Large General Reactive Multicomponent Transport Processes in Porous Media: Modeling, Analysis and Efficient Simulation

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Scaling Up and Modeling for Transport and Flow in Porous Media
in honor of Alain Bourgeat
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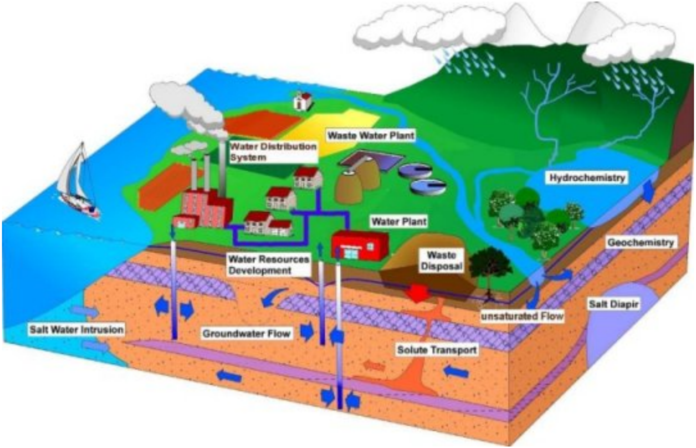
Outline

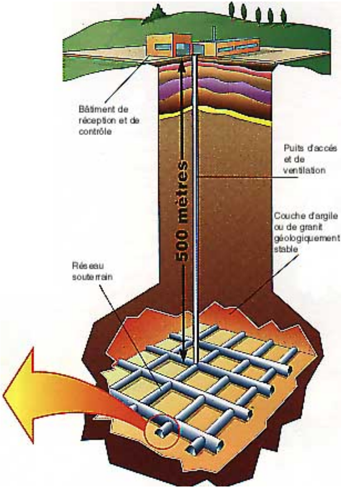
Framework


Waste Water Plant
Water Distribution System
Hydrochemistry
Water Plant
Geochemistry
Waste Disposal
Water Resources Development
Salt Diapir
unsaturated Flow
Salt Water Intrusion
Groundwater Flow
Solute Transport

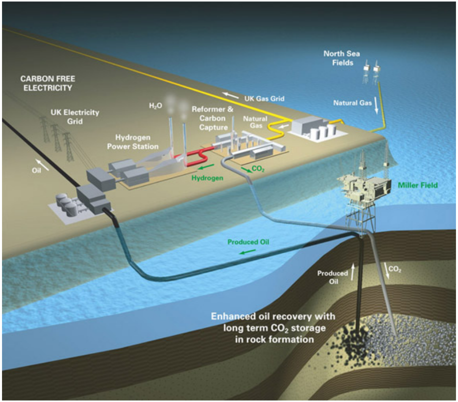
Contaminant Transport and Remediation

- Fate of pollutants by transport and transformation: protection of groundwater and soils
- Organic pollutants : microbially catalysed redox reactions : natural attenuation
- Variant : Enhanced natural attenuation
- Technical in situ remediation : Reactive walls
- Contaminants in phase (LNAPL or DNAPL) : Multiphase flow problem and reactive transport problem
- Redox reaction chains (redox zone formation) and coupling to geochemical background : Large multispecies reactive solute transport problem
- In special situations: Back coupling to fluid flow

Nuclear waste disposal



$\mathrm{CO_2}$-Sequestration in exploited oil/gas-fields



Part I Modelling: Fluid Flow in Porous Media

Example: Saturated–unsaturated flow *(Richards equation)* for pressure ψ (scaled to length) and water flux $\mathbf{q}$

$$\partial_t \Theta(\psi) + \nabla \cdot \mathbf{q} = Q$$

$$\mathbf{q} + K_s k_{rw}(\psi) \nabla(\psi + z) = 0$$

Parameter functions: Water content Θ and conductivity k_{rw} : monotone increasing in ψ, constant for $\psi \geq 0$ (saturated)
$\Rightarrow$ *(strongly) nonlinear* and *degenerated:* elliptic-parabolic

Mass Transport – General Formulation

Transport of solutes dissolved in water, including advection, dispersion, diffusion and general reaction terms:

$$\partial_t(\Theta c_i) - \nabla \cdot (\mathbf{D}\nabla c_i - \mathbf{q}c_i) = \Theta \sum_{j=1}^{N_R} \nu_{ij} R_j .$$

Shorthand: $Lc := -\nabla \cdot (\mathbf{D}\nabla c - \mathbf{q}c)$

Notation:

Θ: volumetric water content, $\mathbf{q}$: water (Darcy) flux,

c_i: solute concentration of ith species, $i \in \{1, \ldots, N_S\}$,

$\mathbf{D}$: diffusion-dispersion tensor, ν_{ij}: stoichiometric coefficient,

R_j: reaction rate expression of the j-th general reaction.

Reaction terms: e.g. for sorption phenomena, decay, may depend on other parameters or concentrations:

$$R_j = R_j(c_1, \ldots, c_{N_S}, x, t, T, \ldots).$$

Biodegradation of Organic Contaminants

Redox processes, catalyzed by microorganisms, depend on the availability and dynamics of electron acceptors (such as oxygen or nitrate), electron donors (an organic substrate), inhibitors, and the biomass (immobile).

→ Multiplicative Monod-model, derived from enzyme kinetics, combines availability terms (left) with inhibition terms (right) to limit exponential bacterial growth (c_{X_r}) and acceptor/donor decay

$$R_r \sim \left(\frac{c_i}{K_i + c_i}\right)\left(\frac{K_{I_j}}{K_{I_j} + c_j}\right) c_{X_r}$$

K_i: Monod half saturation concentration,
K_{I_j}: inhibition concentration.

Multicomponent Geochemical Kinetics

Rate expression of the rth elementary kinetic reaction, formulated with the help of rate constants for forward and backward reaction k_f and k_b under the common assumption of mass action kinetics:

$$R_r = \left(k^f \prod_i c_i^{-\nu_{ir}} - k^b \prod_j c_j^{\nu_{jr}} \right) .$$

Index i: reactants (educts, with stoichiometric coefficients $\nu_{ir} < 0$),
Index j: product species.

Note: rate constants may vary by several orders of magnitude.

Immobile Species

Immobile species: attached to (surface of) soil matrix (porous skeleton), e.g. biomass, sorbed (cat)ions,...

$$\partial_t(\varrho \overline{c}_i) = \Theta \sum_{j=1}^{N_R} \nu_{ij} R_j.$$

Notation:
ϱ: bulk density,
$\overline{c}_i$: concentration of ith immobile species related to mass, $i \in \{1, \dots, \overline{N}_S\}$,
ν_{ij}: stoichiometric coefficient,
R_j: reaction rate expression of the j-th general reaction.
Reaction terms: e.g. for sorption phenomena, decay, may depend on other parameters or concentrations, also nonlocally:

$$R_j = R_j(c_1, \dots, c_{N_S}, \overline{c}_1, \dots, \overline{c}_{\overline{N}_S}, x, t, T).$$

Fast Reactions

E. g. for sorption reaction

$$\partial_t(\Theta c_i) - \nabla \cdot (\mathbf{D}\nabla c_i - \mathbf{q} c_i) = -\Theta R = -\Theta k Q,$$

$$\partial_t(\varrho \overline{c}_i) = \Theta R = \Theta k Q.$$

For large rate parameter k: Quasistationary approximation

$$Q(c_1, \dots, c_{N_S}, \overline{c}_1, \dots, \overline{c}_{\overline{N}_S}, x, t, T) = 0.$$

Equilibrium description by algebraic equation (AE)
Elimination of rate expression e.g. for sorption:

$$\partial_t(\Theta c_i) + \partial_t(\varrho \overline{c}_i) - \nabla \cdot (\mathbf{D}\nabla c_i - \mathbf{q} c_i) = 0.$$

Quasistationary situation :

$$Q(c_1, \ldots, c_{N_S}, \overline{c}_1, \ldots, \overline{c}_{\overline{N}_S}, x, t, T) = Q(c_i, \overline{c}_i) = 0 \Leftrightarrow \overline{c}_i = \varphi(c_i).$$

Quasilinear equation :

$$\partial_t(\Theta c_i) + \partial_t(\varrho\varphi(c_i)) - \nabla \cdot (\mathbf{D}\nabla c_i - \mathbf{q} c_i) = 0.$$

φ: equilibrium sorption characteristic : sorption isotherm

Precipitation/Dissolution

What is Missing...?

Precipitation/dissolution (of minerals)

Quasistationary approximation: leads to complementarity system

Example:

$$A + B \rightleftarrows \overline{C}$$

A, B: dissolved species, c_A, c_B: concentration (= activity)

$\overline{C}$: precipitated species, $c_{\overline{C}}$: concentration (activity = 1)

$$(k - c_A c_B) c_{\overline{C}} = 0, \quad k - c_A c_B \geq 0, \quad c_{\overline{C}} \geq 0$$

Kinetics: set-valued rate function, consistent with equilibrium condition

System of Equations

$$
\begin{aligned}
\partial_t(\Theta \mathbf{c}) + L\mathbf{c} &= \Theta \mathbf{S}_{1,kin}\mathbf{r}_{kin}(\mathbf{c},\bar{\mathbf{c}}) + \Theta \mathbf{S}_{1,eq}\mathbf{r}_{eq} \\
\partial_t(\Theta \bar{\mathbf{c}}) &= \Theta \mathbf{S}_{2,kin}\mathbf{r}_{kin}(\mathbf{c},\bar{\mathbf{c}}) + \Theta \mathbf{S}_{2,eq}\mathbf{r}_{eq} \\
\phi_{mob}(\mathbf{c}) &= \mathbf{0} \\
\phi_{sorp}(\mathbf{c},\bar{\mathbf{c}}_{nmin}) &= \mathbf{0}
\end{aligned}
$$

$$(\psi_j(\mathbf{c}) = 0 \text{ and } \bar{c}_{min,j} \geq 0) \text{ or } (\psi_j(\mathbf{c}) \geq 0 \text{ and } \bar{c}_{min,j} = 0)$$

$$\phi_j(\mathbf{c},\bar{\mathbf{c}}) = -\ln(K_j) + \sum_{i=1}^{I+\bar{I}} s_{eq,ij} \ln(c_i)$$

$$\psi_j(\mathbf{c}) = -\ln(K_j) + \sum_{i=1}^{I} s_{eq,ij} \ln(c_i)$$

(Stoichiometric coefficient of minerals positive)

Reformulation of the equilibrium condition

Equilibrium Condition for a Mineral

$$(\psi_j(\mathbf{c}) = 0 \text{ and } \bar{c}_{min,j} \geq 0) \text{ or } (\psi_j(\mathbf{c}) \geq 0 \text{ and } \bar{c}_{min,j} = 0)$$

Equivalent to *Complementary Condition*

$$\psi_j(\mathbf{c}) \cdot \bar{c}_{min,j} = 0 \text{ and } \psi_j(\mathbf{c}) \geq 0 \text{ and } \bar{c}_{min,j} \geq 0$$

Equivalent to equation $\varphi(\psi_j(\mathbf{c}), \bar{c}_{min,j}) = 0$
$\varphi : \mathbb{R}^2 \to \mathbb{R}$ function with $\varphi(a,b) = 0 \Leftrightarrow (ab = 0 \wedge a \geq 0 \wedge b \geq 0)$
One possible choice: $\varphi(a,b) := \min\{a,b\}$

Equivalent equilibrium condition for a mineral

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Columns of the stoichiometric matrix sorted in the following way

$$\begin{aligned}\mathbf{S}_1 &= \begin{pmatrix}\mathbf{S}_{1,eq} & \mathbf{S}_{1,kin}\end{pmatrix} = \begin{pmatrix}\mathbf{S}_{1,mob} & \mathbf{S}_{1,sorp} & \mathbf{S}_{1,min} & \mathbf{S}_{1,kin}\end{pmatrix}\\ \mathbf{S}_2 &= \begin{pmatrix}\mathbf{S}_{2,eq} & \mathbf{S}_{2,kin}\end{pmatrix} = \begin{pmatrix}\mathbf{0} & \mathbf{S}_{2,sorp} & \mathbf{S}_{2,min} & \mathbf{S}_{2,kin}\end{pmatrix}\end{aligned}$$

Assumption

$$\mathbf{S}_{2,min} = \begin{pmatrix}\mathbf{0}\\ \mathbf{I}\end{pmatrix}, \qquad \mathbf{S}_{2,sorp} = \begin{pmatrix}\tilde{\mathbf{S}}_{2,sorp}\\ \mathbf{0}\end{pmatrix}$$

Part II Analysis: Existence of a Global Solution of the Analytical Problem

Model-Restriction:

– All reactions kinetic, mass action law, forward-backward formulation

– All species mobile

$$\partial_t u + Lu = SR(u)$$

Theorem (Global Existence):

For arbitrary $T > 0$, a solution on $[0, T]$ exists

Application of Schaefer's fixed point theorem

Choose $X := W_p^{2,1}(Q_T) := \{u | u, \nabla u, \nabla^2 u, \partial_t u \in L^p(Q_T)\}, \quad p > 3,$

$Q_T := (0, T) \times \Omega,$

$$Z : W_p^{2,1}(Q_T) \longrightarrow W_p^{2,1}(Q_T), \quad u \longmapsto v,$$

where v is the solution of $\partial_t v + \mathcal{L} v = SR(u)$.

Challenge: Prove a priori estimate for Z: Lyapunov technique, i.e., find functional φ s.th. $t \mapsto \varphi(u(t))$ is non-increasing

Preliminary consideration: Regard batch situation $\partial_t u = SR(u)$
First step: Prove that any solution fulfils $u > 0$.
Then: For the construction of the **Lyapunov functional** φ:

Inspired by the Gibbs free energy choose $\varphi(u) := \sum_{i=1}^{I} (\mu_i^0 - 1 + \ln u_i)\, u_i + e^{1-\mu_i^0}$,

where the constant vector μ^0 is a solution of $S^t \mu^0 = -\ln K$, K =vector of equil. const.
Properties: $\nabla\varphi(u) = \mu^0 + \ln u, \quad \varphi(u) \geq 0, \quad \varphi(u) \geq |u|$

Test the batch problem with $\nabla\varphi$:

$$\begin{aligned} \frac{d}{dt}\varphi(u(t)) &= (\partial_t u, \nabla\varphi(u(t))) = (SR(u(t)), \mu^0 + \ln u(t)) \\ &= (R(u(t)), S^t\mu^0 + S^t \ln u(t)) \\ &= -(R(u(t)), \ln K - S^t \ln u(t)) \leq 0, \end{aligned}$$

since $[R(u)]_i \gtreqless 0 \Leftrightarrow [\ln K - S^t \ln u]_i \gtreqless 0$,
i.e., $\varphi(u(t)) \leq \varphi(u(t_0)) = \text{const}\ \forall t \geq t_0$
$\Rightarrow |u(t)| \leq \varphi(u(t)) \leq \text{const}$

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Generalization to the PDE-case

- Use $\Phi(u) := \int_\Omega \varphi(u)\,dx = \int_\Omega [\sum_{i=1}^{I} (\mu_i^0 - 1 + \ln u_i)\,u_i + e^{1-\mu_i^0}]\,dx, \Phi(u) \geq \|u\|_{L^1(\Omega)}$
- Check that Φ 'behaves well' with advective term, diffusive term
  $\Rightarrow \Phi(u(t)) \leq \Phi(u(t_0)) = \text{const}\ \forall t \geq t$
  $\Rightarrow \|u(t)\|_{L^1(\Omega)} \leq \Phi(u(t)) \leq \text{const}$
- Does "$\|u(t)\|_{L^1(\Omega)} \leq \text{const} \overset{???}{\Rightarrow} \|SR(u)\|_{L^p(\Omega)} \leq \text{const}$" hold?
  If so:
  $W_p^{2,1}(Q_T)$-estimate for sol. of FP-equation $\partial_t u + \mathcal{L}u = SR(u)$ follows from linear parabolic theory.
- If $R(u)$ is highly nonlinear:
  Replace $\Phi(u) := \int_\Omega \varphi(u(x))\,dx$ by $\tilde{\Phi}(u) := \int_\Omega \varphi(u(x))^r\,dx$ (r sufficiently large)
  $\tilde{\Phi}$ also 'behaves well' w.r.t. advective, diffusive, reactive term.
  Now: $\tilde{\Phi}(u) \geq \|u\|_{L^r(\Omega)}^r$!!

