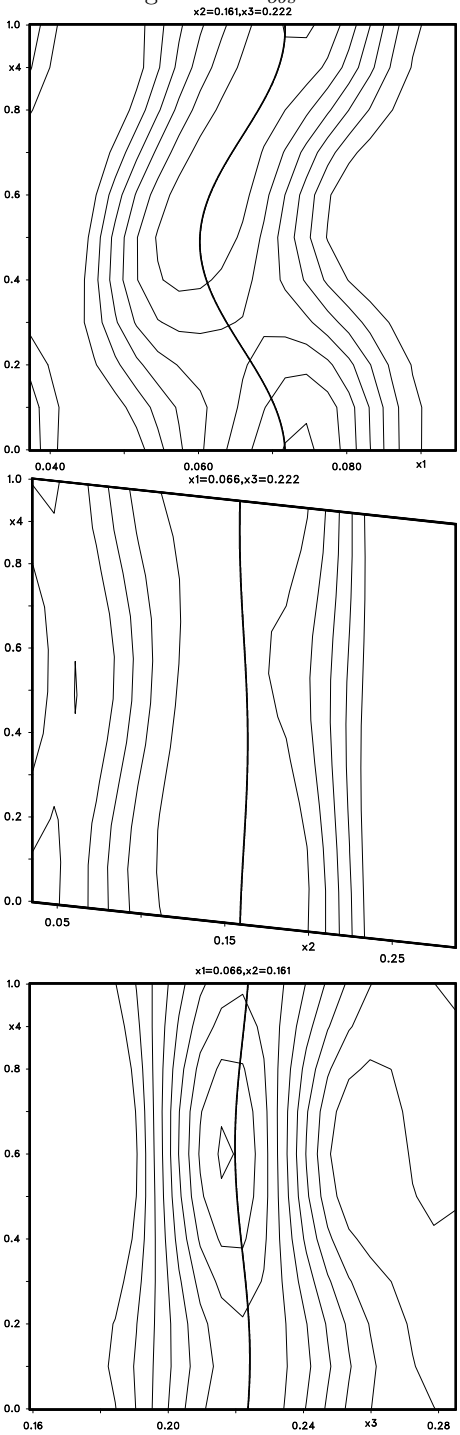


Figure 52: ρ_{MEM} O9

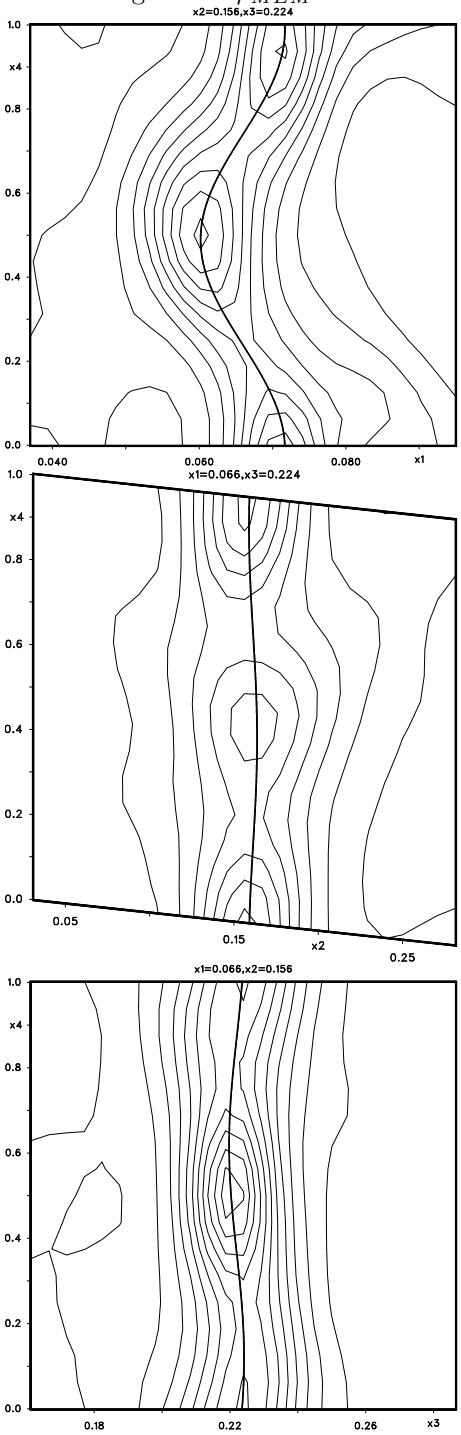


Figure 53: F_{obs} O6

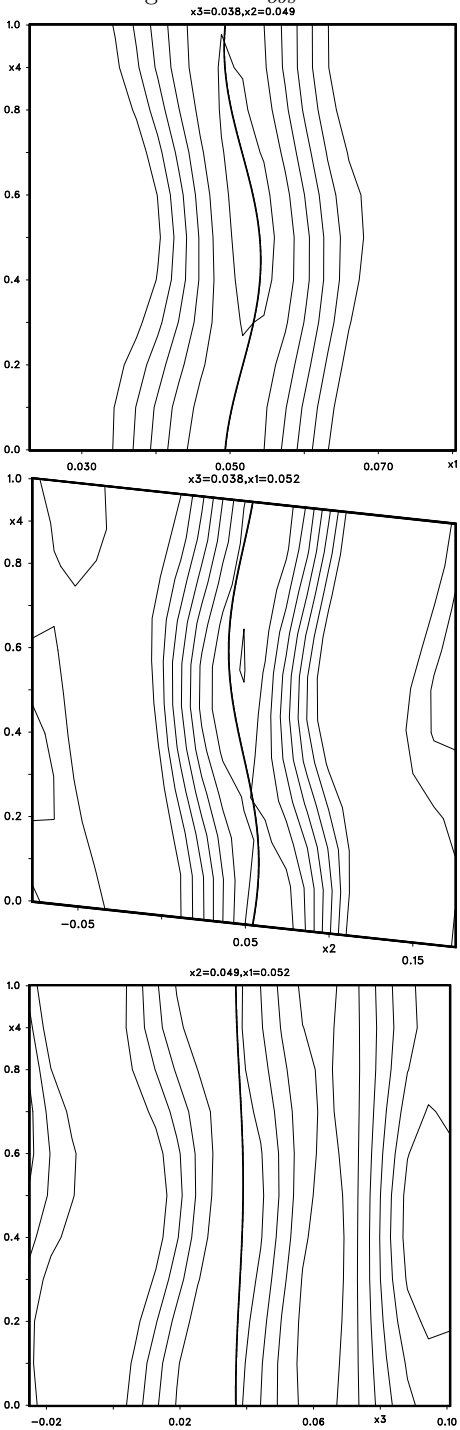


Figure 54: ρ_{MEM} O6

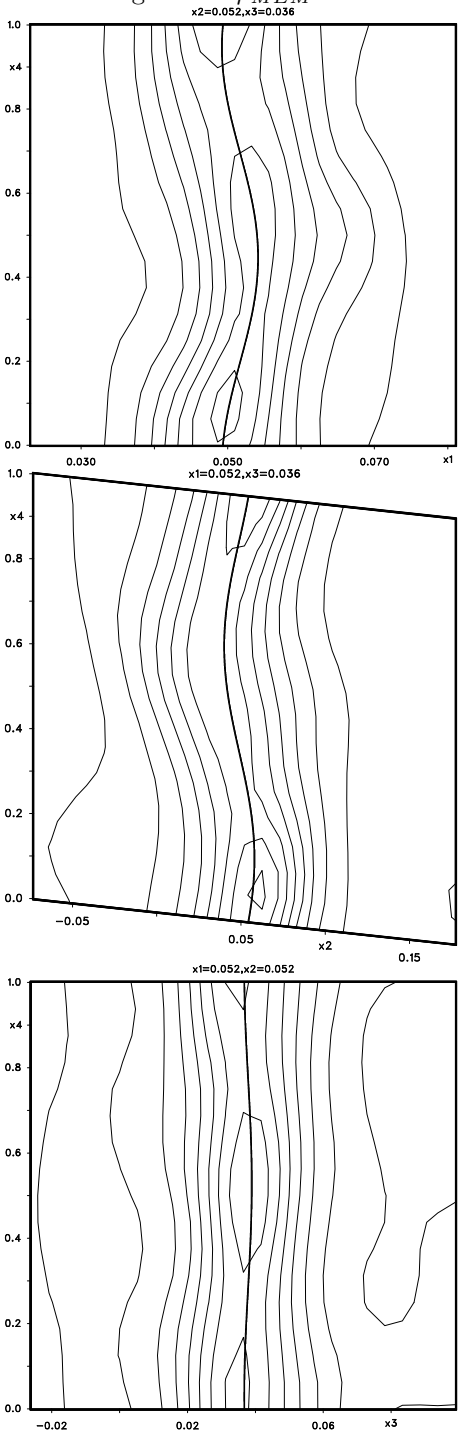


Figure 55: F_{obs} Ga2

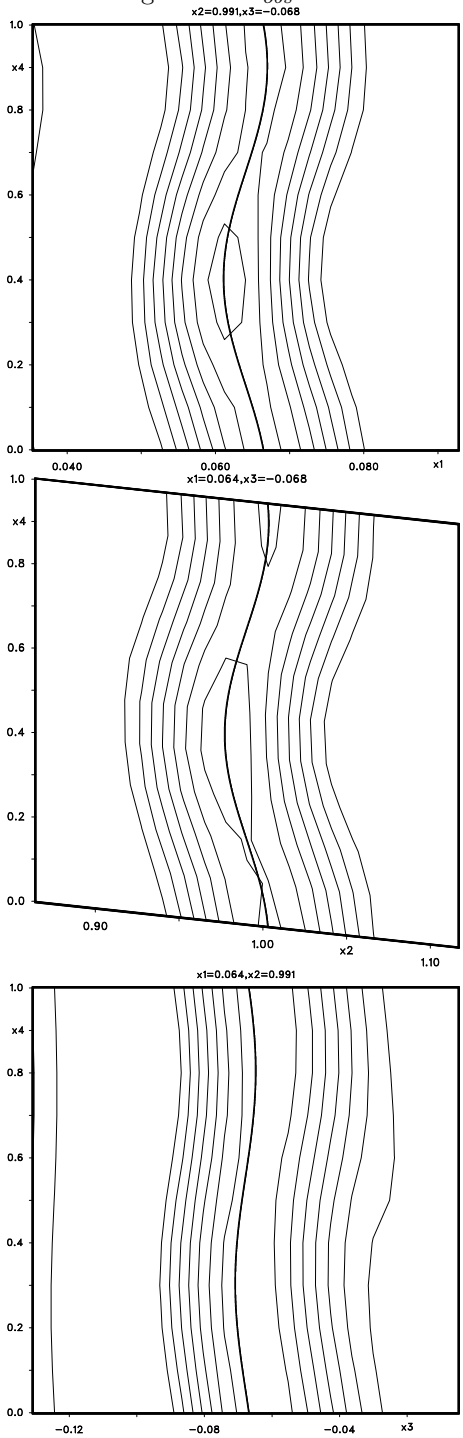


Figure 56: ρ_{MEM} Ga2

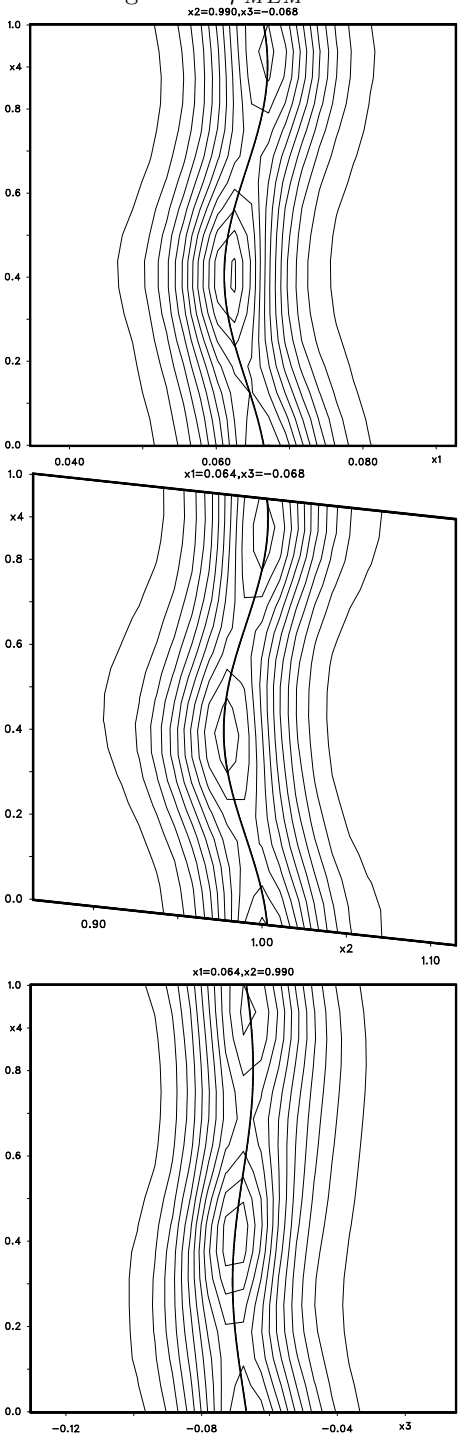


Figure 57: F_{obs} O15

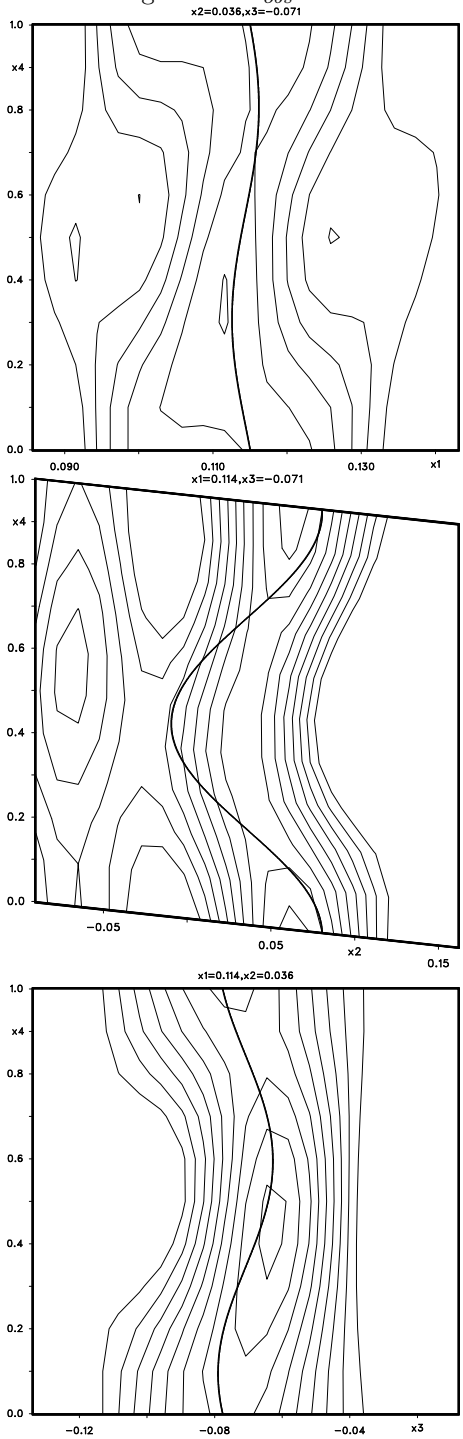


Figure 58: ρ_{MEM} O15

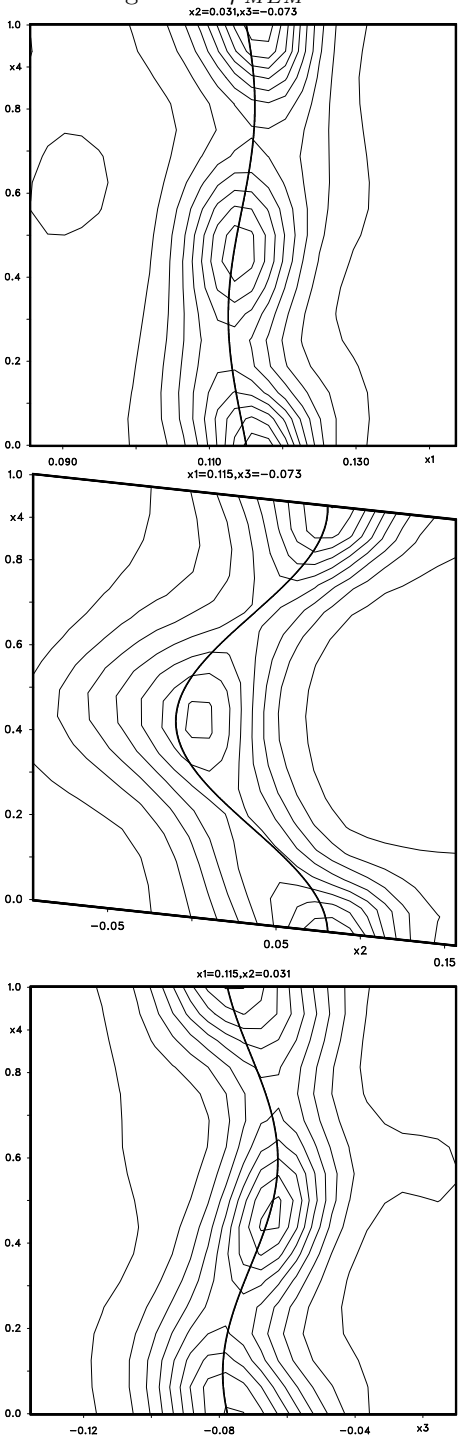


Figure 59: F_{obs} O3

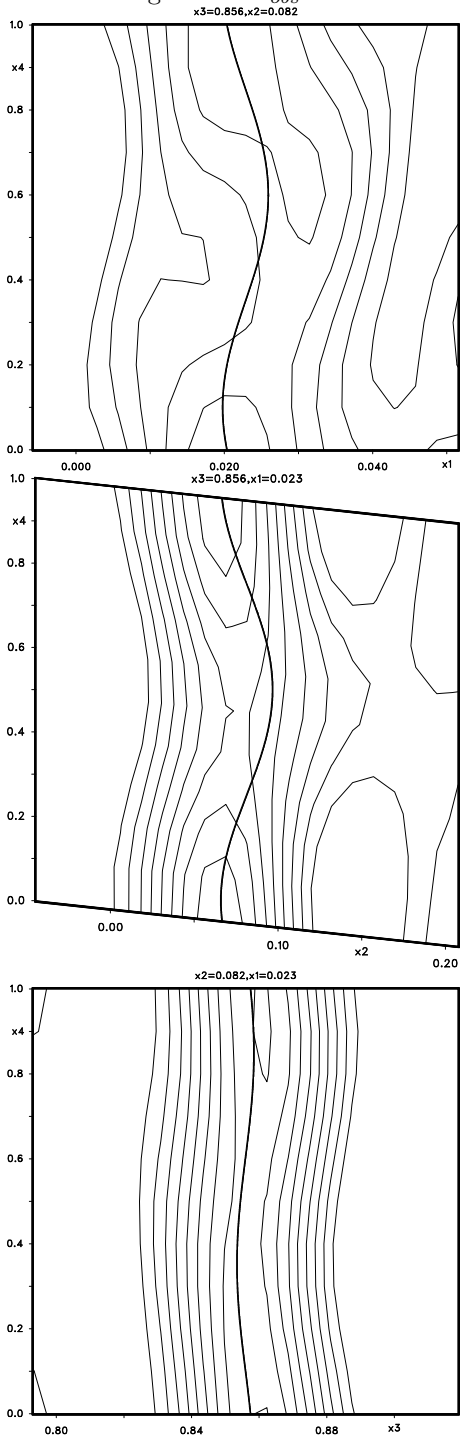


Figure 60: ρ_{MEM} O3

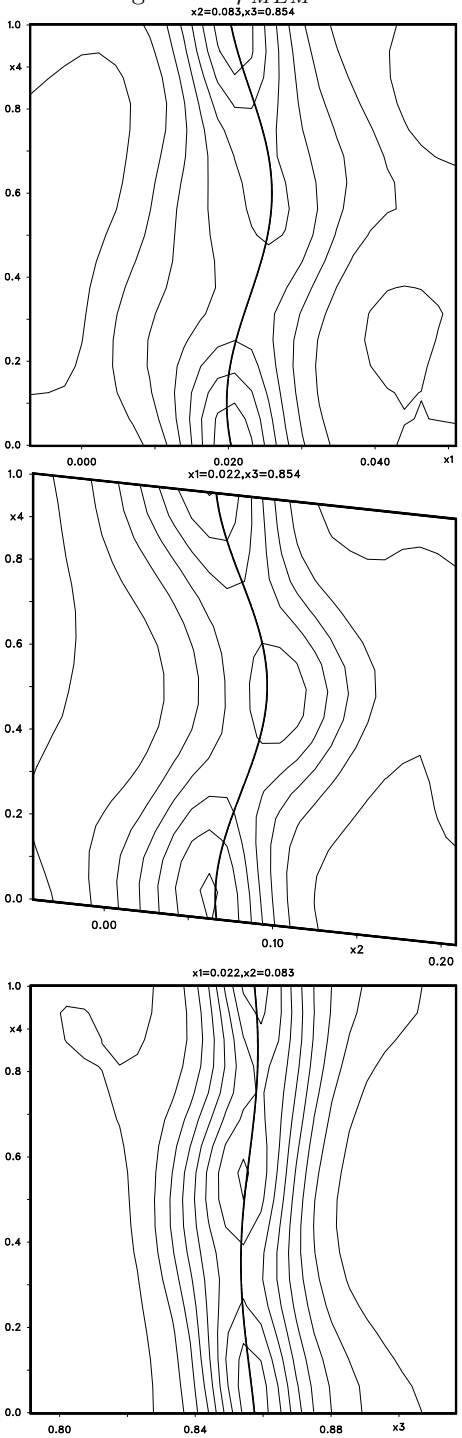


Figure 61: F_{obs} O11

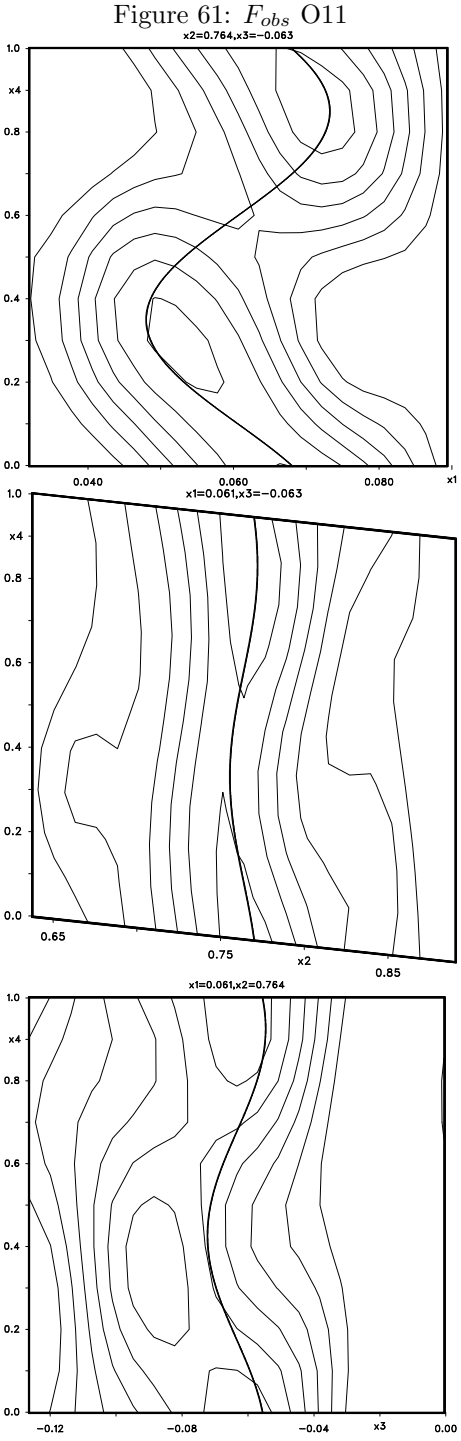


Figure 62: ρ_{MEM} O11

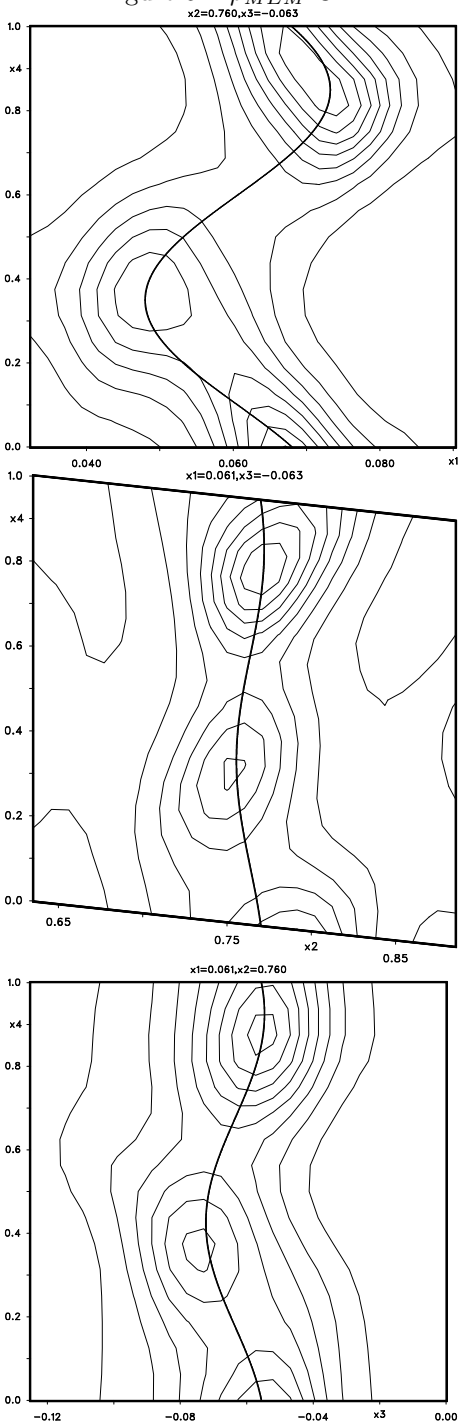


Figure 63: F_{obs} Ga1

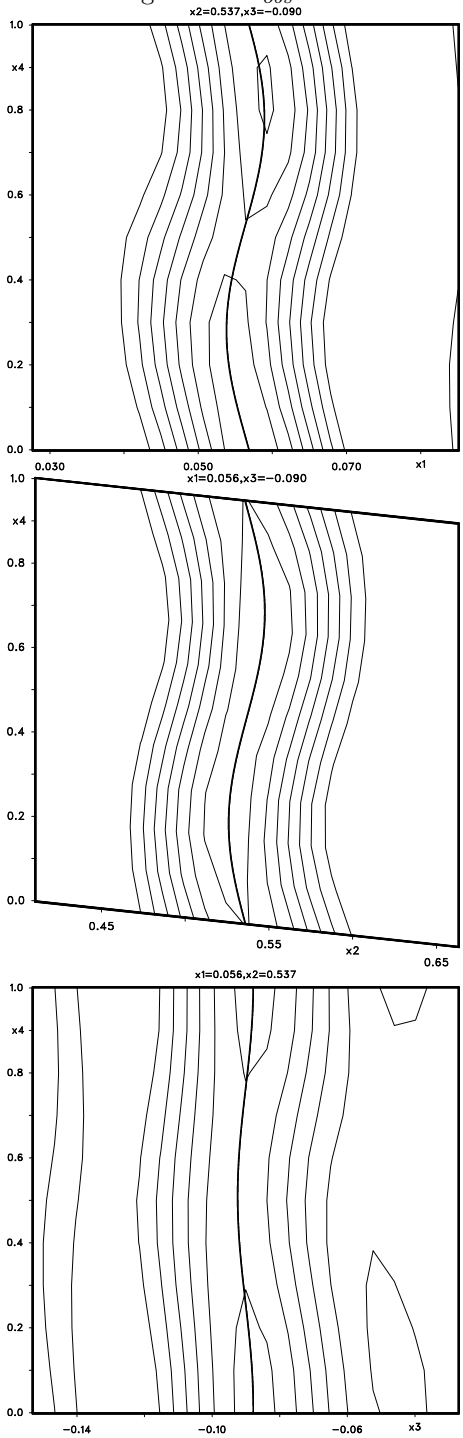


Figure 64: ρ_{MEM} Ga1

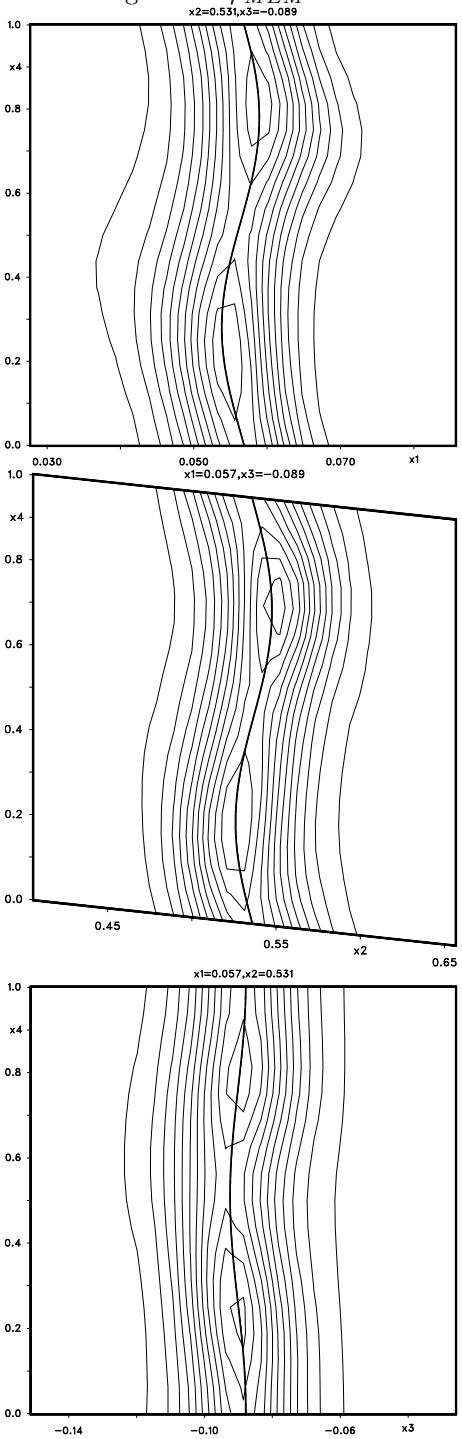


Figure 65: F_{obs} O14