  Estimate for $\tilde{\Phi} \Rightarrow$ estimate for $\|u\|_{L^r(\Omega)} \Rightarrow$ estimate for $\|SR(u)\|_{L^p(\Omega)}$
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Some technical difficulties:

- Definition of $\Phi, \tilde{\Phi}$ requires "ln u". But only $u \geq 0$ is known.
  $\Rightarrow$ Use $u_\delta := u + \delta, \ \ \delta > 0$, let $\delta \to 0$.
- Some steps require that u_δ is approximated by a smooth function

Extensions to

- mobile-immobile (PDE-ODE) model
  (if interphase exchange terms are (sub)linear, or if coupling is one-way)
- equilibrium problem (PDE-AE)

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Part III Numerical Methods: Approach

Outline

- Time discretization
  (not only by one-step methods)
- time-discrete **nonlinear** flow problem in hybrid mixed variational form: discretization with (lowest order) Raviart–Thomas or BDM elements
  static condensation by solution of local nonlinear problems
- time discrete nonlinear transport problem: discretization with mixed finite elements or conformal finite elements or finite volumes
- Newton's method **to solve resulting nonlinear discrete equations (Global Implicit Approach)**
- multigrid method to solve linear subproblems within Newton's method

Solution Methods

for space-and time-discrete nonlinear set of equation $\mathbf{f}(\mathbf{c}) = \mathbf{0}$

# of unknowns: $N * N_S$

spatial degrees of freedom * #Species

1. Full Newton's Method (Global Implicit Approach GI(A).)

$$\mathbf{Df}\left(\mathbf{c}^{(k)}\right)\boldsymbol{\delta}^{(k)} = -\mathbf{f}\left(\mathbf{c}^{(k)}\right),$$

with functional matrix $\mathbf{Df}(\mathbf{c}) = (\partial_j f_i(\mathbf{c}))_{ij}$

$$\mathbf{c}^{(k+1)} := \mathbf{c}^{(k)} + \boldsymbol{\delta}^{(k)}.$$

each iteration: assembly and solution of linear system of equation of same size and sparsity structure as nonlinear problem

Special form of $f(u)$

$$\mathbf{f}(\mathbf{c}) \quad = \quad \mathbf{Dc} \quad + \quad \mathbf{Ac} \quad + \quad \mathbf{g}(\mathbf{c}) \quad - \quad \mathbf{b} \quad - \quad \mathbf{Dc}^{old}$$

time spatial reaction
discretization nonlinearity

2. Iterative Operator Splitting

iterative substeps:

i) *transport step:*
$(\mathbf{D} + \mathbf{A})\mathbf{c}^{k+1,1} = \mathbf{b} - \mathbf{g}(\mathbf{c}^k) - \mathbf{Dc}^{old}$
— decouples in species: N_S subproblem of size N —

ii) *reaction step:*
$\mathbf{Dc}^{k+1} + \mathbf{g}(\mathbf{c}^{k+1}) = \mathbf{b} - \mathbf{Ac}^{k+1,1} - \mathbf{Dc}^{old}$
— decouples in spatial nodes: N subproblem of size N_S —

If only one Newton step for reaction step, then sparsened Newton method with

i) $\mathbf{D} + \mathbf{A} + D\mathbf{g}(\mathbf{c}^k) \rightarrow \mathbf{D} + \mathbf{A}$

ii) $\mathbf{D} + \mathbf{A} + D\mathbf{g}(\mathbf{c}^k) \rightarrow \mathbf{D} + D\mathbf{g}(\mathbf{c}^k)$
i.e. with fixed sparsening

3. <u>Noniterative Operator Splitting</u>
   i) *transport step*
   $(\mathbf{D} + \mathbf{A}) + \mathbf{c}^{,1} = \mathbf{b} + \mathbf{D}\mathbf{c}_{old}$
   ii) *reaction step*
   $\mathbf{D}\mathbf{c} + g(\mathbf{c}) = \mathbf{b} + \mathbf{D}\mathbf{c}^{,1}$

1. solves exact discrete nonlinear problem with local quadratic convergence
2. solves exact discrete nonlinear problem with ?
3. does not solve exact discrete nonlinear problem
   consistency error $O(\Delta t)$ (other version $O(\Delta t^2)$)

Modified Newton's Method by Sparsening of Reaction Network

Approximation of Jacobian

→ benefit from decoupled subsets in the linear solver

→ respect 'process-preserving' complete problem in Newton step (in contrast to (noniterative) operator splitting techniques!)

$$\mathbf{c}^{(k+1)} := \mathbf{c}^{(k)} - \left(D\mathbf{f}\left(\mathbf{c}^{(k)}\right) + \Delta\left(\mathbf{c}^{(k)}\right)\right)^{-1} \left(\mathbf{f}\left(\mathbf{c}^{(k)}\right)\right) .$$

Then (under standard assumptions) $\exists\, C > 0$:

$$\|\mathbf{e}^{(k+1)}\| \le C \left(\|\mathbf{e}^{(k)}\|^2 + \|\Delta(\mathbf{c}^{(k)})\| \|\mathbf{e}^{(k)}\| \right) ,$$

with $\mathbf{e}^{(k)} := \mathbf{c}^{(k)} - \mathbf{c}^*$.

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Goal:

Neglect couplings through reactions where possible (slow kinetics, vanishing concentrations, stationary states)
→ reducible Jacobian
→ independent solution of parts, e.g.:

sparsity pattern of A_{ii} for a reaction system with 12 species:

$$\begin{array}{rcl}
\mathrm{A}+\mathrm{B} & \rightleftharpoons & \mathrm{C}\,, \\
\mathrm{C} & \leftrightarrow & \mathrm{D}+\mathrm{I}\,, \\
\mathrm{D}+\mathrm{E} & \rightleftharpoons & \mathrm{F}\,, \\
\mathrm{G}+\mathrm{H} & \rightleftharpoons & \mathrm{I}\,, \\
\mathrm{I} & \leftrightarrow & \mathrm{J}\,, \\
\mathrm{J}+\mathrm{K} & \rightleftharpoons & \mathrm{L}\,.
\end{array}
\qquad
\begin{array}{c}
\mathrm{A}\\ \mathrm{B}\\ \mathrm{C}\\ \mathrm{D}\\ \mathrm{E}\\ \mathrm{F}\\ \mathrm{G}\\ \mathrm{H}\\ \mathrm{I}\\ \mathrm{J}\\ \mathrm{K}\\ \mathrm{L}
\end{array}
\left(\begin{array}{cccccc|cccccc}
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Tradeoff between

- → computational savings from solving smaller problems with less coupled components, and
- → possible deterioration of the convergence of the Newton iteration for the decoupled system (only approximated Jacobian):

Reduction of l_2-norm of defect (y–axis) per Newton step (x–axis) in coupled (A...L) and uncoupled (ABC)...(JKL) case
12 species,
left: time step $dt = 0.05$,
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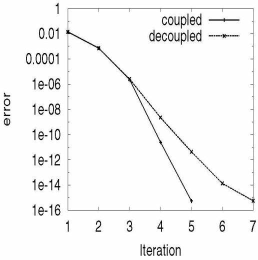
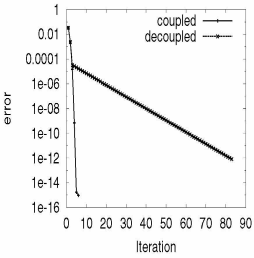


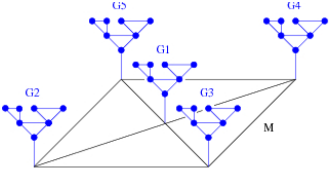


Adaptive Strategies

Algorithm should choose appropriately in every time step:

1. time step size Δt
   (simple heuristic criterion based on number of Newton steps)
2. connectivity pattern of the subsystems based on a suitable decoupling strategy.
   - decouple as much as possible,
   - avoid significant increase in number of Newton steps,
   - decoupling algorithm itself should be efficient.

Decoupling strategy



note: due to large number of spatial nodes it is impossible to analyse all local reaction graphs $\mathcal{R}_{K_i}$ seperately

$\Rightarrow$ Seek for common, global connectivity pattern through all nodes K_i.
$\Rightarrow$ match together local reaction graphs to a representing one $\widetilde{\mathcal{R}}$.
Thus:

$$A \mapsto \widetilde{A} \qquad \text{with} \qquad \widetilde{A} \in \mathbb{R}^{N_S,N_S},$$

$\widetilde{A}$: adjacency matrix of a non-oriented graph (upper triangular form).

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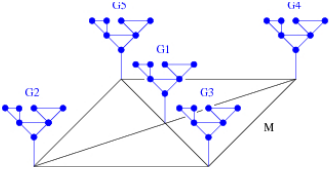

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Decoupling strategy

- efficient partitioning of small matrix $\widetilde{A}$: $O\left(d_{\mathcal{R}}^{max} N_S \log N_S\right)$ [algorithm of Stoer and Wagner]
- to identify global weak couplings between species:

$$\widetilde{A}_{ij} := \begin{cases} \max\limits_{k,l\in\{1,\ldots,n\}(*)} \{\left|A_{kl}\right|, \left|A_{lk}\right|\} & \text{for } i=1,\ldots,N_S,\ j=i,\ldots,N_S, \\ 0 & \text{else.} \end{cases}$$

  (*) : k same species as i, l same species as j .
  Weight of the edges of $\widetilde{\mathcal{R}}$: max. of *all local* reaction graphs $\mathcal{R}_{K_i}$.

- neglect edges in $\widetilde{A}$ with small weight, if connectivity graph is thus split in independent parts:

$$\left(\widetilde{A}_{neglect}\right)_{ij} \leq \epsilon_B^{rel} \left|\widetilde{A}\right| \qquad \forall i,j=1,\ldots,N_S$$

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2D Simulation: 12 species - 6 reactions

Performance for 12 species example

Reactions with $Da = (1000, 1, 1000, 1000, 1, 1000)$.

Solver	configuration	NS/TS	Ass	LS	Ges
SuperLU	$(A \dots L)$	3, 0	304	2371	2679
SuperLU	$(ABC) \dots (JKL)$	3, 0	327	200	531
BiCGStab	$(A \dots L)$	3, 0	303	125	433
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direct solver with decoupling strategy in the range of iterative solver - gain for iterative solver modest

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2D Reactive Barrier: Problem Setting

21 species and 10 reactions:

Nr	Reaction		
1	$Fe^0\,(s) + CrO_4^{2-} + 6H^+$	$\rightarrow$	$Fe^{3+} + Cr\,(OH)_2^+ + 2H_2O$
2	$Fe^0\,(s) + 0,3025\,C_2HCL_3$ $+1,2325\,H^+$	$\rightarrow$	$Fe^{2+} + 0,07\,C_2H_2Cl_2$ $+0,2325\,C_2H_6 + 0,7675\,Cl^-$
3	$Fe^0\,(s) + C_2H_2Cl_2 + H^+$	$\rightarrow$	$Fe^{2+} + C_2H_3Cl + Cl^-$
4	$Fe^0\,(s) + \frac{1}{2}\,C_2H_3Cl + \frac{3}{2}\,H^+$	$\rightarrow$	$Fe^{2+} + \frac{1}{2}\,C_2H_6 + \frac{1}{2}\,Cl^-$
5	$Fe^0\,(s) + \frac{1}{4}\,O_2\,(aq) + 3H^+$	$\rightarrow$	$Fe^{3+} + \frac{1}{2}\,H_2O + H_2\,(aq)$
6	$Fe^0\,(s) + \frac{3}{8}\,NO_3^- + \frac{15}{4}\,H^+$	$\rightarrow$	$Fe^{3+} + \frac{3}{8}\,NH_4^+ + \frac{9}{8}\,H_2O$
7	$Fe^0\,(s) + \frac{1}{4}\,SO_4^{2-} + \frac{9}{4}\,H^+$	$\rightarrow$	$Fe^{2+} + \frac{1}{4}\,HS^- + H_2O$
8	$Fe^0\,(s) + \frac{1}{2}\,CH_2O + 2H^+$	$\rightarrow$	$Fe^{2+} + \frac{1}{2}\,CH_4\,(aq) + \frac{1}{2}\,H_2O$
9	$Fe^0\,(s) + \frac{1}{4}\,CO_3^{2-} + \frac{5}{2}\,H^+$	$\rightarrow$	$Fe^{2+} + \frac{1}{4}\,CH_4\,(aq) + \frac{3}{4}\,H_2O$
10	$Fe^0\,(s) + 2H^+$	$\rightarrow$	$Fe^{2+} + H_2\,(aq)$

2D Barrier: Reactions

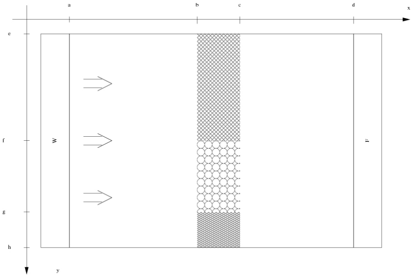
Rate constants and Damköhler numbers:

Nr	$\log k$	Da
1	$6,0$	$4,00 \cdot 10^{12}$
2	$-3,1$	$3,18 \cdot 10^{3}$
3	$-4,1$	$3,18 \cdot 10^{2}$
4	$-3,3$	$2,00 \cdot 10^{3}$
5	$6,5$	$1,26 \cdot 10^{13}$

Nr	$\log k$	Da
6	$-2,5$	$1,26 \cdot 10^{4}$
7	$-3,5$	$1,26 \cdot 10^{3}$
8	$-4,7$	$7,98 \cdot 10^{1}$
9	$-4,7$	$7,98 \cdot 10^{1}$
10	$-7,3$	$2,00 \cdot 10^{-1}$

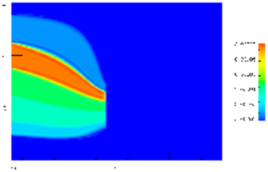
left boundary: Dirichlet conditions,
right boundary: homogeneous Neumann

2D Reactive Barrier: Simulation

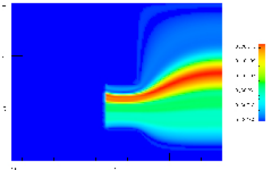


Domain with permeable, reactive barrier and unpermeable region

29700 elements, grid Peclet number 2.02



species CrO_4^{2-}



product species $Cr\,(OH)_2^+$

2D Reactive Barrier: Performance

Computation times of 2D barrier problem: fixed and adaptive time steps and connectivity graphs

Δt	decoup	TS	NS/TS	Ass	$Auto$	LS	N_T	Tot
fixed	no	70	11, 9	346	–	1116	1	1530
fixed	yes	70	12, 8	378	5	365	13	775
varied	no	39	13, 4	213	–	842	1	1098
varied	yes	39	13, 7	223	3	290	13	533

TS	number of time steps	NS	number of Newton steps
Ass	time for assembling	$Auto$	time for decoupling algorithm
LS	time for linear solver	N_T	number of subsystems
Tot	total CPU time		

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The Reduction Scheme

Transformation of concentration variables such that

- part of the system becomes linear and decouples from rest ("reaction invariants")
- elimination of unknown rate functions for equilibrium reactions
- (significantly) reduced nonlinear coupled system, further reduction by (algorithmic) resolution of local equations (from equilibrium reactions and kinetic reaction of immobile species) (Direct Substitution Approach)

Scope of the method:

- can handle couplings of mobile/immobile species and kinetic/equilibrium reactions including mineral reactions,
- no limitations due to the stoichiometry,
- produces no couplings under the transport operator

Applying the reduction scheme

- Replacing $\mathbf{S}_i$ by $\mathbf{S}_i^*\mathbf{A}_i$ with $\mathbf{S}_i^*$ maximal system of linear independent columns of $\mathbf{S}_i$
- Taking linear combination of the PDEs and ODEs separately in each block by multiply the PDE block with

$$(\mathbf{B}_1^T\mathbf{S}_1^*)^{-1}\mathbf{B}_1^T\,, \qquad (\mathbf{S}_1^{\perp\,T}\mathbf{B}_1^{\perp})^{-1}\mathbf{S}_1^{\perp\,T}$$

and the ODE block with

$$(\mathbf{B}_2^T\mathbf{S}_2^*)^{-1}\mathbf{B}_2^T\,, \qquad (\mathbf{S}_2^{\perp\,T}\mathbf{B}_2^{\perp})^{-1}\mathbf{S}_2^{\perp\,T}$$

Conditions for $\mathbf{B}_i$

  - same size as $\mathbf{S}_i^*$
  - columns linear independent
  - $\mathrm{span}\{\mathbf{B}_1^{\perp}, \mathbf{S}_1^*\} = \mathbb{R}^I$ and $\mathrm{span}\{\mathbf{B}_2^{\perp}, \mathbf{S}_2^*\} = \mathbb{R}^{\bar{I}}$

Simplest choice $\mathbf{B}_i = \mathbf{S}_i^*$

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Orthogonal complement $\mathbf{A}^\perp$: maximal system of linear independent vectors perpendicular on all columns of $\mathbf{A}$

➡ ${\mathbf{A}^\perp}^T\mathbf{A} = \mathbf{0}$, $\operatorname{span}\{\mathbf{A}^\perp, \mathbf{A}\} = \mathbb{R}^n$

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Simplest choice $\mathbf{B}_i = \mathbf{S}_i^*$

Applying the Reduction Scheme

- Elimination of $\mathbf{r}_{eq}$ by taking linear combinations between PDEs and ODEs
- Introduction of new variables

$$\xi = \begin{pmatrix} \xi_{mob} \\ \xi_{sorp} \\ \xi_{min} \\ \xi_{kin} \end{pmatrix} := \left(\mathbf{B}_1^T \mathbf{S}_1^*\right)^{-1} \mathbf{B}_1^T \mathbf{c}\,, \qquad \eta := \left({\mathbf{S}_1^\perp}^T \mathbf{B}_1^\perp\right)^{-1} {\mathbf{S}_1^\perp}^T \mathbf{c}\,,$$

$$\bar{\xi} = \begin{pmatrix} \bar{\xi}_{sorp} \\ \bar{\xi}_{min} \\ \bar{\xi}_{kin} \end{pmatrix} := \left(\mathbf{B}_2^T \mathbf{S}_2^*\right)^{-1} \mathbf{B}_2^T \bar{\mathbf{c}}\,, \qquad \bar{\eta} := \left({\mathbf{S}_2^\perp}^T \mathbf{B}_2^\perp\right)^{-1} {\mathbf{S}_2^\perp}^T \bar{\mathbf{c}}$$

$$\tilde{\xi}_{sorp} := \xi_{sorp} - \bar{\xi}_{sorp}\,, \qquad \tilde{\xi}_{min} := \xi_{min} - \bar{\xi}_{min}$$

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Transformed System of Equations

$$\begin{aligned}
\partial_t(\Theta\eta) + L\eta &= \mathbf{0} \\
\tilde{\xi}_{sorp} &= \xi_{sorp} - \bar{\xi}_{sorp} \\
\tilde{\xi}_{min} &= \xi_{min} - \bar{\xi}_{min} \\
\partial_t(\Theta\tilde{\xi}_{sorp}) + L\xi_{sorp} &= \Theta(\mathbf{A}_{1,sorp} - \mathbf{A}_{2,sorp})\mathbf{r}_{kin}(\mathbf{c},\bar{\mathbf{c}}) \\
\partial_t(\Theta\tilde{\xi}_{min}) + L\xi_{min} &= \Theta\mathbf{A}_{1,min}\mathbf{r}_{kin}(\mathbf{c},\bar{\mathbf{c}}) \\
\partial_t(\Theta\xi_{kin}) + L\xi_{kin} &= \Theta\mathbf{A}_{1,kin}\mathbf{r}_{kin}(\mathbf{c},\bar{\mathbf{c}}) \\
\partial_t(\Theta\bar{\eta}) &= \mathbf{0} \\
\partial_t(\Theta\bar{\xi}_{kin}) &= \Theta\mathbf{A}_{2,kin}\mathbf{r}_{kin}(\mathbf{c},\bar{\mathbf{c}}) \\
\phi_{mob}(\mathbf{c}) &= \mathbf{0} \\
\phi_{sorp}(\mathbf{c},\bar{\mathbf{c}}_{nmin}) &= \mathbf{0} \\
\min\{\psi_j(\mathbf{c}),\bar{c}_{min,j}\} &= 0, \quad j = 1,\ldots,J_{min}
\end{aligned}$$

$$\mathbf{c} = \mathbf{S}_{1,mob}\xi_{mob} + \mathbf{S}_{1,sorp}(\tilde{\xi}_{sorp} + \bar{\xi}_{sorp}) + \mathbf{S}_{1,min}(\tilde{\xi}_{min} + \bar{\xi}_{min}) + \mathbf{S}^{*}_{1,kin}\xi_{kin} + \mathbf{B}_1^{\perp}\eta$$

$$\bar{\mathbf{c}}_{nmin} = \tilde{\mathbf{S}}_{2,sorp}\bar{\xi}_{sorp} + \mathbf{S}^{*}_{2,kin}\bar{\xi}_{kin} + \mathbf{B}_2^{\perp}\bar{\eta}\,, \quad \bar{\mathbf{c}}_{min} = \bar{\xi}_{min}$$

Efficiency in Realistic Model Problems

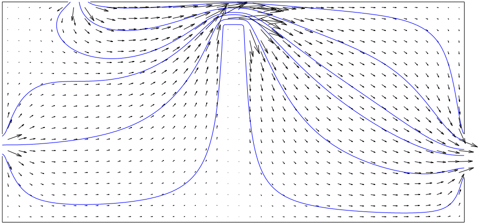
	metal-hydrolysis	EDTA-problem	biodegradation-chain	MoMaS-benchmark
# species $(I+\bar{I})$	9	14	7	12
# PDEs/ODEs in canonical form $(I+\bar{I}-J_{eq})$	3	9	7	5
# coupled nonlin. PDEs in new reduction scheme	1	6	2	2
cpu red./cpu non-red.	16%	$\sim 50\%$	$22-33\%$	–

MoMaS Benchmark:Problem Formulation 2D Case

- Domain $\Omega = (0, 2.1) \times (0, 1)$
- Anisotropic dispersion:

	Medium A	Medium B
Longitudinal β_l	10^{-2}	$6 \cdot 10^{-2}$
Transversal β_t	10^{-3}	$6 \cdot 10^{-3}$

- In Medium B by a factor of 10^{-3} lower conductivity
- Layer of Medium B over 90% of the height of the domain
  - ➥ Narrow passage
- Two inflow and one outflow zone



Chemical Reactions

Three different reaction networks

"Easy test case":

- 9 mobile and 3 immobile species
- Only equilibrium reactions: 5 with only mobile species, 2 sorption equilibrium reactions, largest equilibrium constant $K = 10^{35}$ ▸ Simulation

"Medium test case":

- 11 mobile and 4 immobile species
- Two more equilibrium reactions, largest exponent 10, and additionally one kinetic mineral reaction ▸ Simulation

"Hard test case":

- 12 mobile and 6 immobile species
- Additionally two equilibrium mineral reactions and one kinetic reaction ▸ Simulation

Software of Other Research Groups

- Comparison of the benchmark results not finished yet
- Results of the other groups out of the comparative talk of J. Carrayrou

Other groups with 2D results:
HYTEC:

- Vincent Lagneau and Jan van der Lee
- Iterative splitting
- Finite Volumes

MIN3P:

- K. U. Mayer and K. T. B MacQuarrie
- Global implicit approach
- Finite Differences

Comparison of CPU Time

CPU time in normalized units (CPU time for multiplication of two 1000×1000 matrices)

test case “Easy Advective 2D”:

	number of nodes	CPU time	“normalized”
HYTEC	7747	5706	17837
MIN3P	5406	4684.4	22960
Reduction scheme	19281	10645.6	10646

test case “Medium Advective 2D”:

	number of nodes	CPU time	“normalized”
MIN3P	5406	4049.1	12934
Reduction scheme	13689	6911.9	6912

Conclusions

Part I: Modelling

- 1,5 phase (also multiphase flows possible)
- homogeneous and heterogeneous reactions
- kinetic or quasi-stationary description
- mineral dissolution and precipitation included
- Monod-type or mass action-type or ... reaction rates

Conclusions

Part II: Analysis

- global in time existence for arbitrary mass action based rate description

Conclusions

Part III: Numerical methods and tools

- locally mass conservative spatial discretizations, in particular mixed finite elements
- application for nonlinear, not for linearized time-discrete problems
- all in one damped Newton's method for multicomponent reactive flow
- feasability also for large problems by
  - selective decoupling by sparsening of reactive network
  - reduction by exact decoupling

Conclusions

Outlook

- pore space changed by reaction: full coupling of fluid flow and reactive transport

Handling of Monod reactions

Reaction rate

$$r_{monod,j}(\mathbf{c},\bar{\mathbf{c}}) = \mu_{max,j}\bar{c}_{X_j} \prod_{i\in M_j} \frac{c_i}{K_{M,ij}+c_i} \prod_{i\in I_j} \frac{K_{I,ij}}{K_{I,ij}+c_i}$$

Equation for biomass

$$\rho\partial_t\bar{c}_{X_j} = \Theta Y_j \left(1 - \frac{\sum_i \bar{c}_{X_i}}{\bar{c}_{X_j,max}}\right) r_{monod,j}(\mathbf{c},\bar{\mathbf{c}}) - d_{X_j}\bar{c}_{X_j}$$

Problem: right hand side of ODE not $\Theta r_{monod,j}(\mathbf{c},\bar{\mathbf{c}})$
Solution: Introduction of two reactions

$$r_1 := r_{monod,j}\,, \qquad r_2 := \left(1 - \frac{\sum_i \bar{c}_{X_i}}{\bar{c}_{X_j,max}}\right) r_{monod,j} - \tilde{d}_{X_j}\bar{c}_{X_j}$$

back

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back

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▸ back

Handling of kinetic minerals

Equation for kinetic mineral

$$\partial_t(\theta \bar{c}_{kinmin,j}) = \begin{cases} \theta r_{kinmin,j}(\mathbf{c}) & \text{for } (\bar{c}_{kinmin,j} > 0) \vee (r_{kinmin,j}(\mathbf{c}) > 0) \\ 0 & \text{for } (\bar{c}_{kinmin,j} = 0) \wedge (r_{kinmin,j}(\mathbf{c}) \leq 0) \end{cases}$$

Equivalent formulation with minimum function

$$\min\left\{\partial_t(\theta \bar{c}_{kinmin,j}) - \theta r_{kinmin,j}(\mathbf{c}), \bar{c}_{kinmin,j}\right\} = 0$$

Replace mineral equilibrium condition

$\min\{\psi_j(\mathbf{c}), \bar{c}_{min,j}\} = 0$ by $\min\left\{\partial_t(\theta \bar{c}_{kinmin,j}) - \theta r_{kinmin,j}(\mathbf{c}), \bar{c}_{kinmin,j}\right\} = 0$

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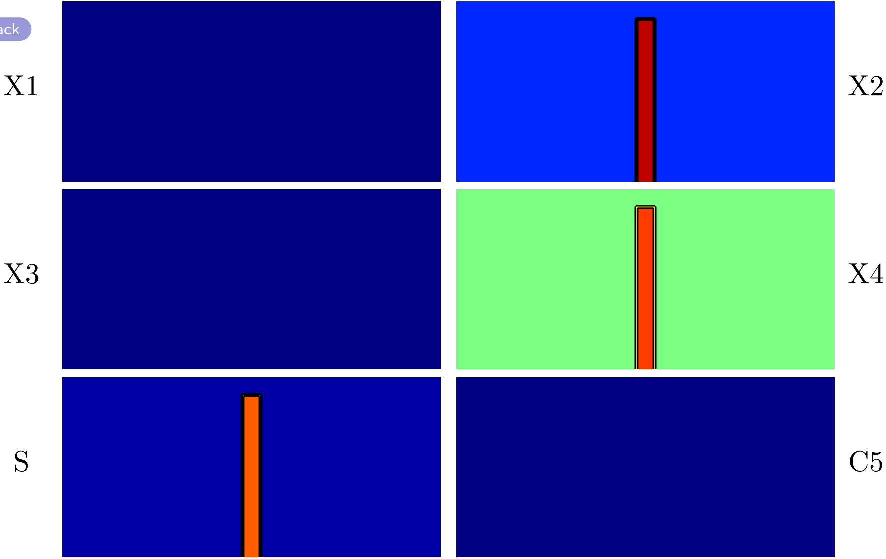

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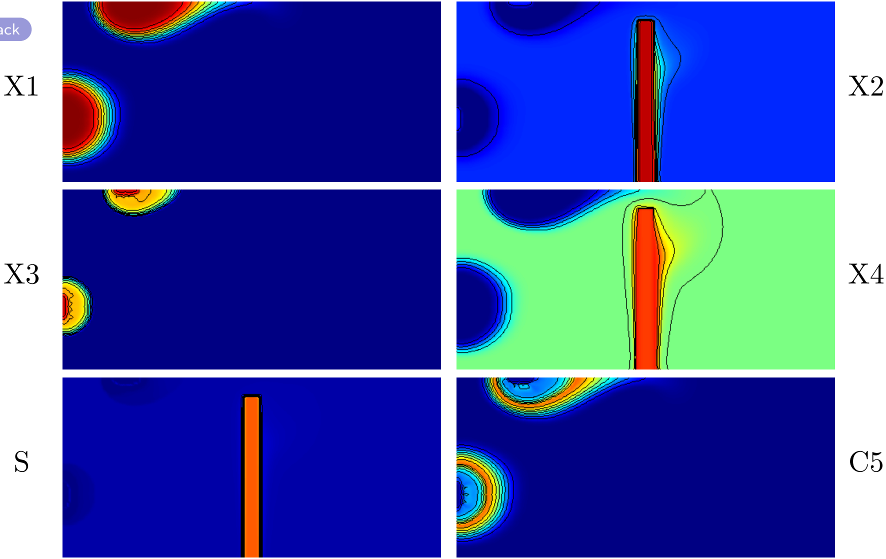

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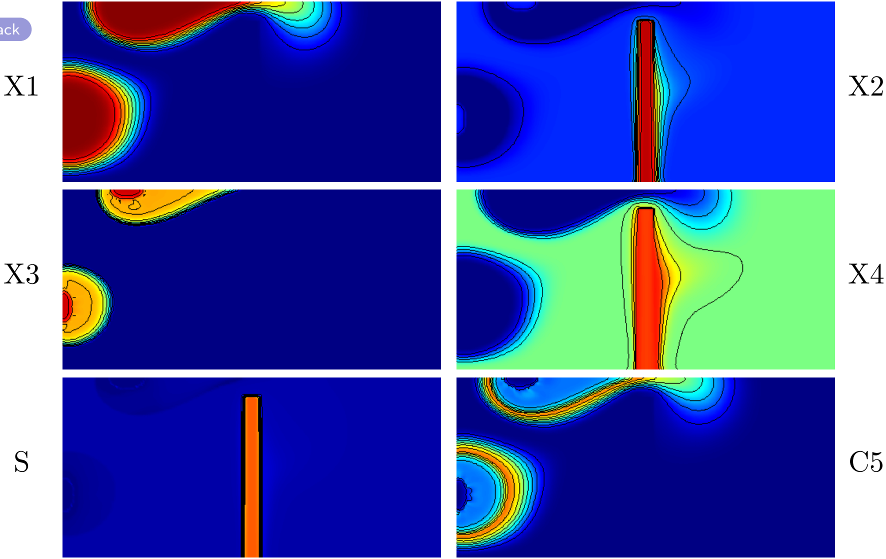

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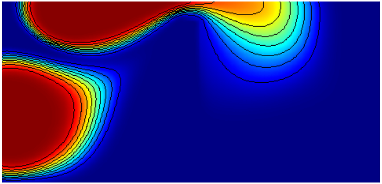

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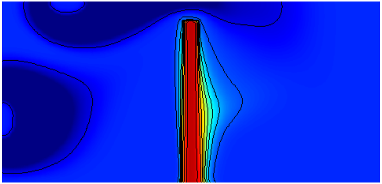

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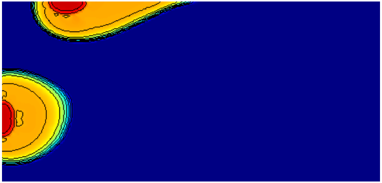

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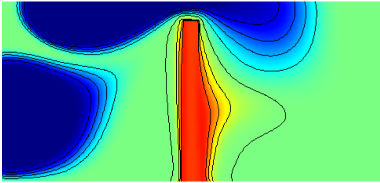

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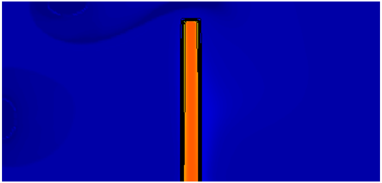

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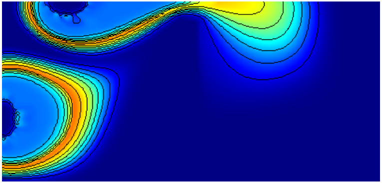