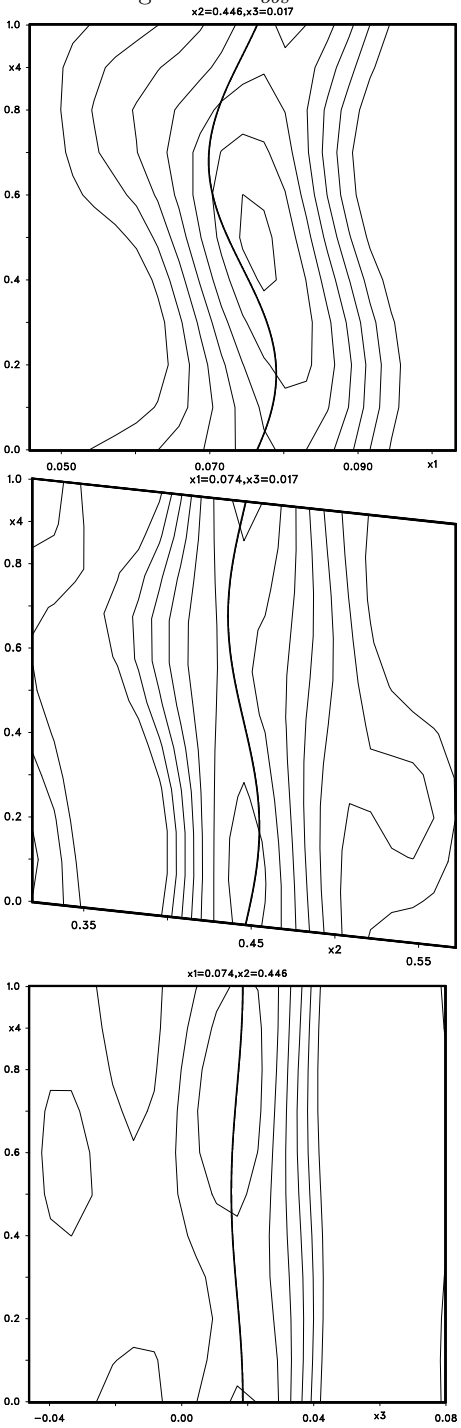


Figure 66: ρ_{MEM} O14

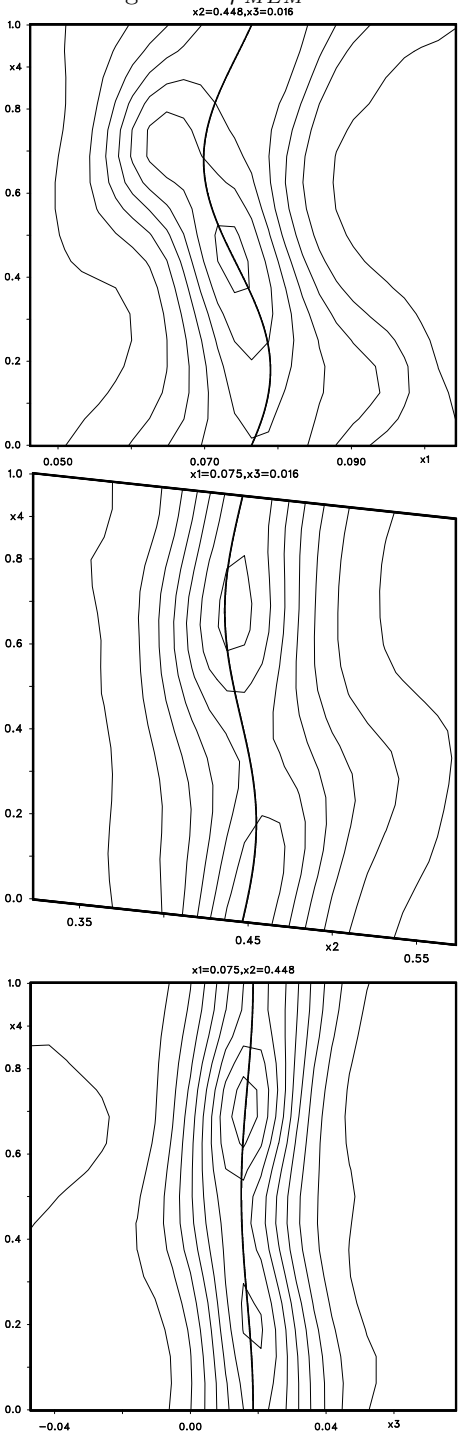


Figure 67: F_{obs} O10

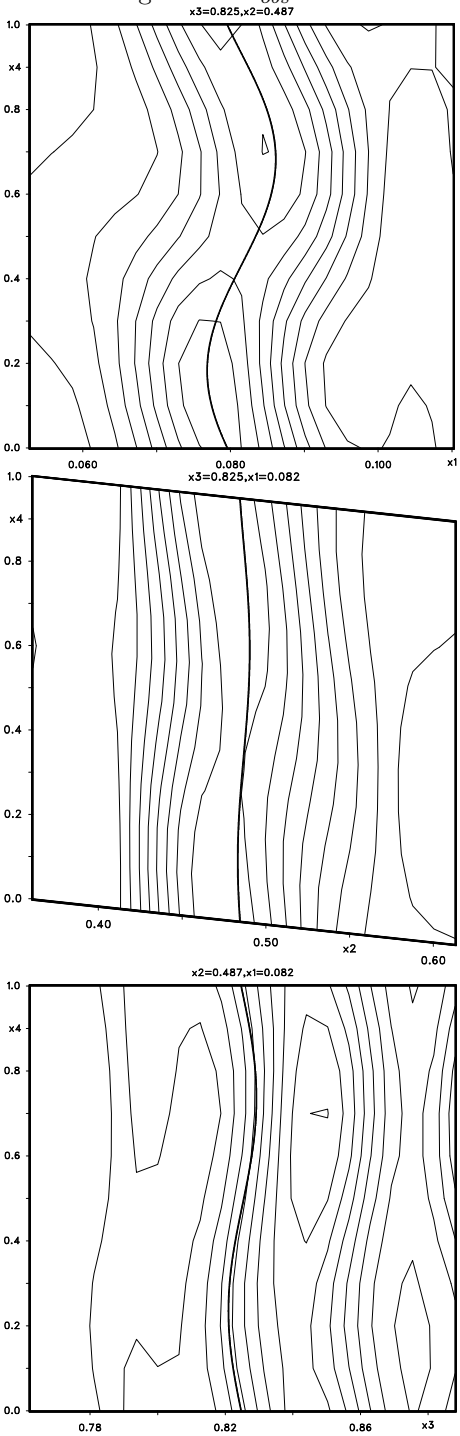


Figure 68: ρ_{MEM} O10

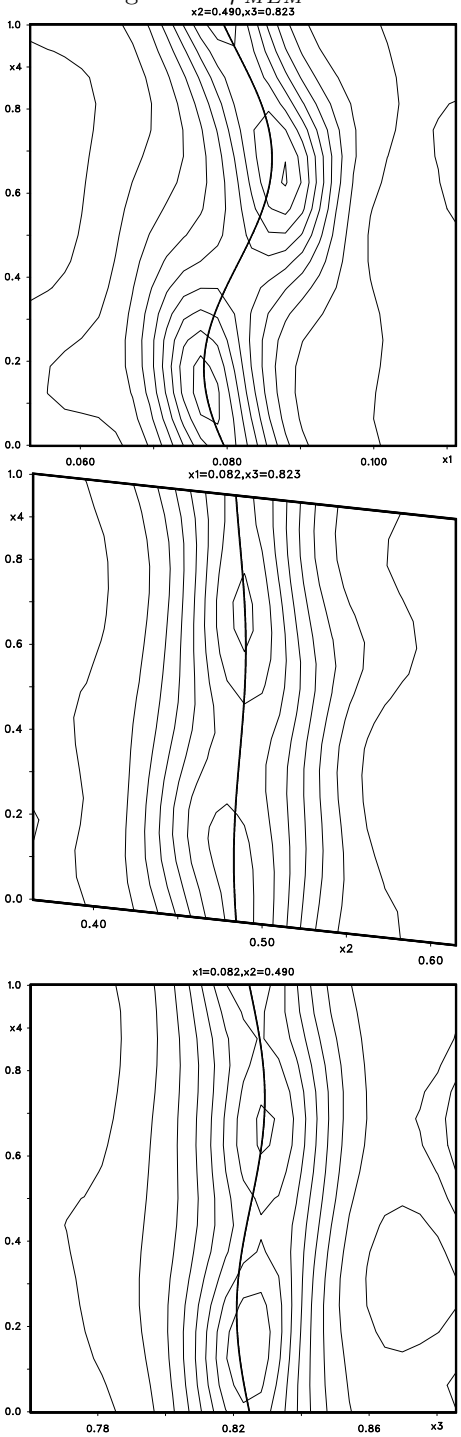


Figure 69: F_{obs} O17

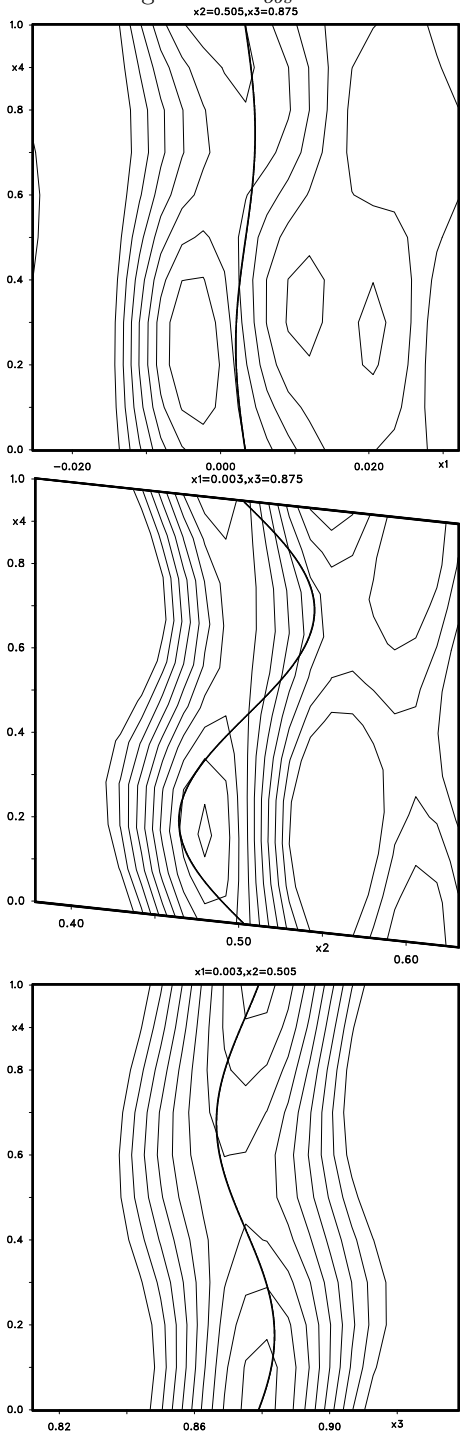


Figure 70: ρ_{MEM} O17

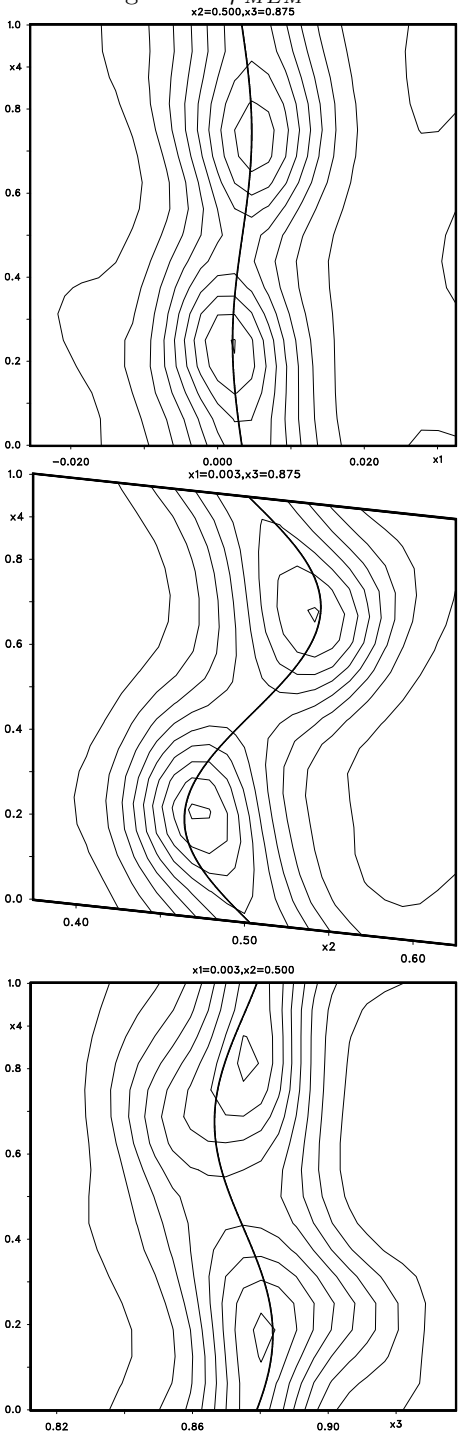


Figure 71: F_{obs} Sr1

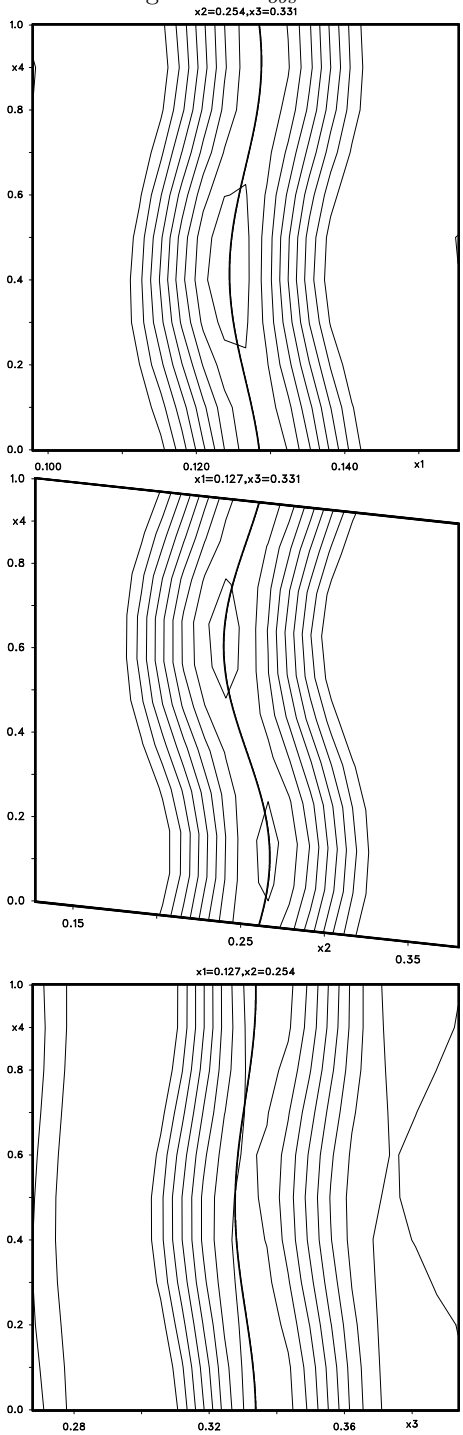


Figure 72: ρ_{MEM} Sr1

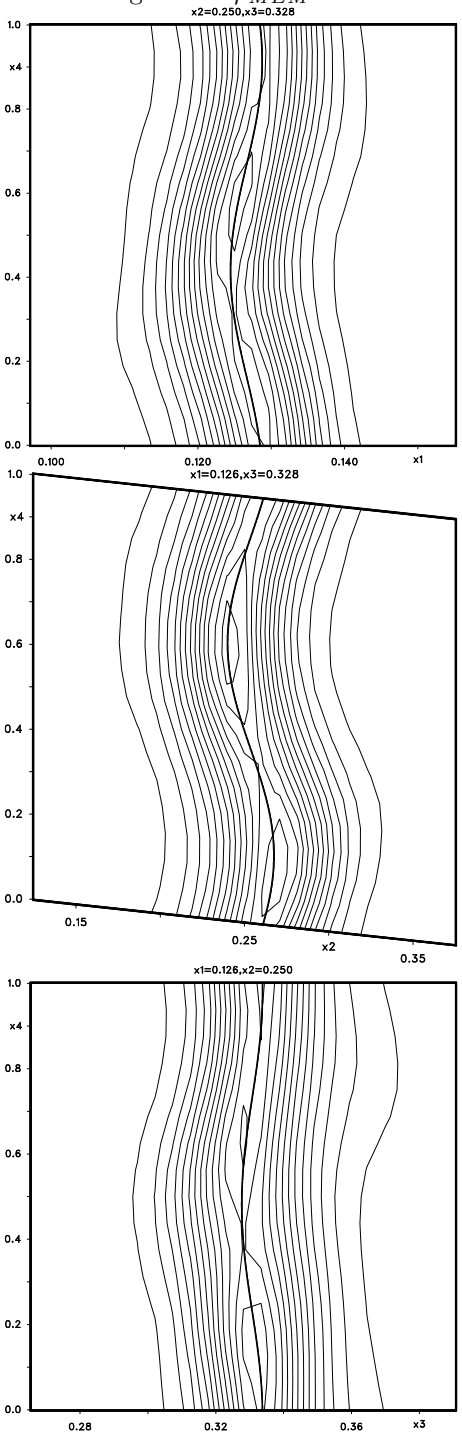


Figure 73: F_{obs} Sr2

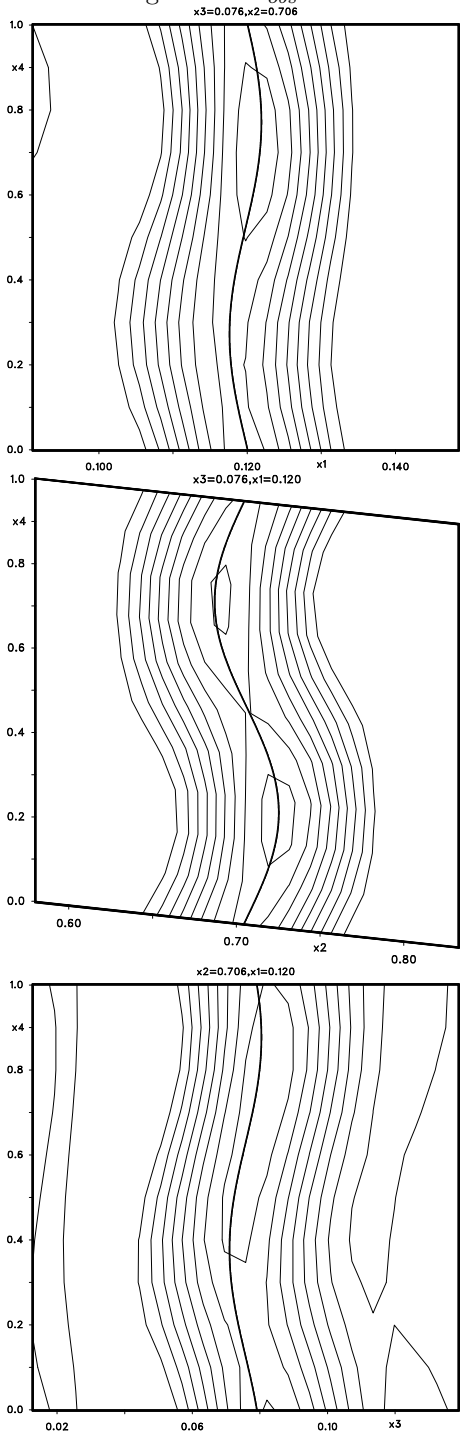


Figure 74: ρ_{MEM} Sr2

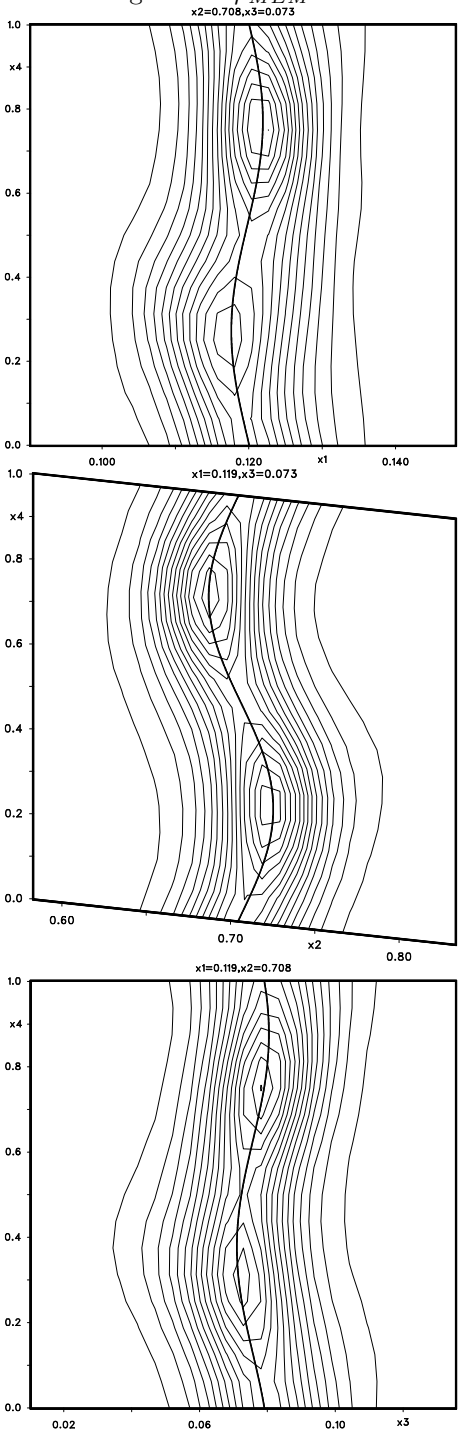


Figure 75: F_{obs} Sr3

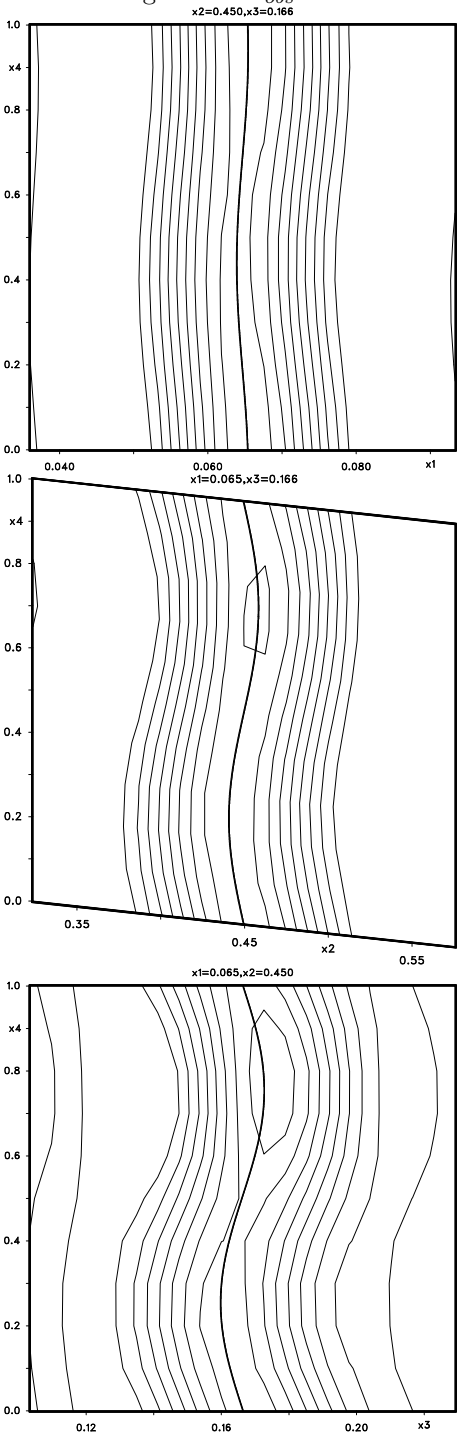


Figure 76: ρ_{MEM} Sr3

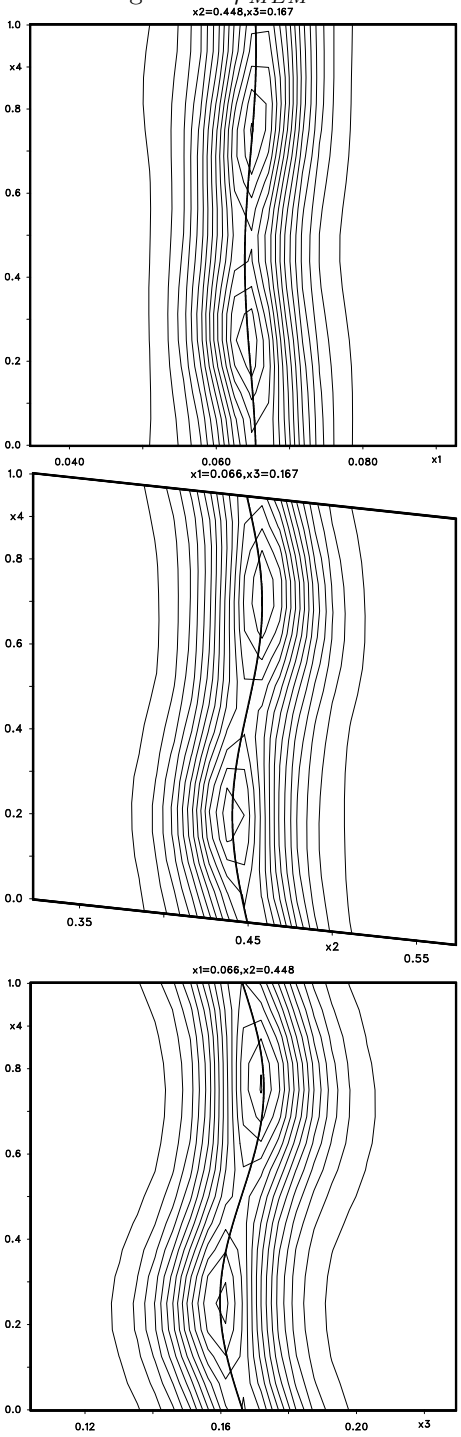


Figure 77: F_{obs} Sr4

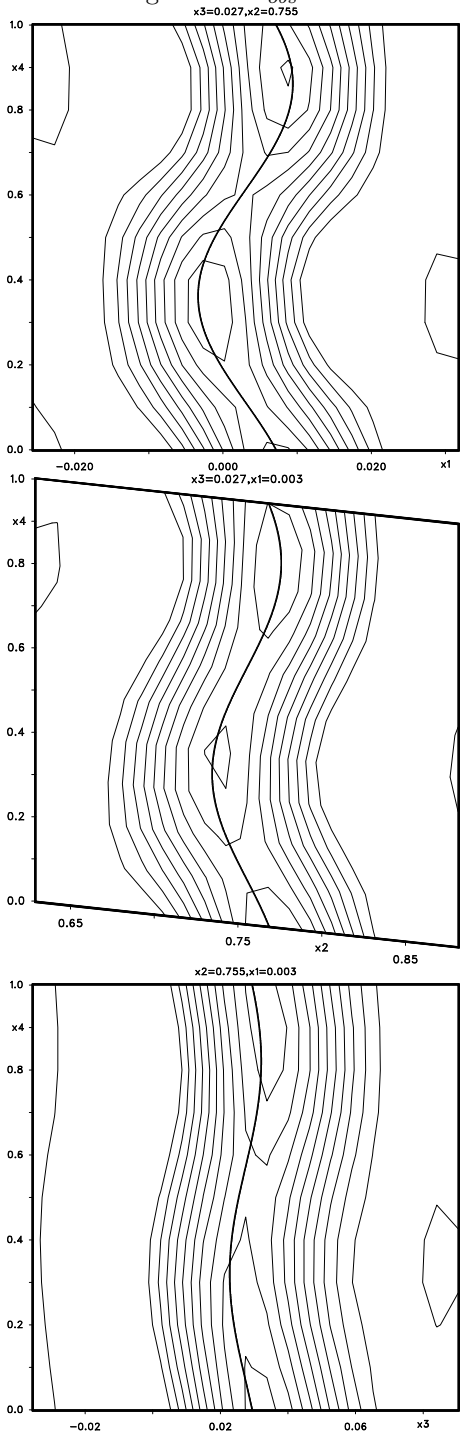


Figure 78: ρ_{MEM} Sr4

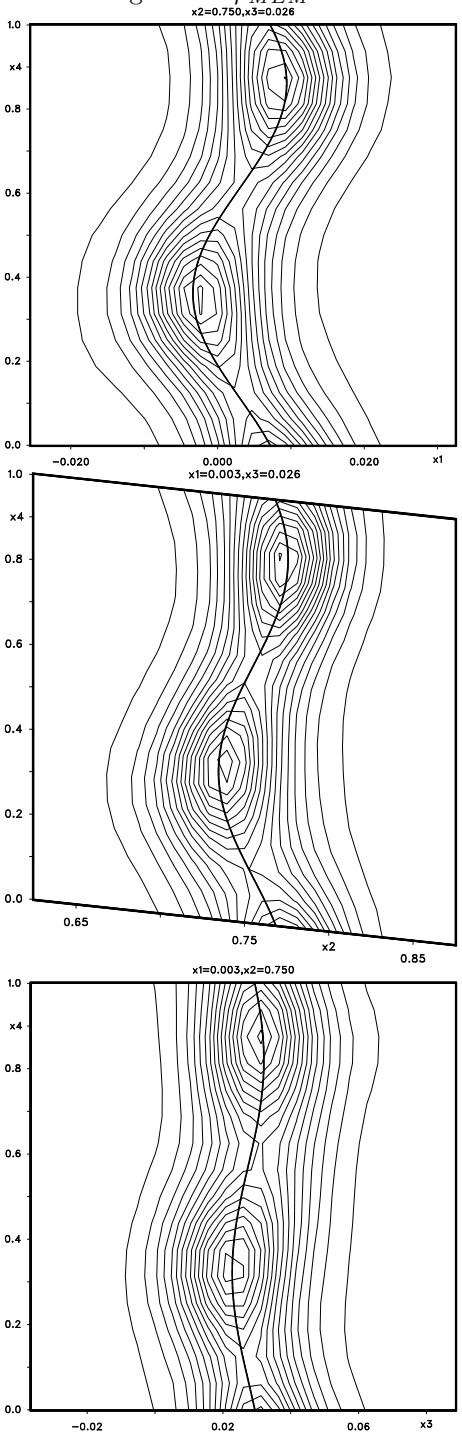


Figure 79: F_{obs} Sr5

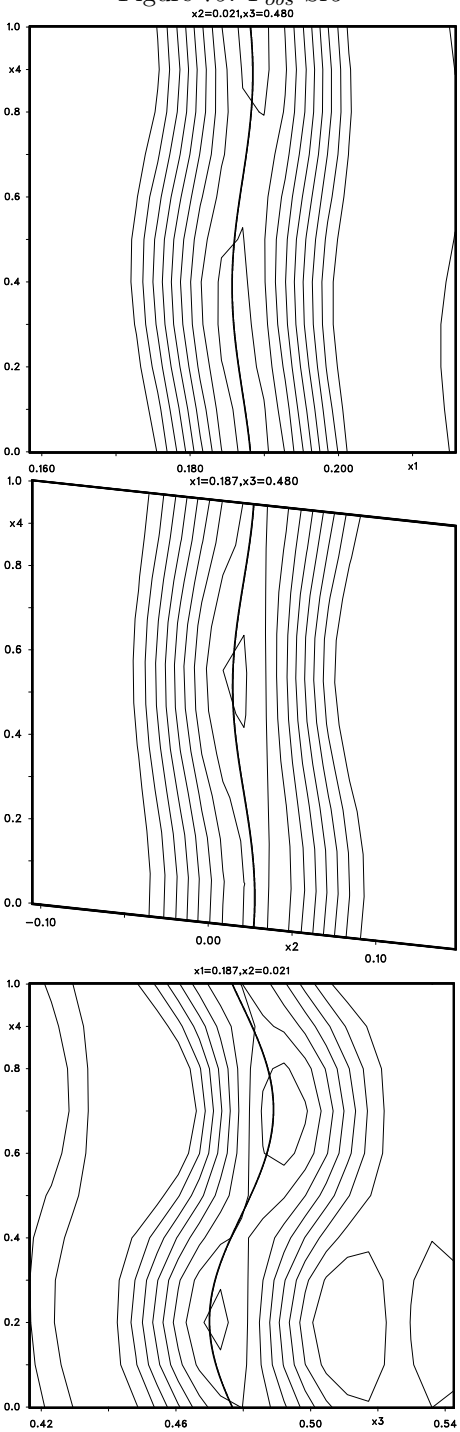