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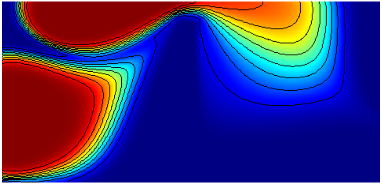
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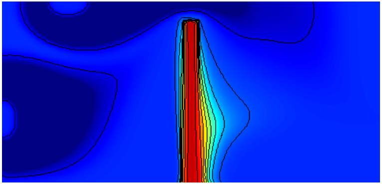
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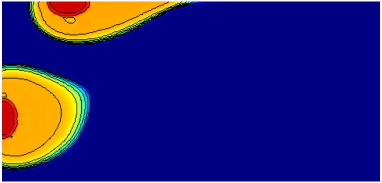
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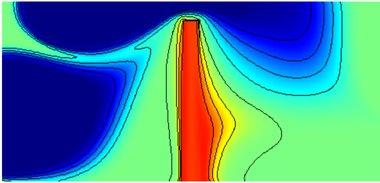
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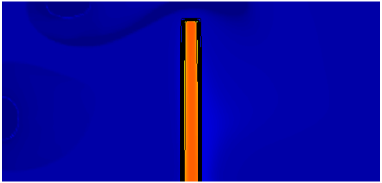
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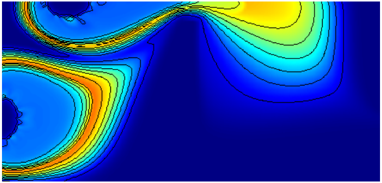
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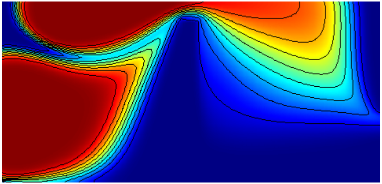

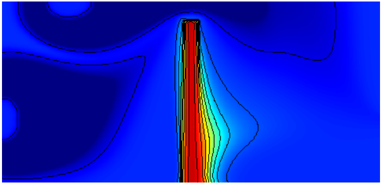

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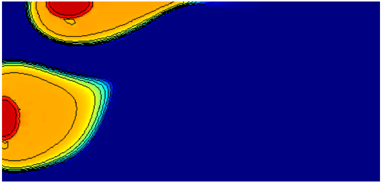

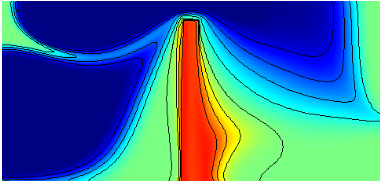

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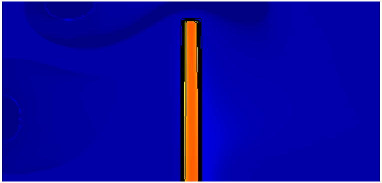

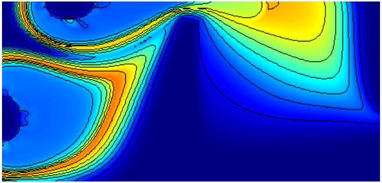

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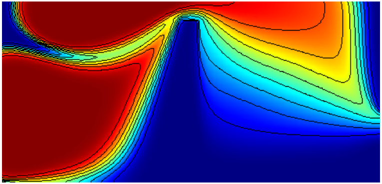

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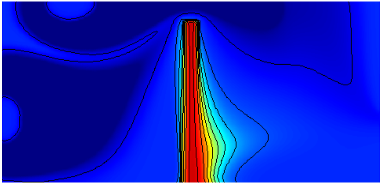

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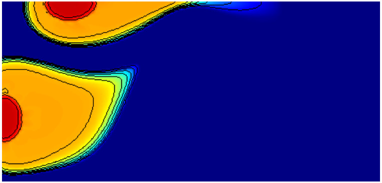

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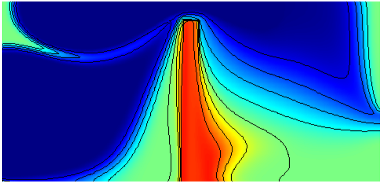

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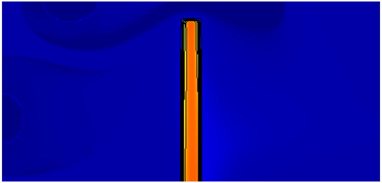

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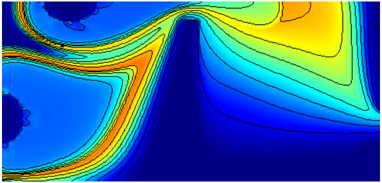

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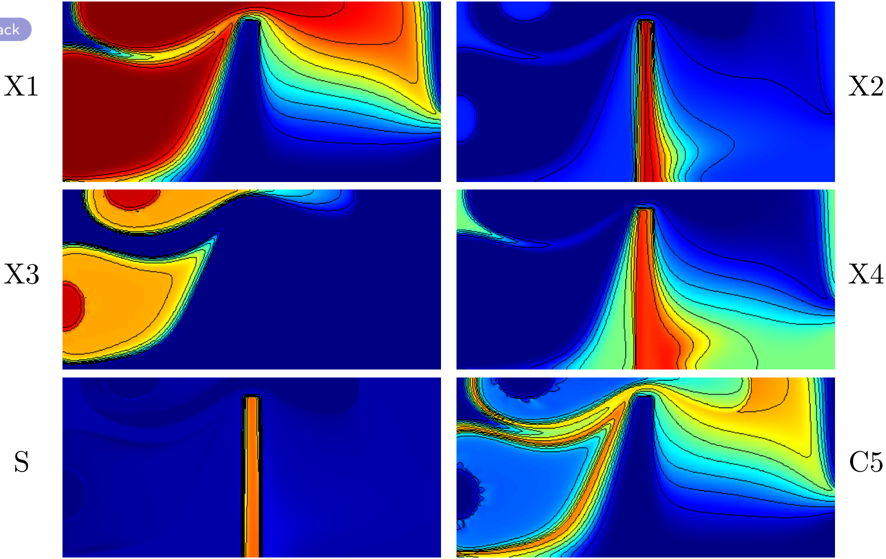

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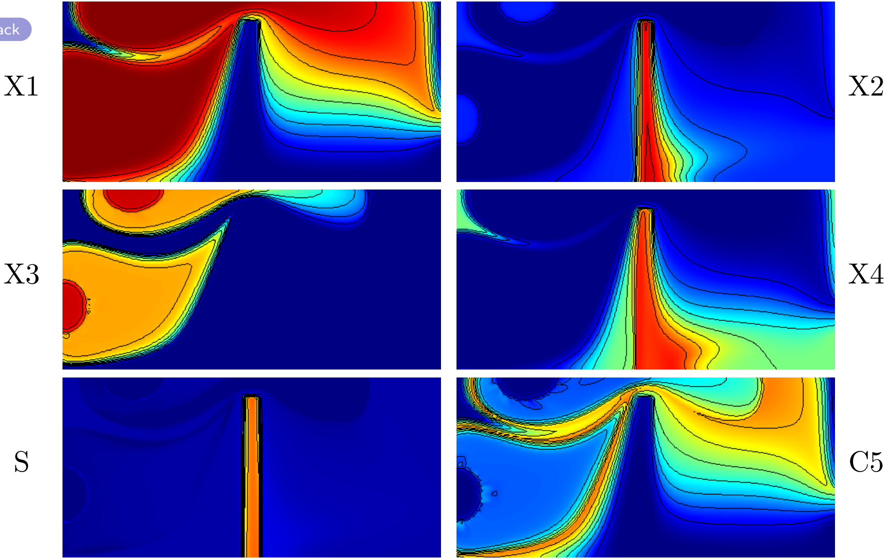

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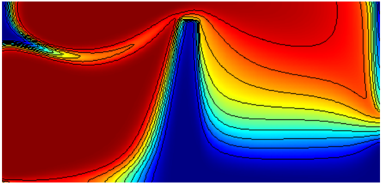
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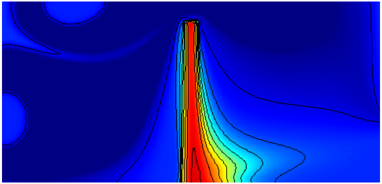
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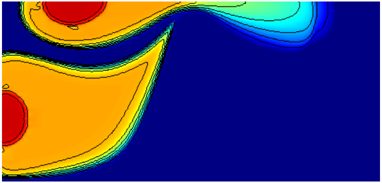
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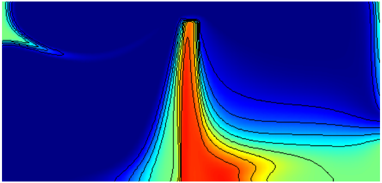
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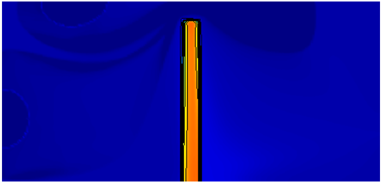
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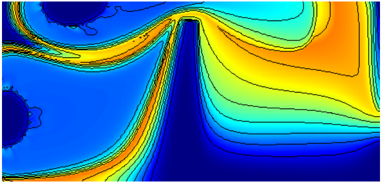
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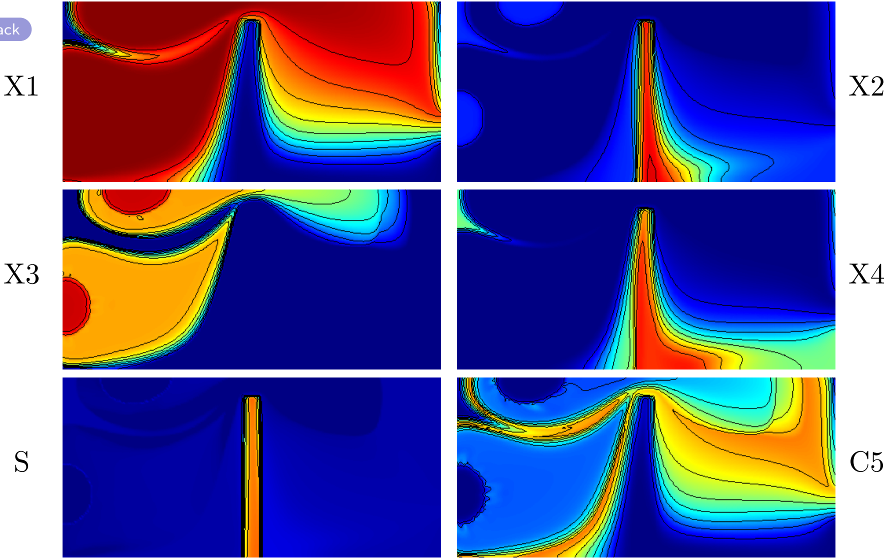

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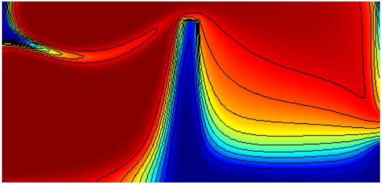

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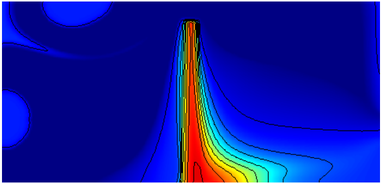

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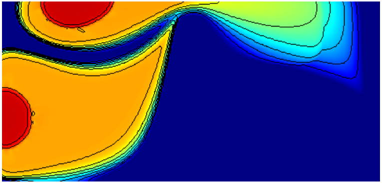

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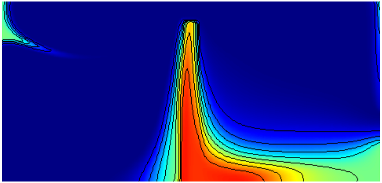

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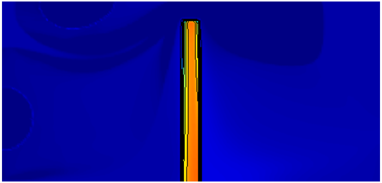

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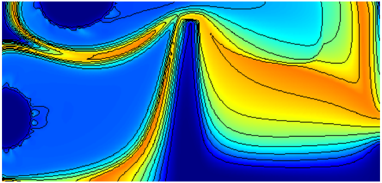

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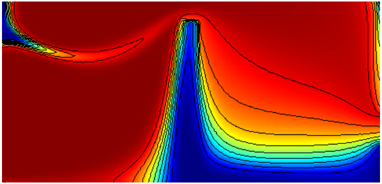

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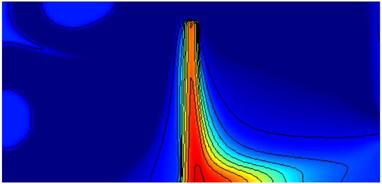

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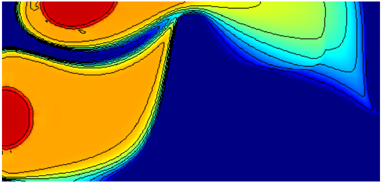

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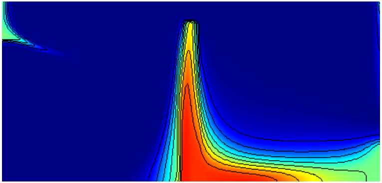

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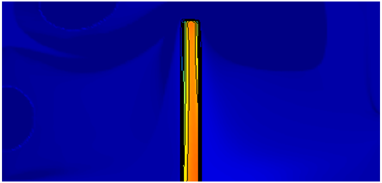

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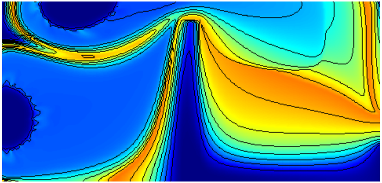

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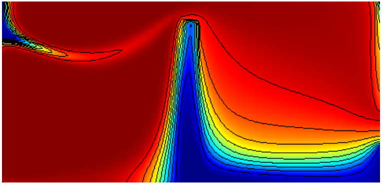

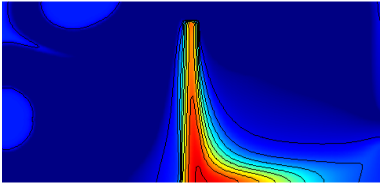

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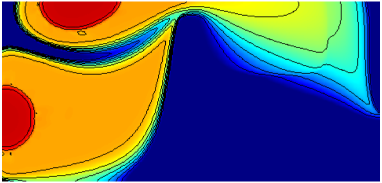

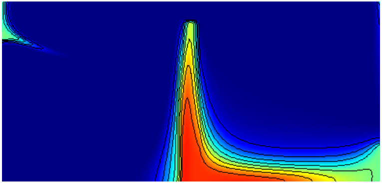

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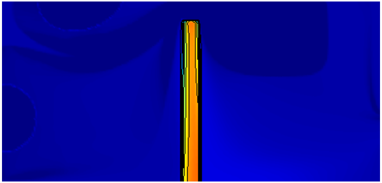

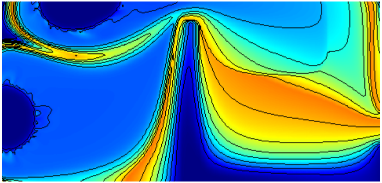

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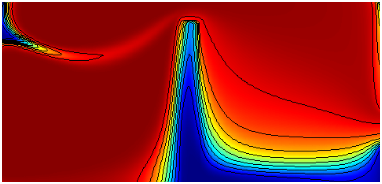

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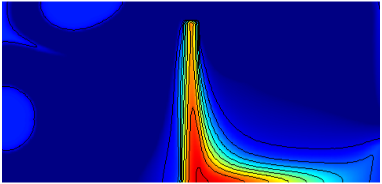

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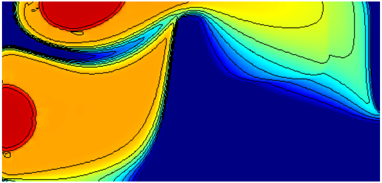

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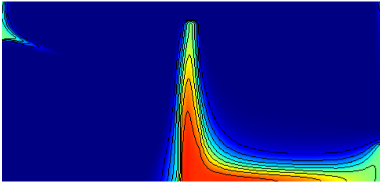

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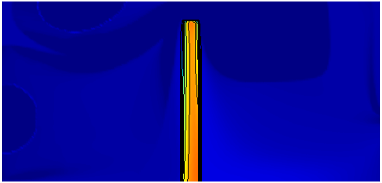

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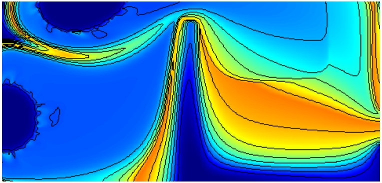

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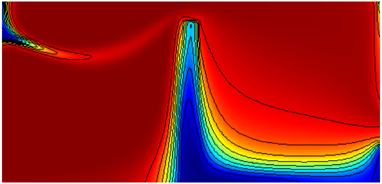

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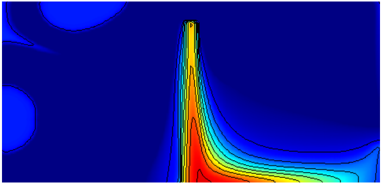

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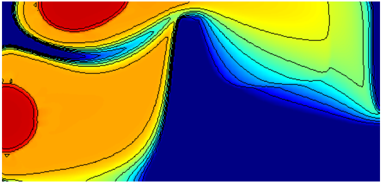

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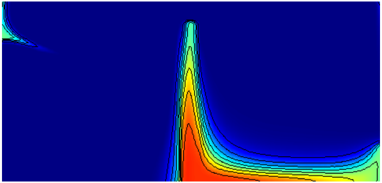

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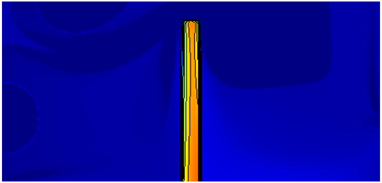

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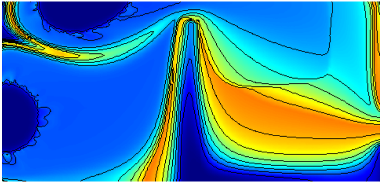

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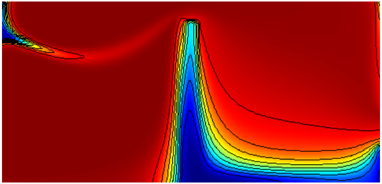

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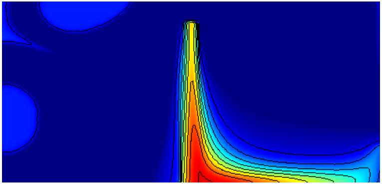

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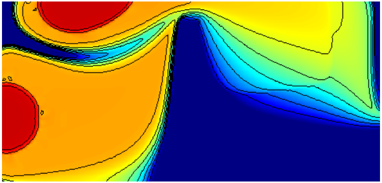

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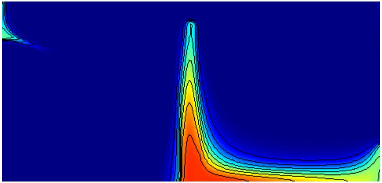

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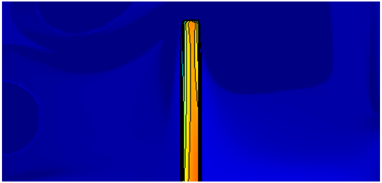

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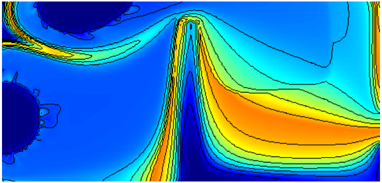

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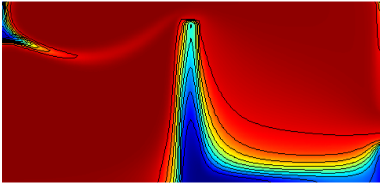

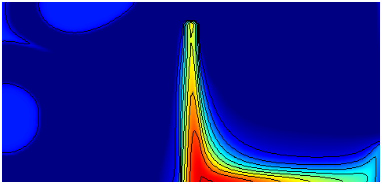

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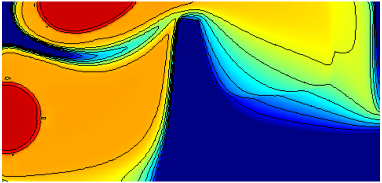

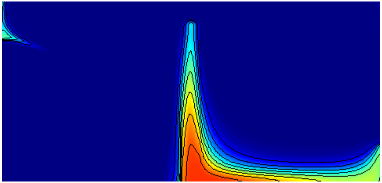

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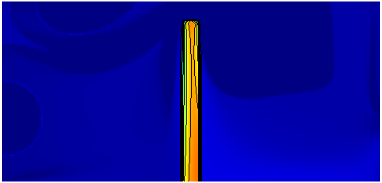

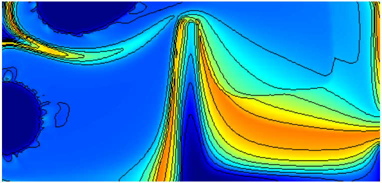

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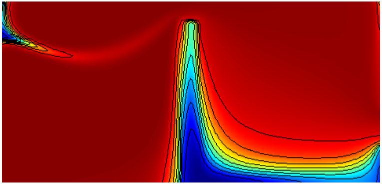

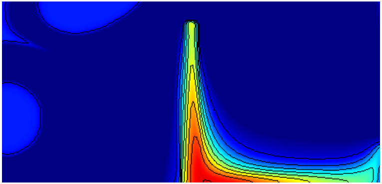

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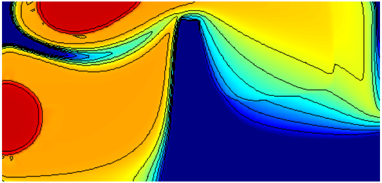

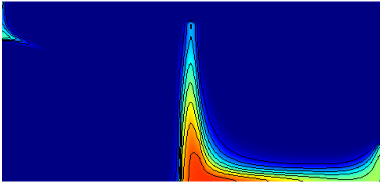

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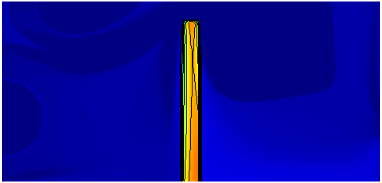

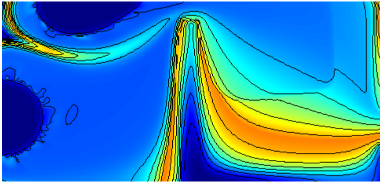

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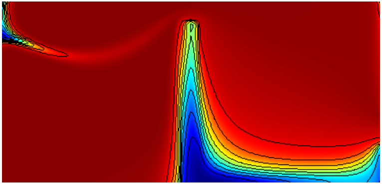
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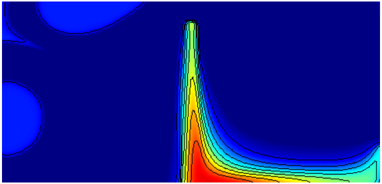
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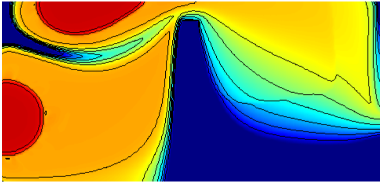
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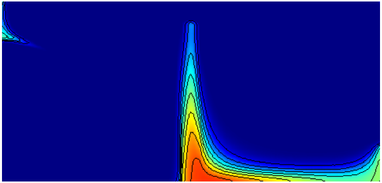
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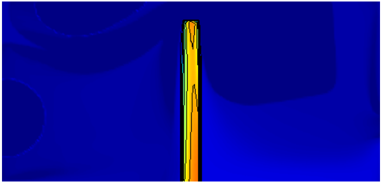
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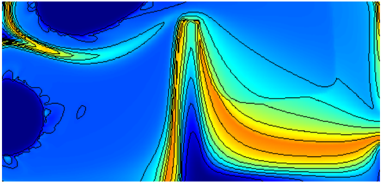
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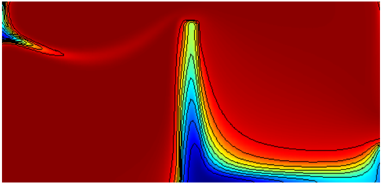

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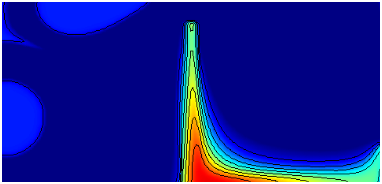

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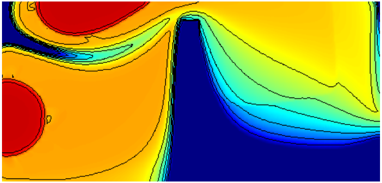

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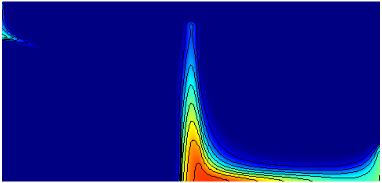

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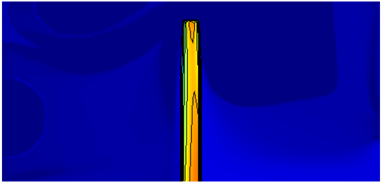

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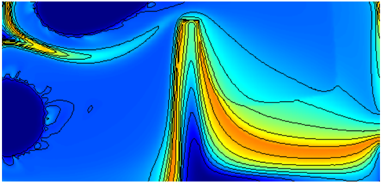

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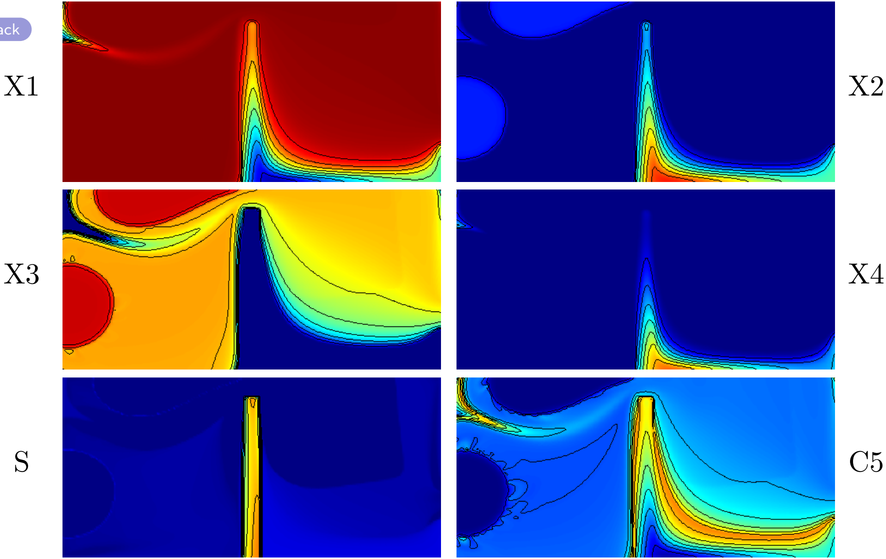

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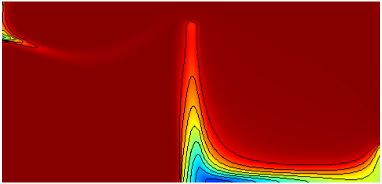

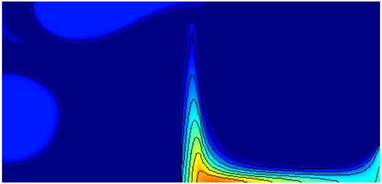

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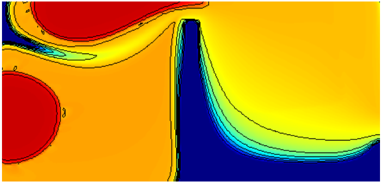

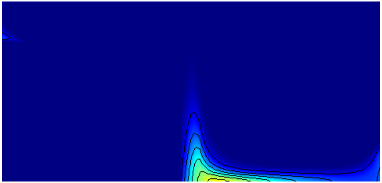

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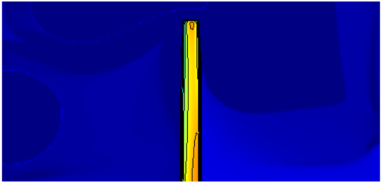

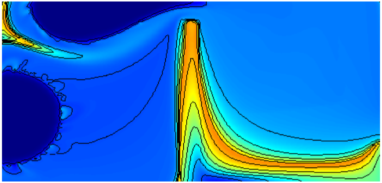

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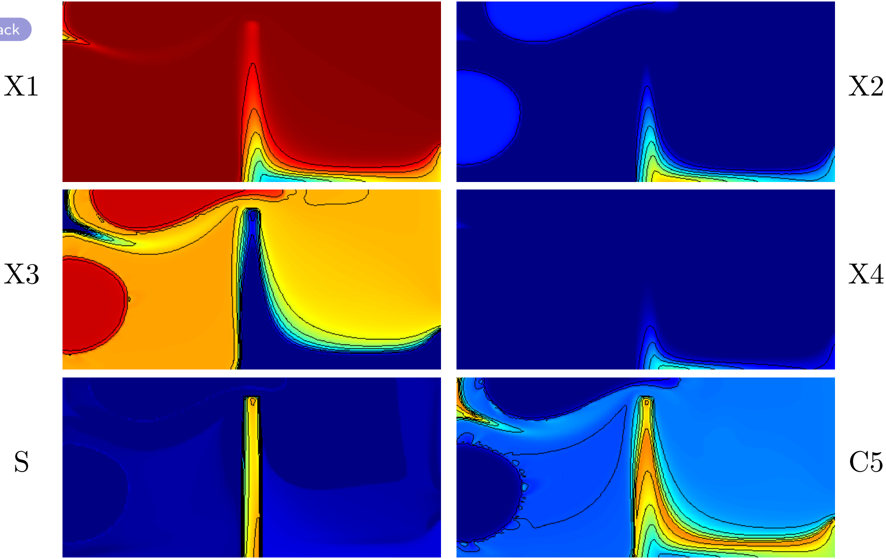

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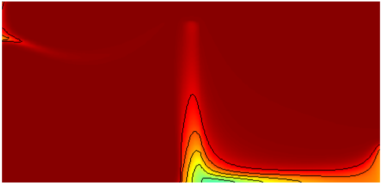

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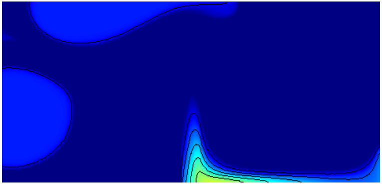

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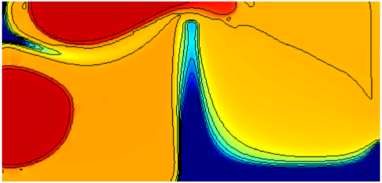

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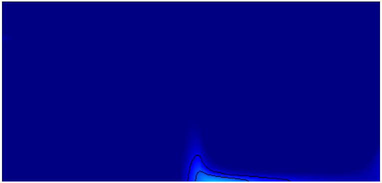

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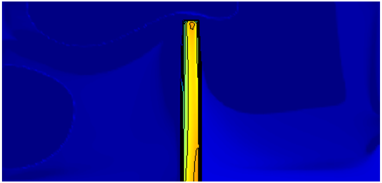

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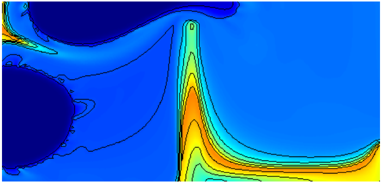

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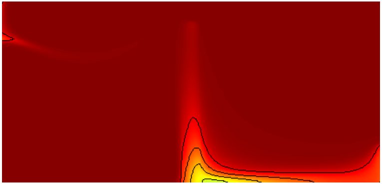

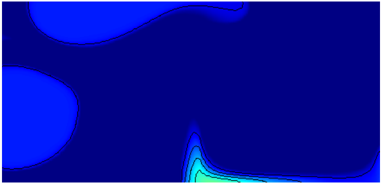

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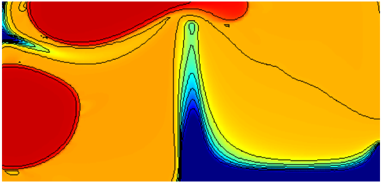

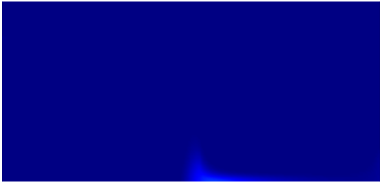

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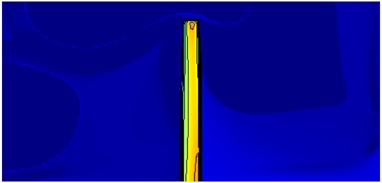