Figure 80: ρ_{MEM} Sr5

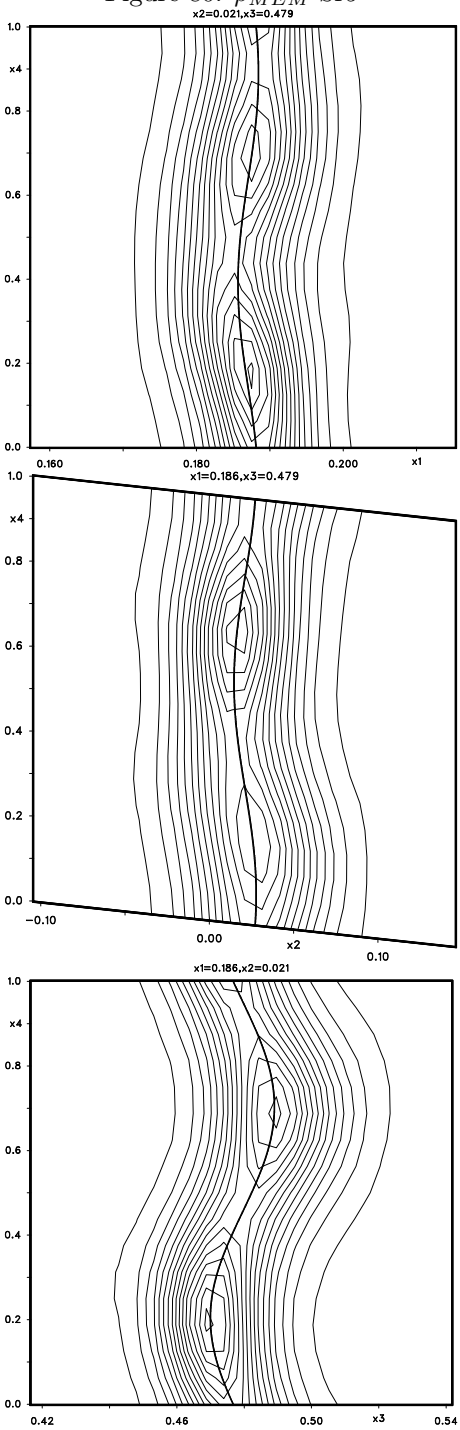


Figure 81: F_{obs} Sr6

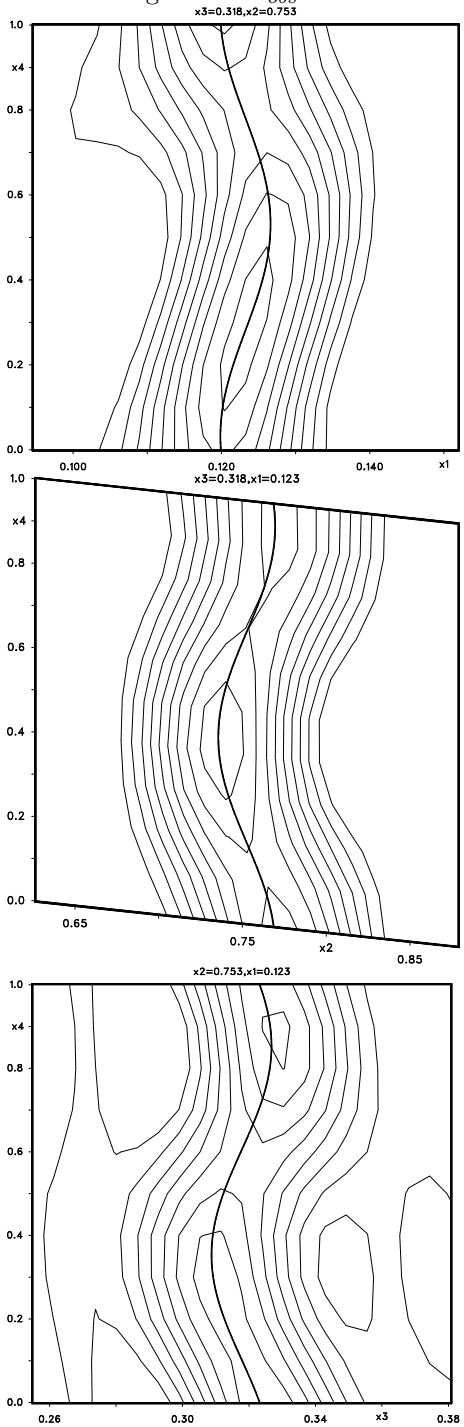


Figure 82: ρ_{MEM} Sr6

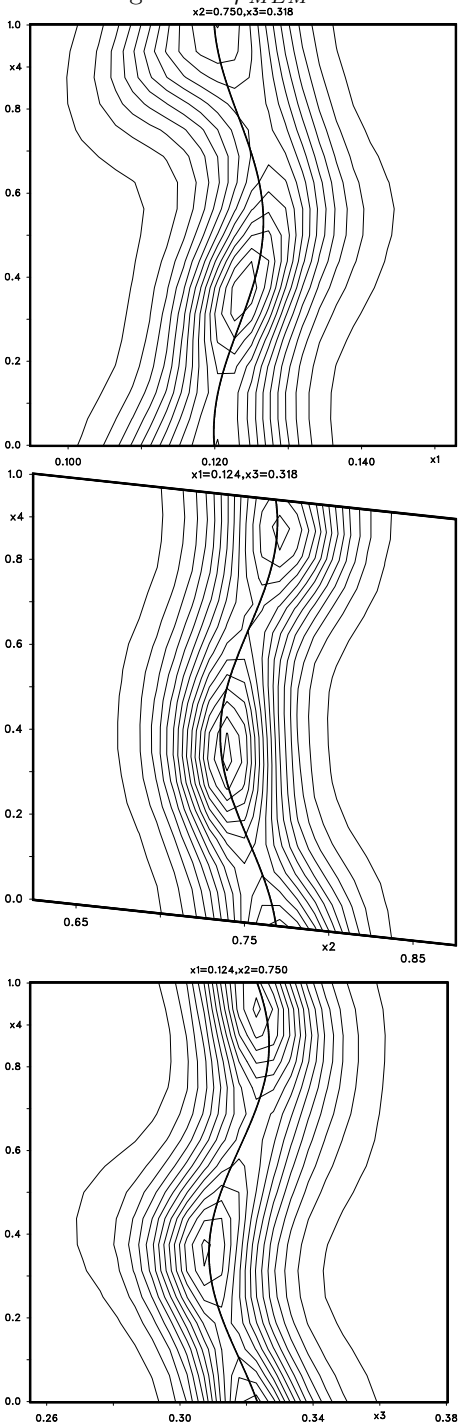


Figure 83: F_{obs} Sr7

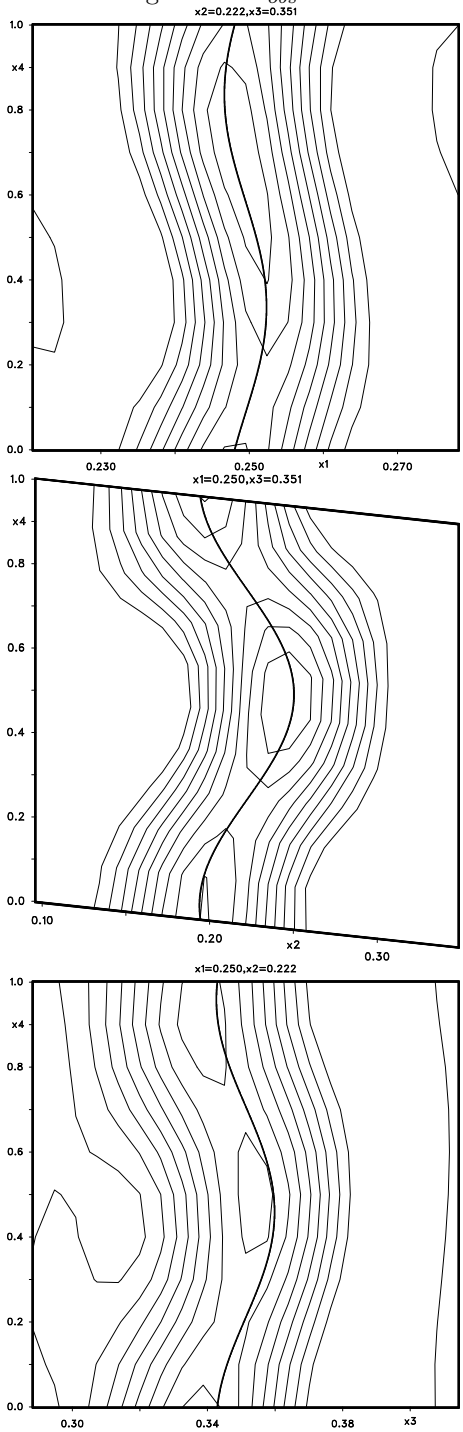


Figure 84: ρ_{MEM} Sr7

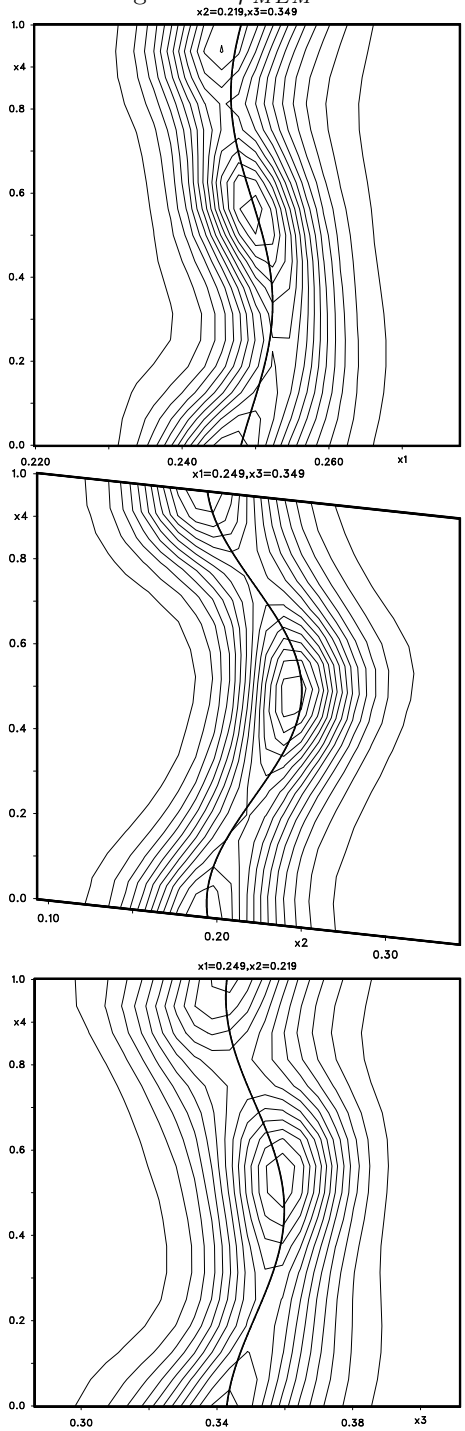


Figure 85: F_{obs} Sr8

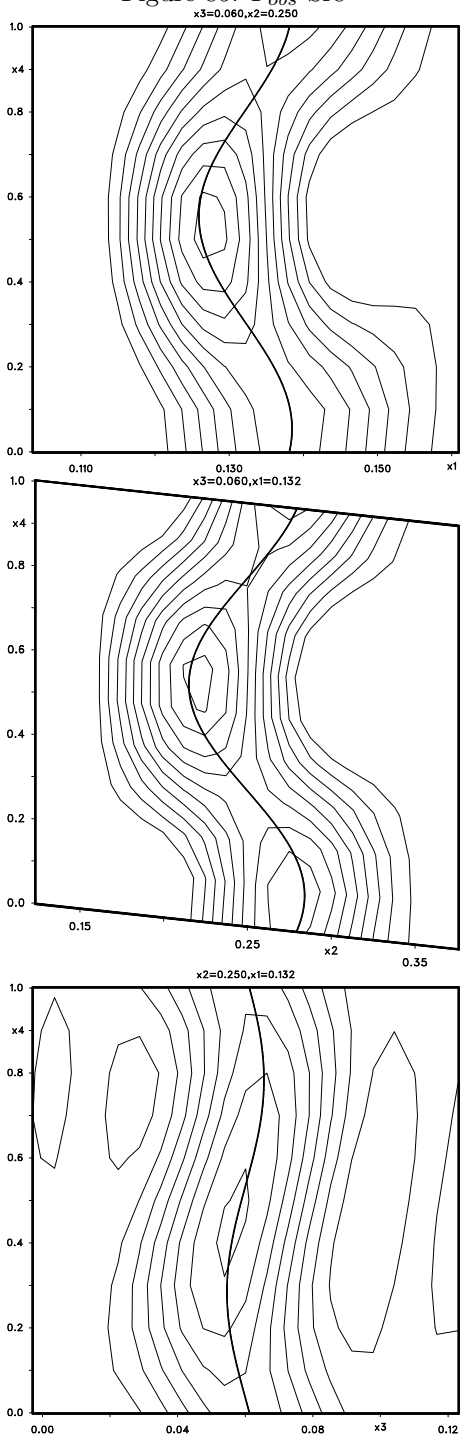


Figure 86: ρ_{MEM} Sr8

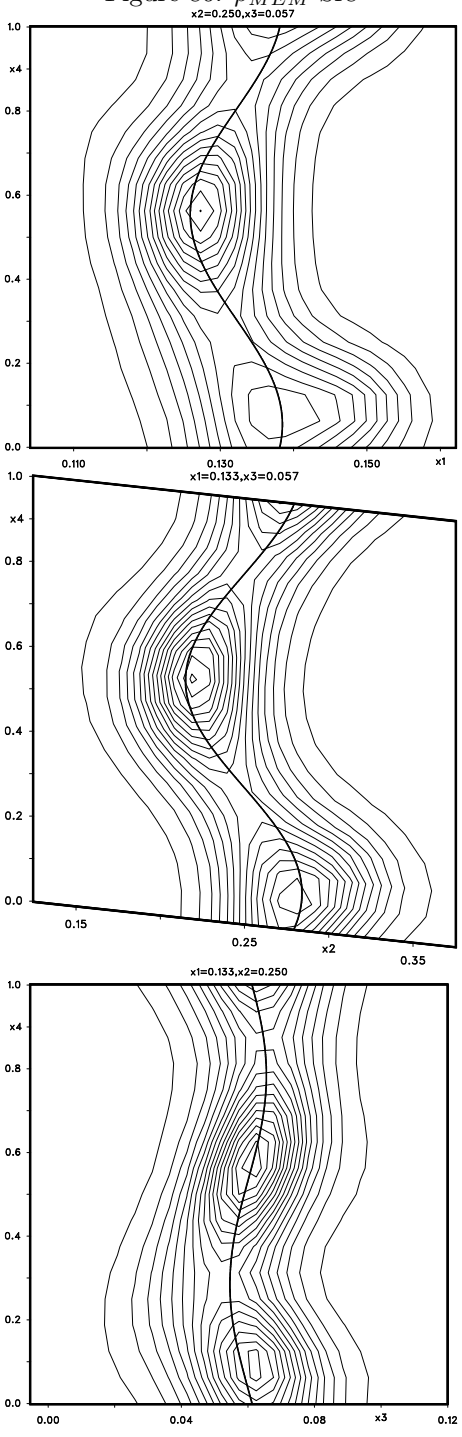