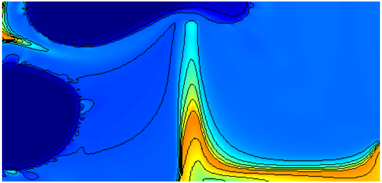

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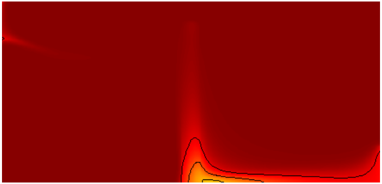

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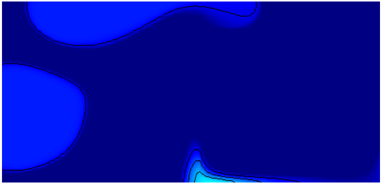

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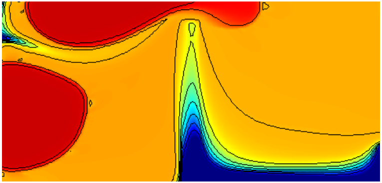

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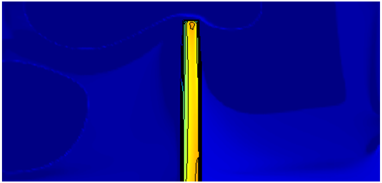

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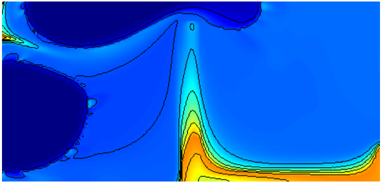

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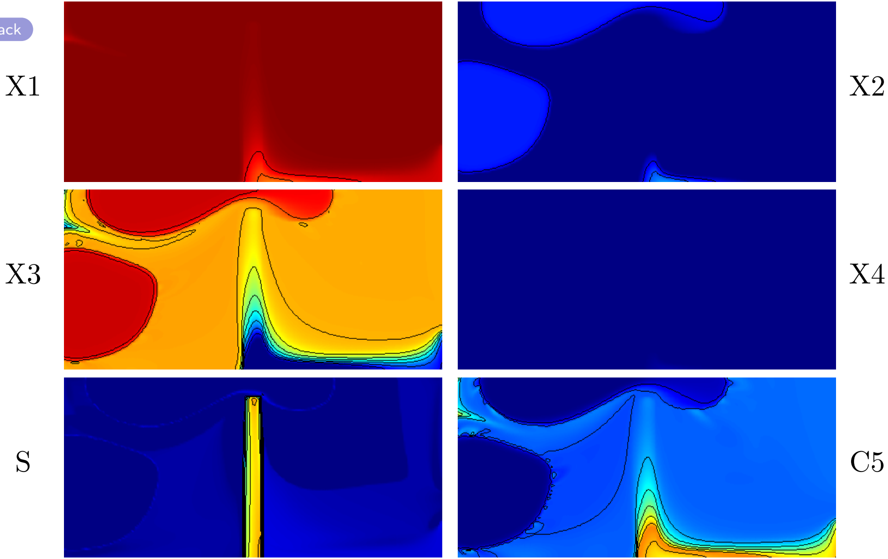

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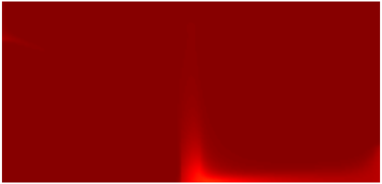

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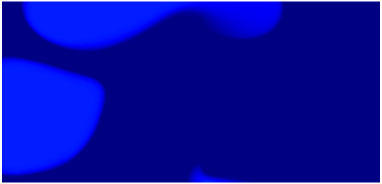

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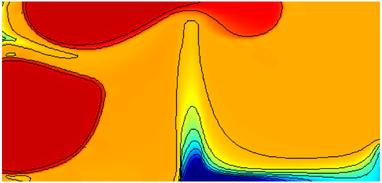

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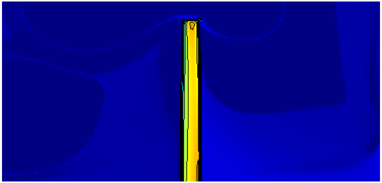

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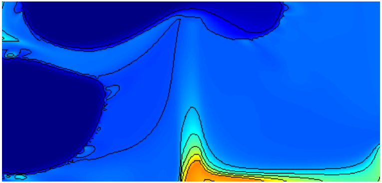

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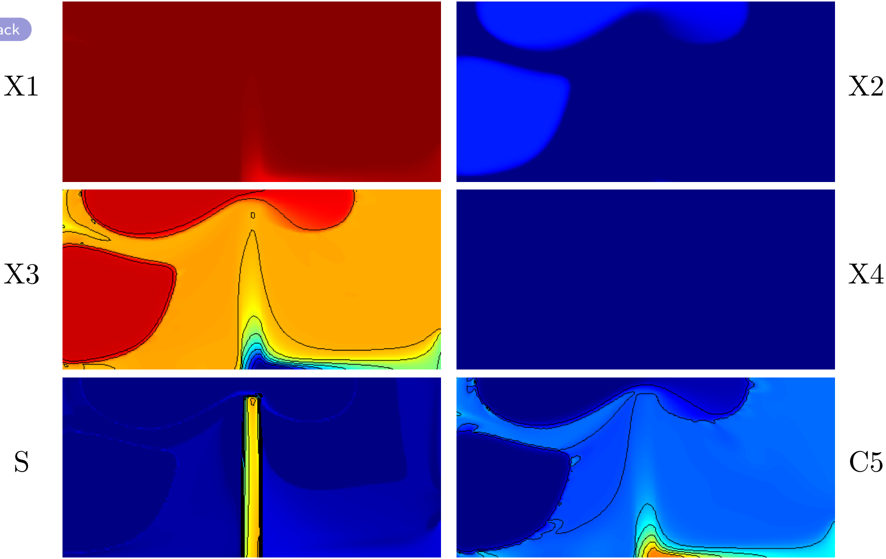

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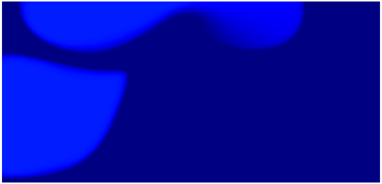

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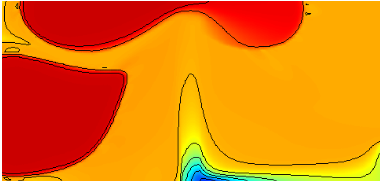

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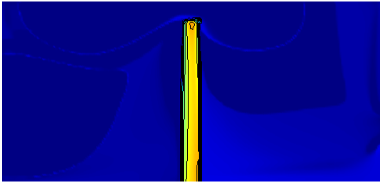

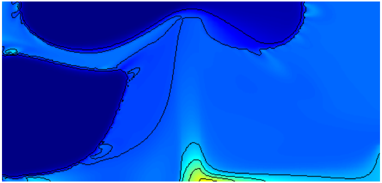

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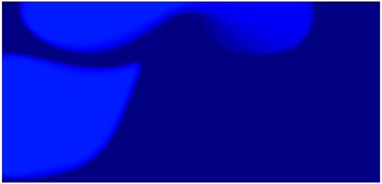

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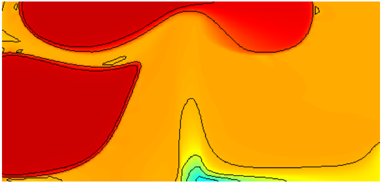

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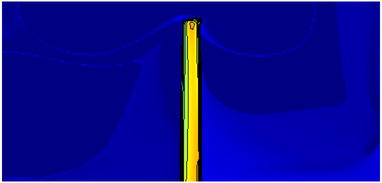

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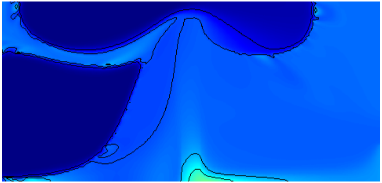

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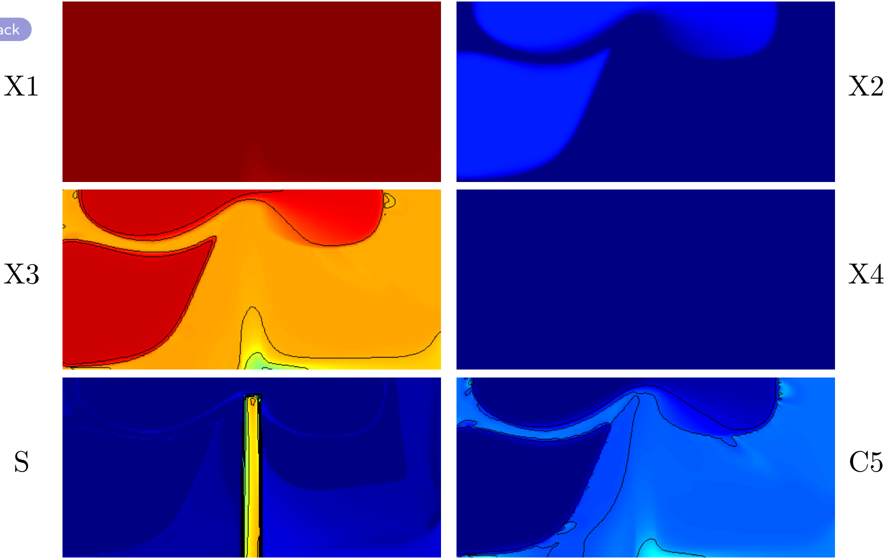

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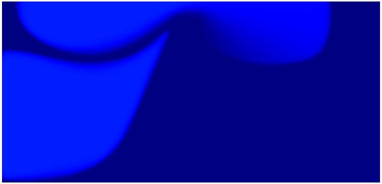

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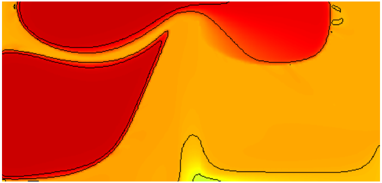

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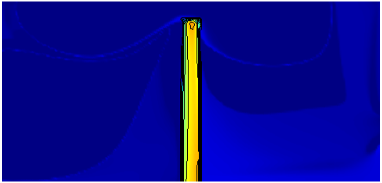

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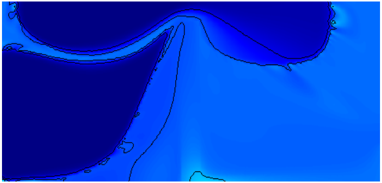

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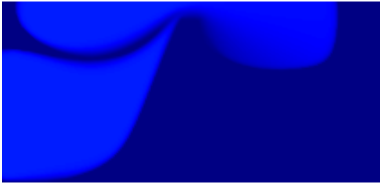

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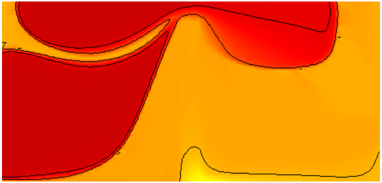

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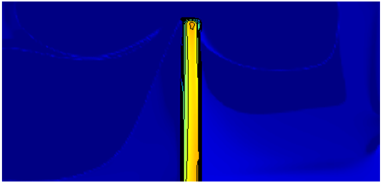

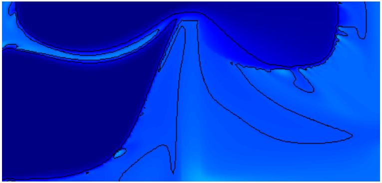

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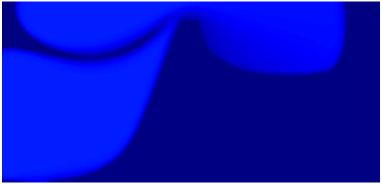

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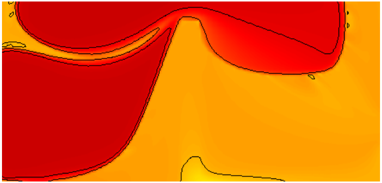

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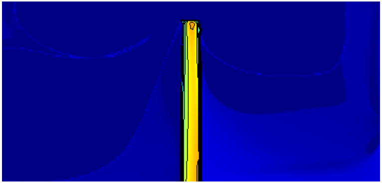

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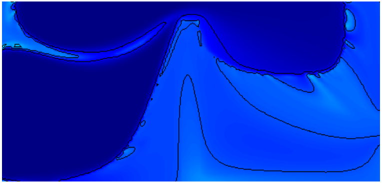

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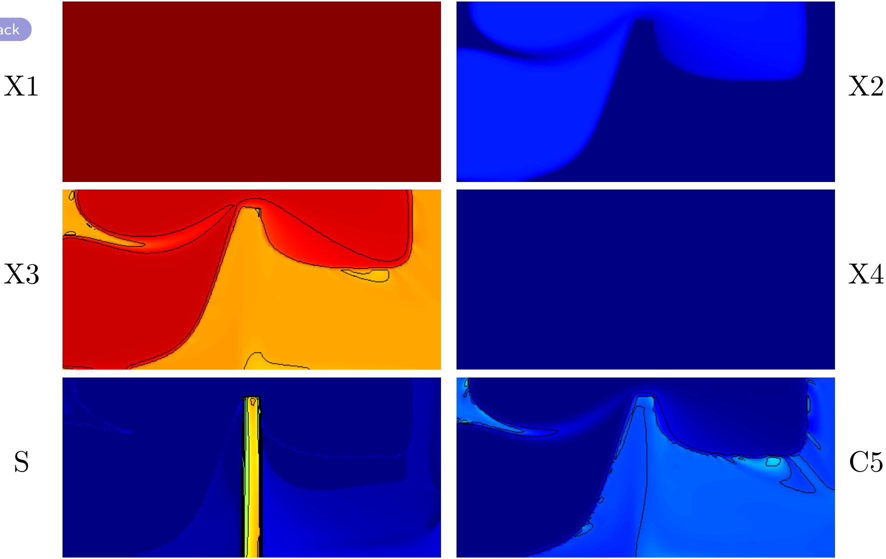

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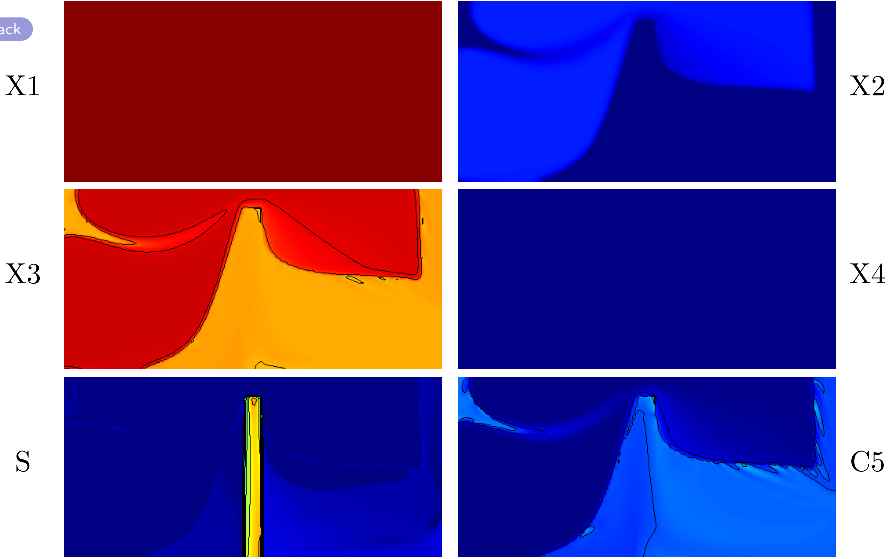

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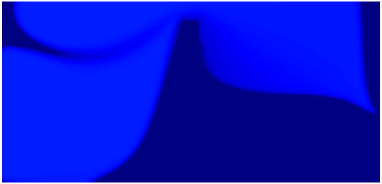

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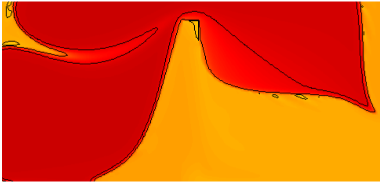

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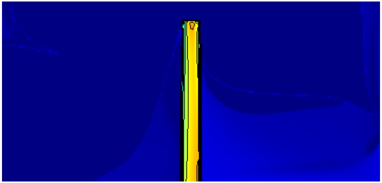

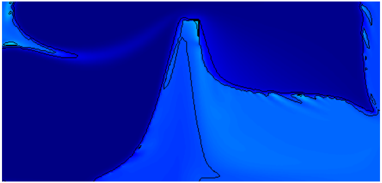

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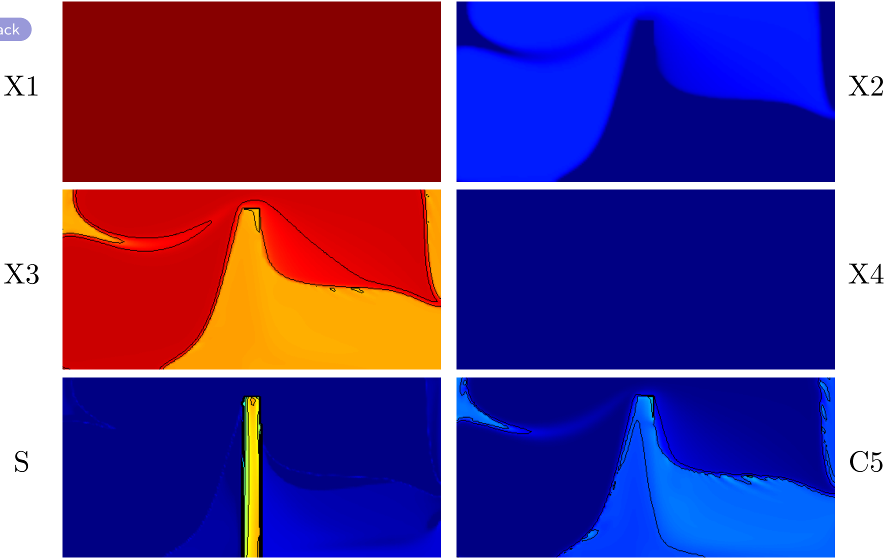

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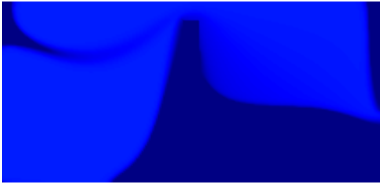

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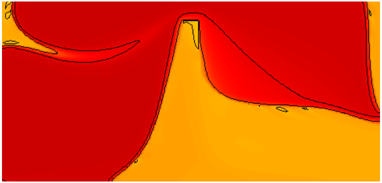

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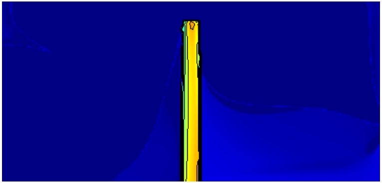

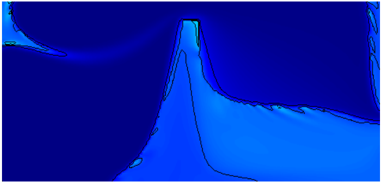

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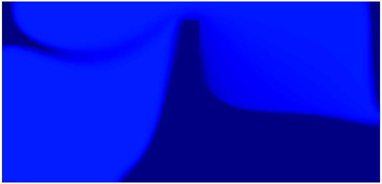

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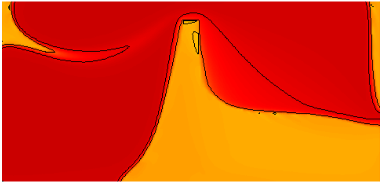

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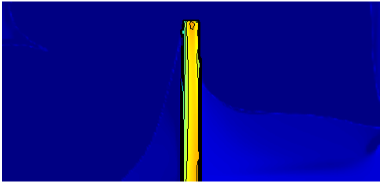

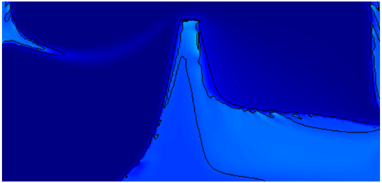

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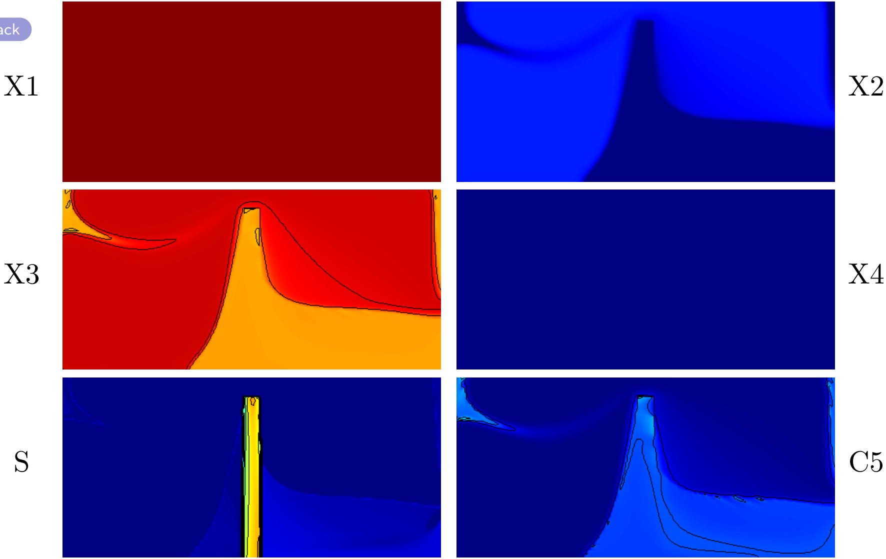

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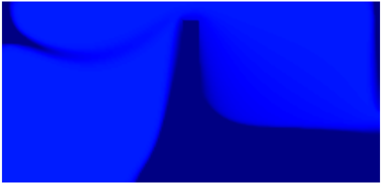

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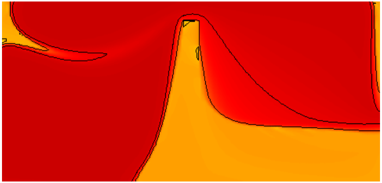

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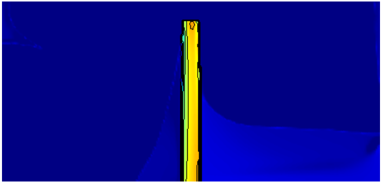

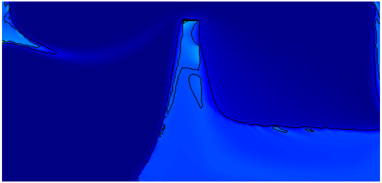

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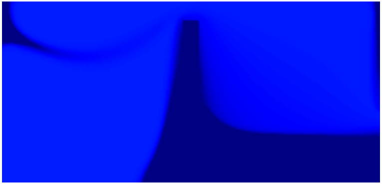

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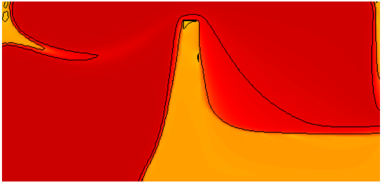

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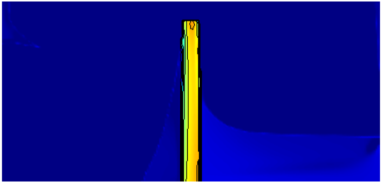

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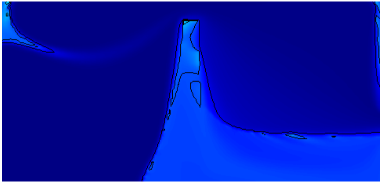

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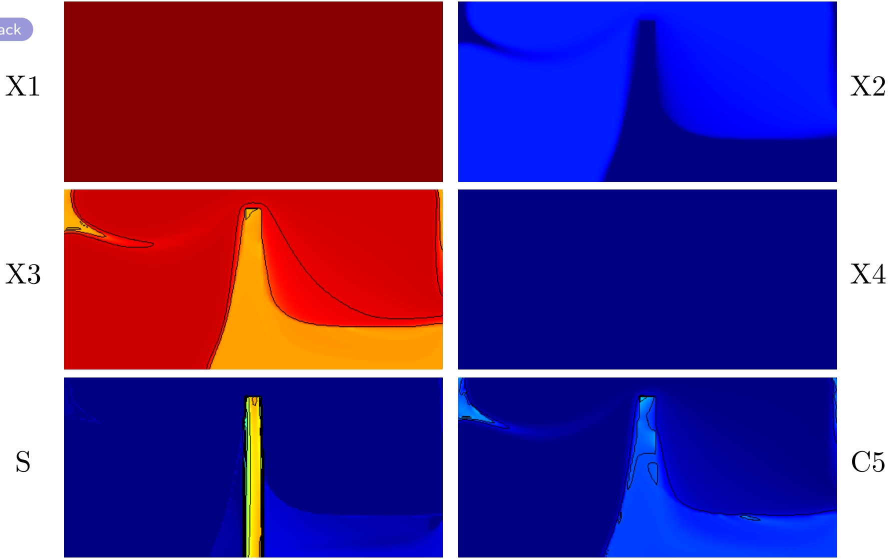

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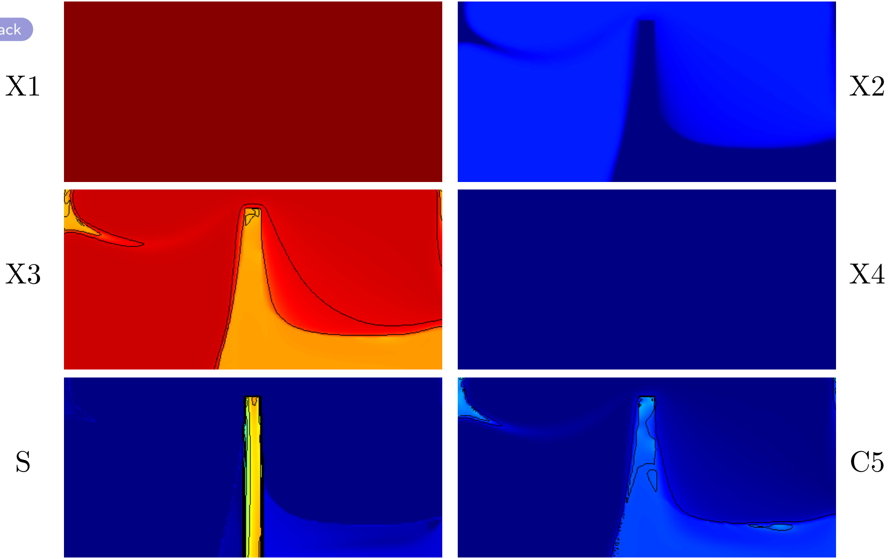

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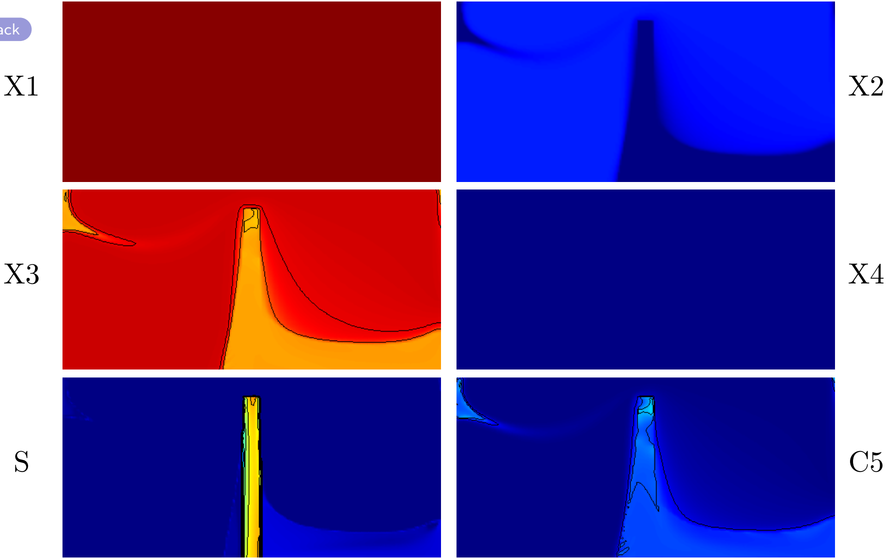

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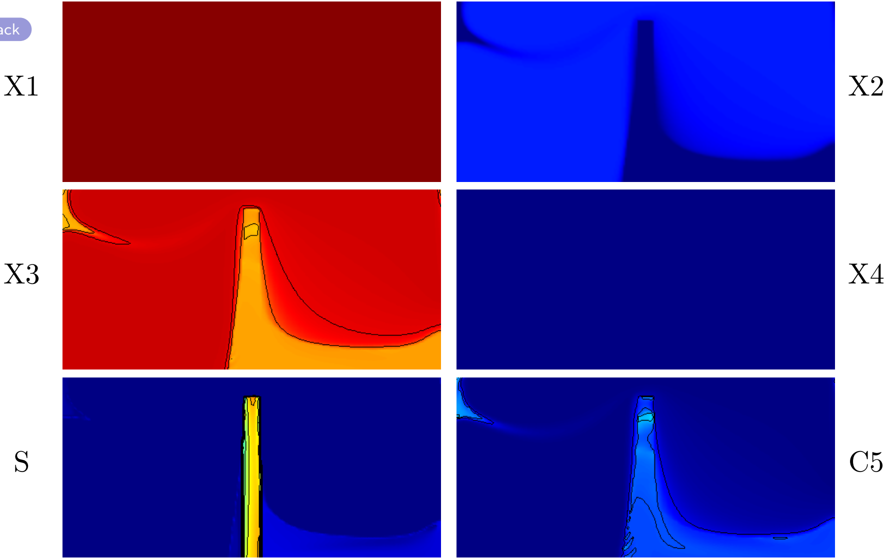

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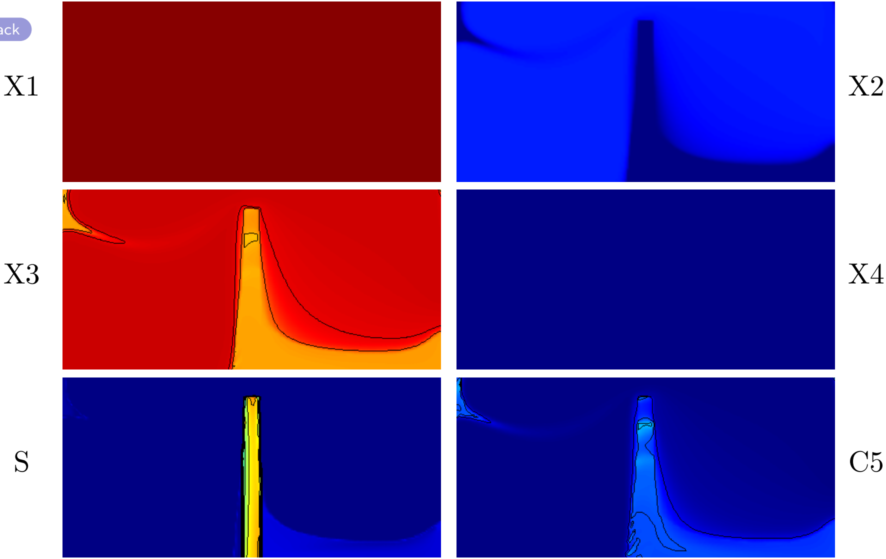

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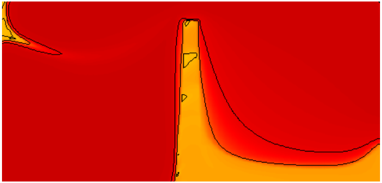

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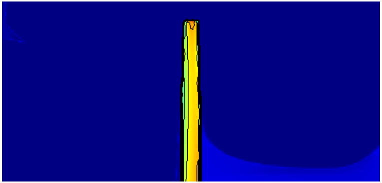

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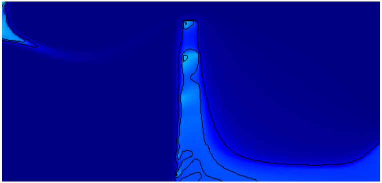

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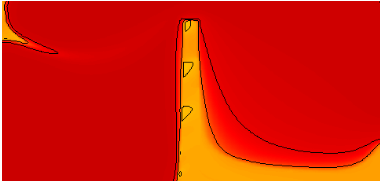

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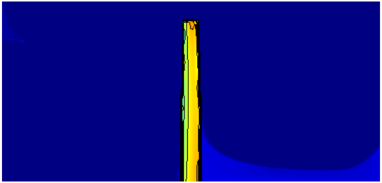