Figure 87: F_{obs} Sr9

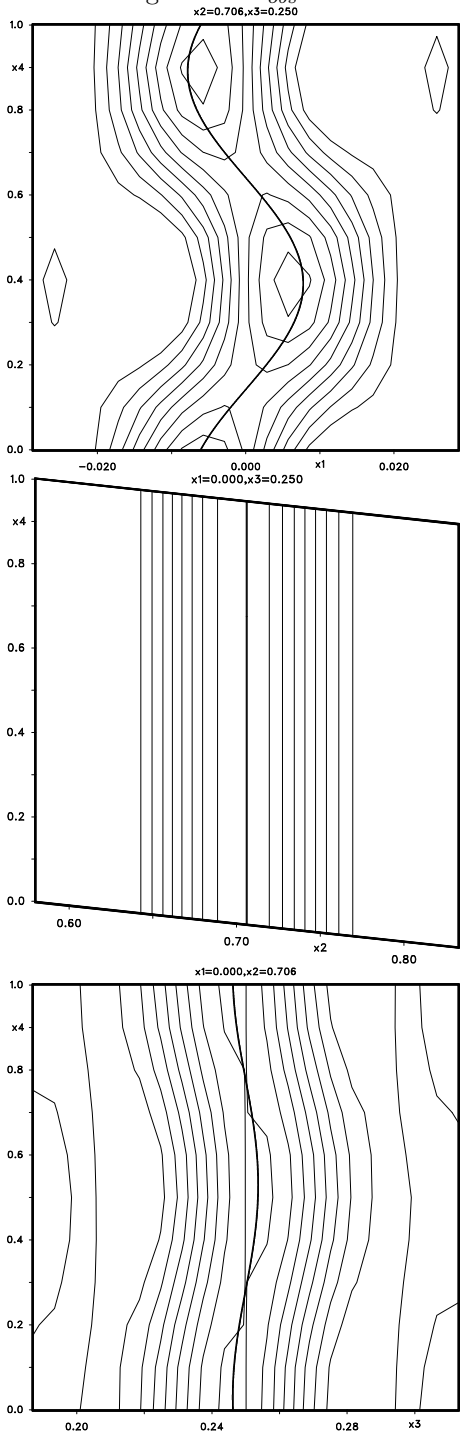


Figure 88: ρ_{MEM} Sr9

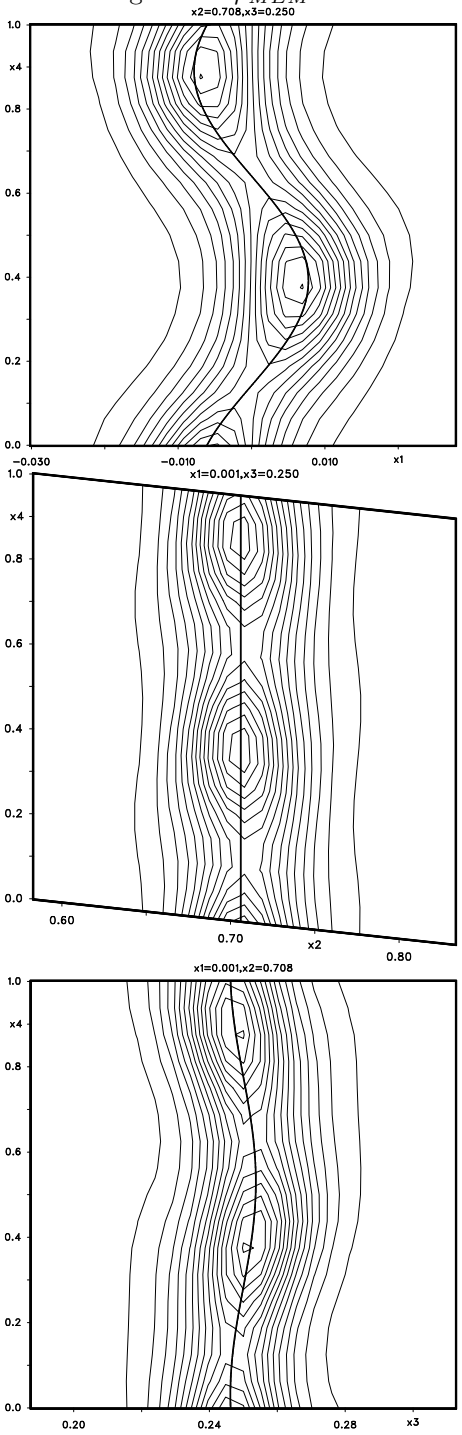


Figure 89: F_{obs} Sr10

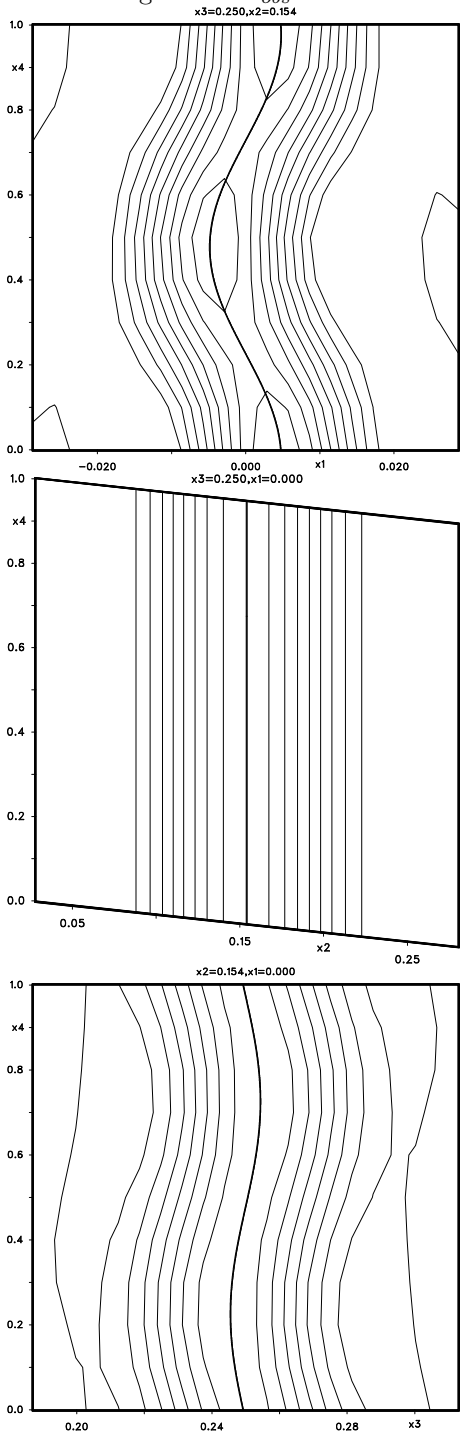


Figure 90: ρ_{MEM} Sr10

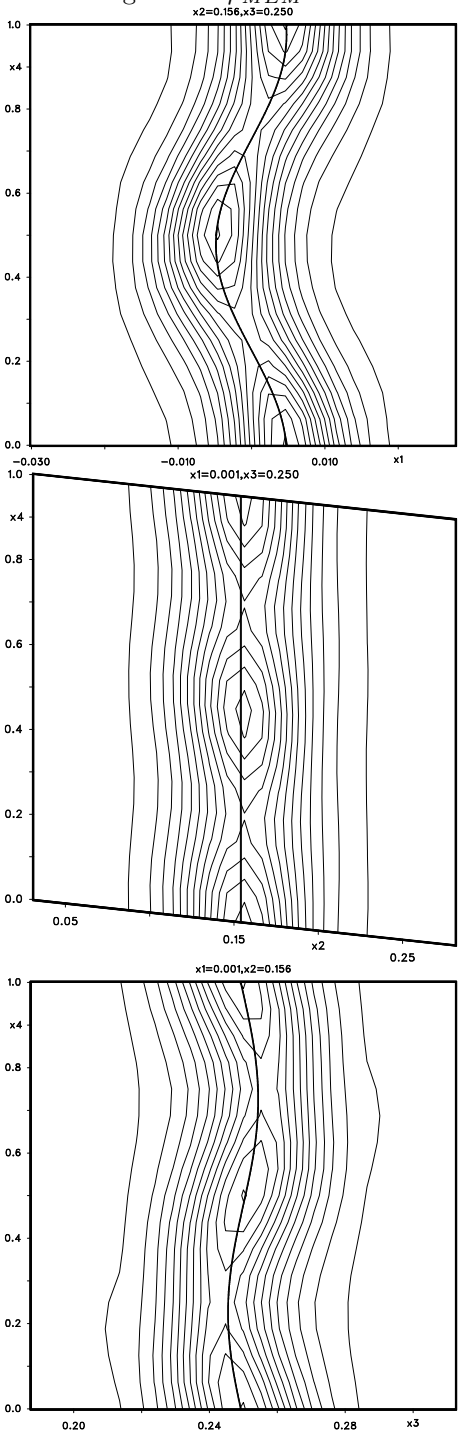


Figure 91: F_{obs} Sr11

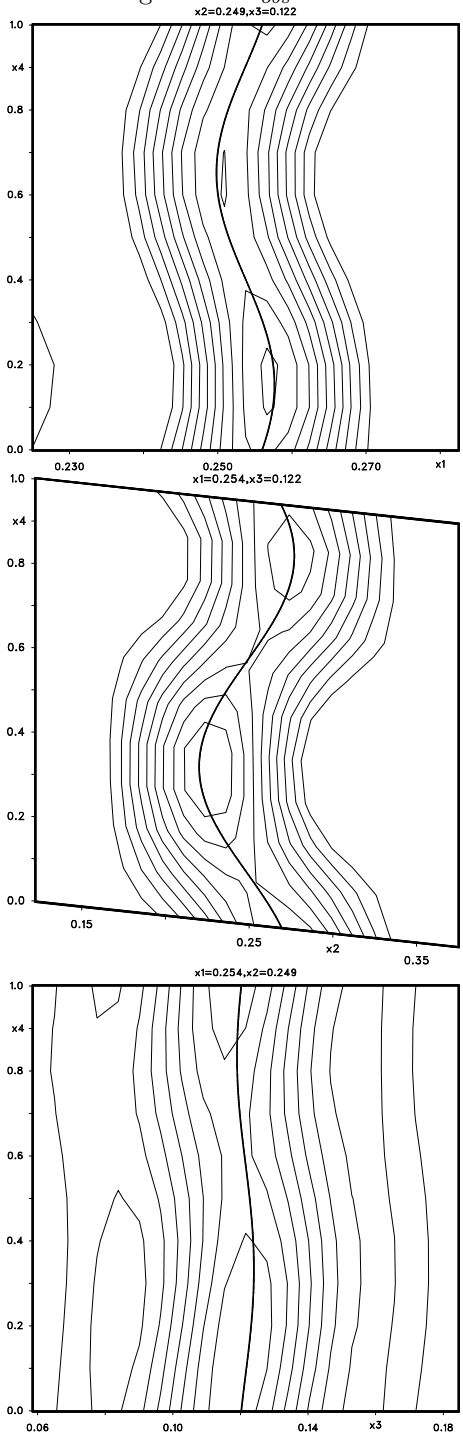
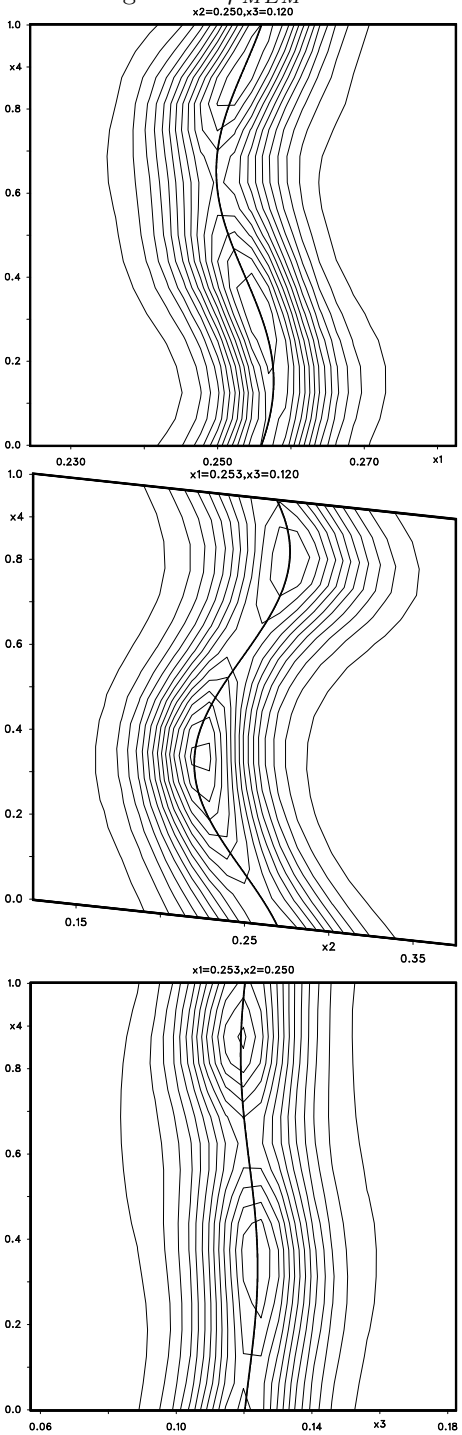


Figure 92: ρ_{MEM} Sr11



References

[1] L. W. Finger, M. Kroeker & B. H. Toby (2007), 'DRAWxtl, an open-source computer program to produce crystal structure drawings', *J. Appl. Crystallogr.* **40**(1), 188–192, doi: 10.1107/S0021889806051557

[2] S. van Smaalen, L. Palatinus & M. Schneider (2003), 'The maximum-entropy method in superspace', *Acta Crystallogr.* **A59**, 459–469, doi: 10.1107/S010876730301434X

[3] M. Sakata & M. Sato (1990), 'Accurate structure analysis by the maximum-entropy method', *Acta Crystallogr.* **A46**, 263–270, doi: 10.1107/S0108767389012377

[4] L. Palatinus & S. van Smaalen (2002), 'The generalized f constraint in the maximum-entropy method — a study on simulated data', *Acta Crystallogr.* **A58**, 559–567, doi:10.1107/S0108767302015556

[5] L. Palatinus & S. van Smaalen (2004), 'Incommensurate modulations made visible by the Maximum Entropy Method in superspace', *Z. Kristallogr.* **219**(11), 719–729, doi:10.1524/zkri.219.11.719.52435

[6] L. Palatinus (2009), 'editm81', personal communication