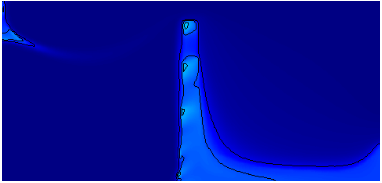

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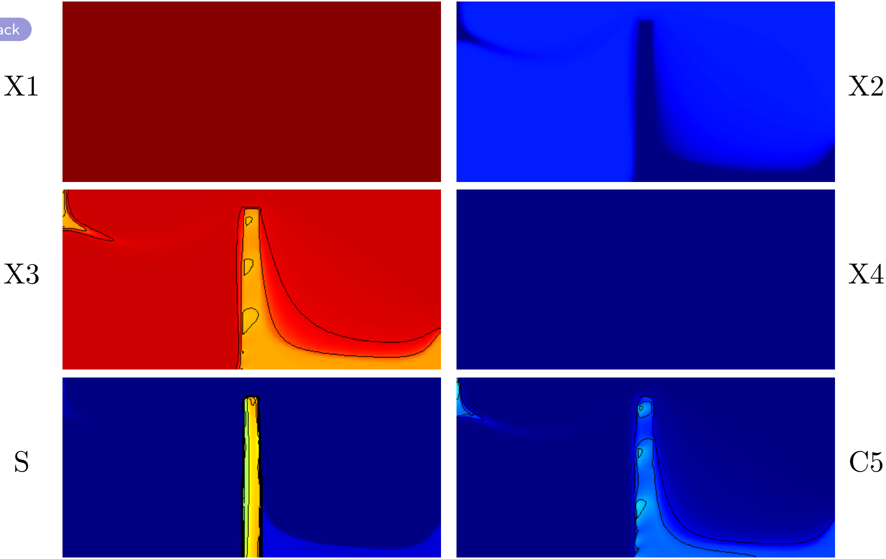

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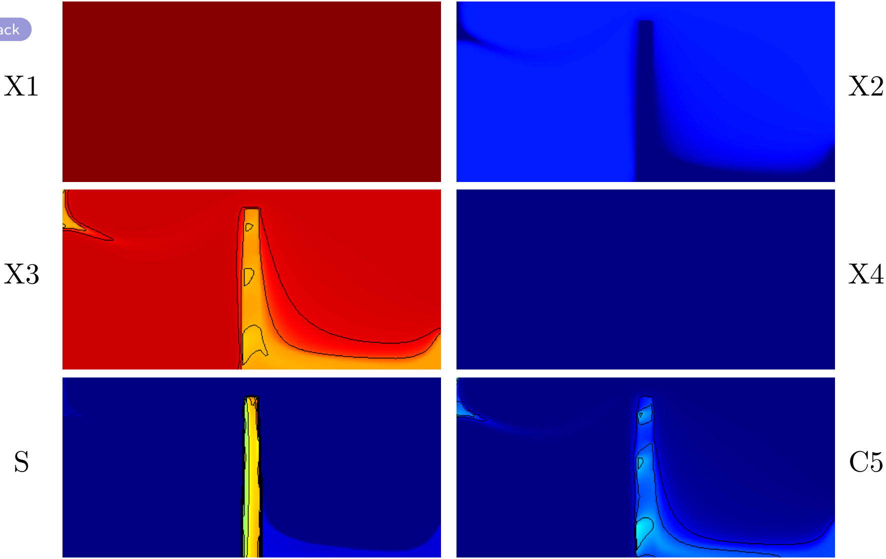

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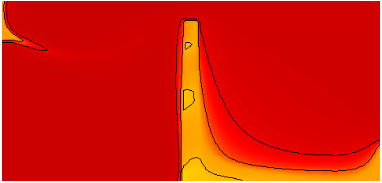

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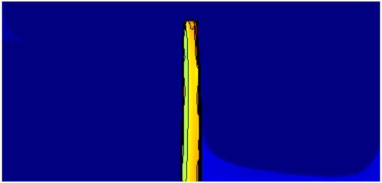

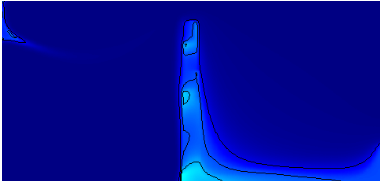

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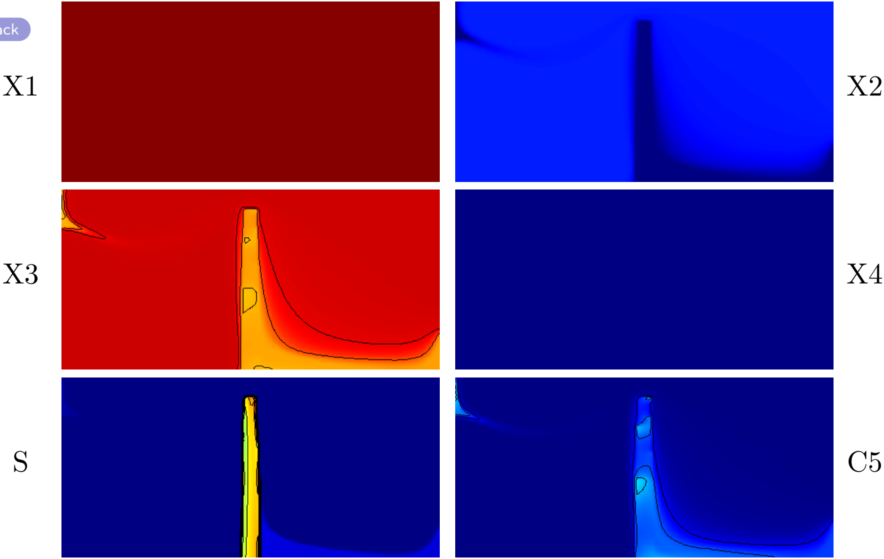

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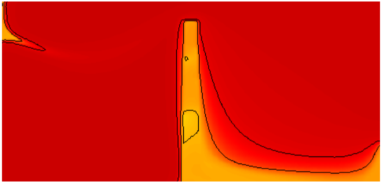

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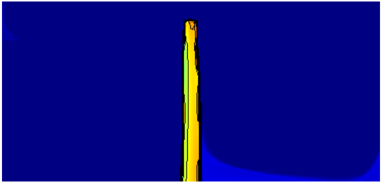

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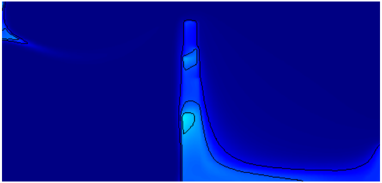

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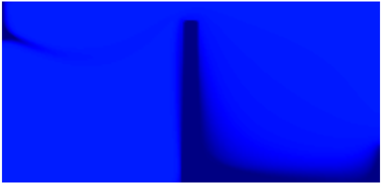

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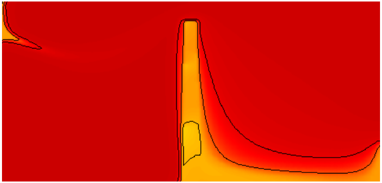

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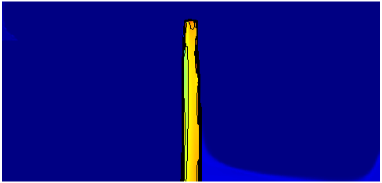

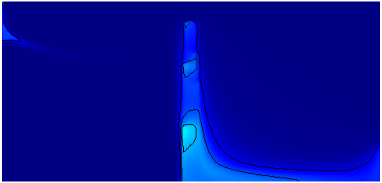

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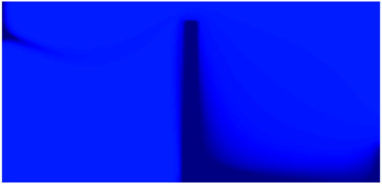
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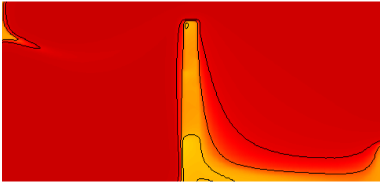
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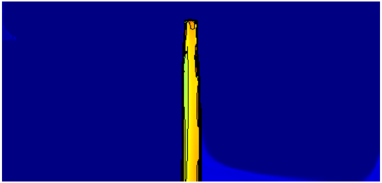
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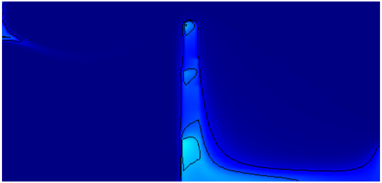
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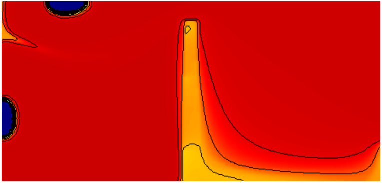

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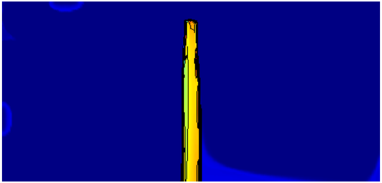

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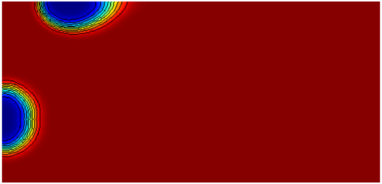

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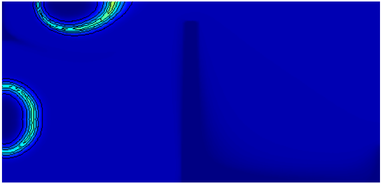

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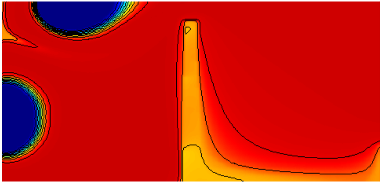

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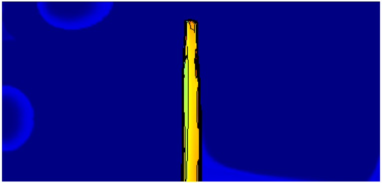

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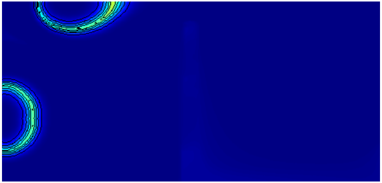

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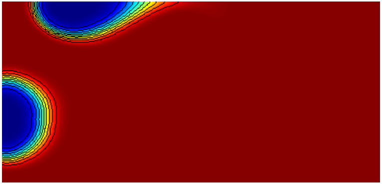

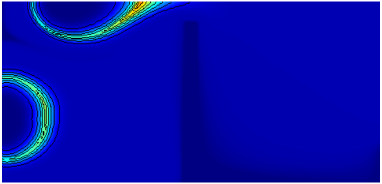

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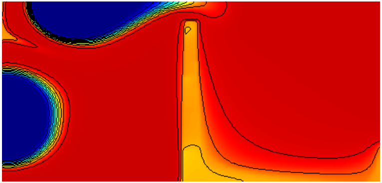

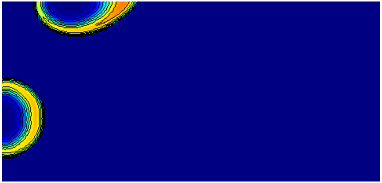

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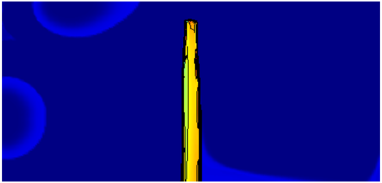

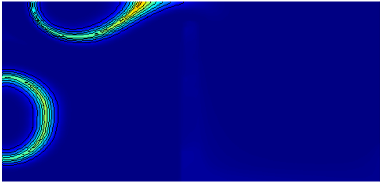

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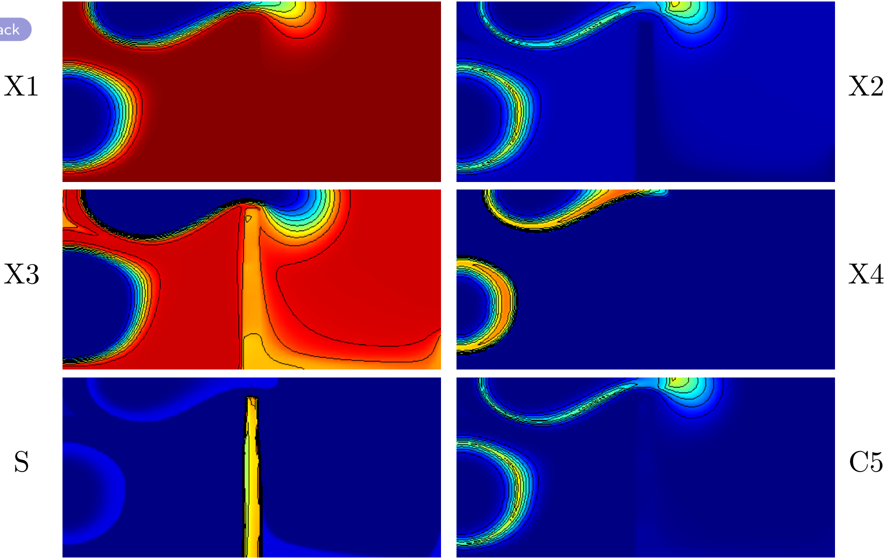

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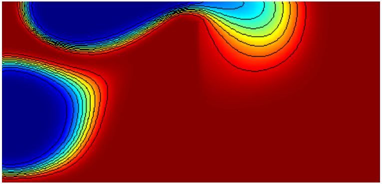

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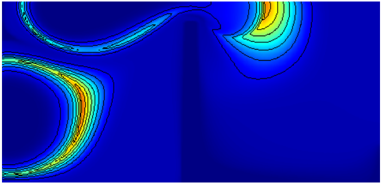

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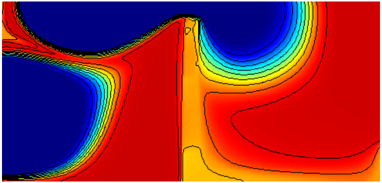

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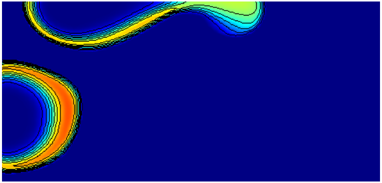

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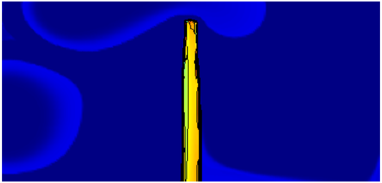

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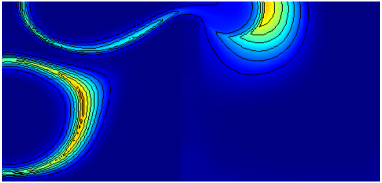

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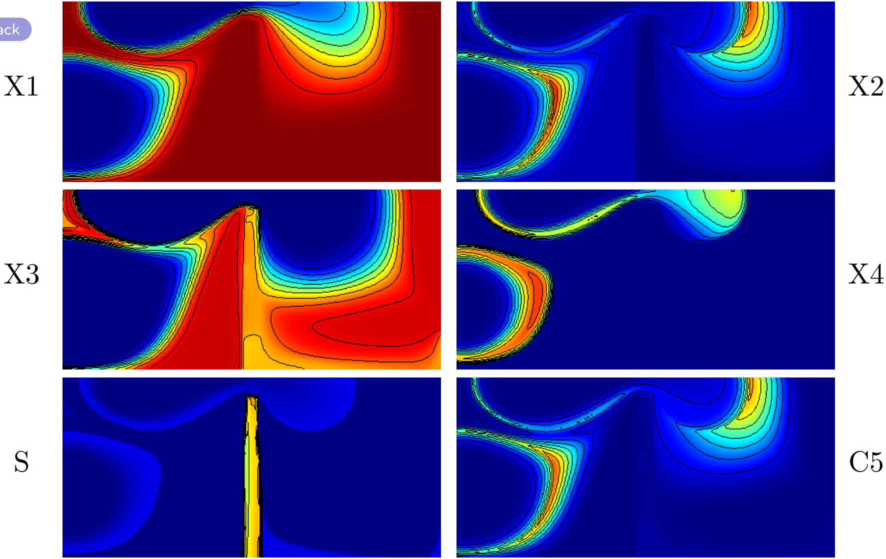

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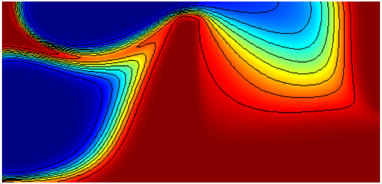

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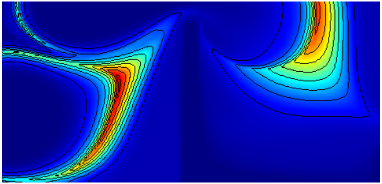

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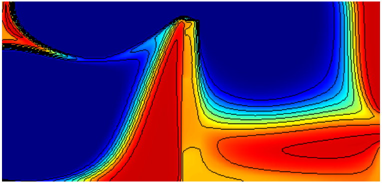

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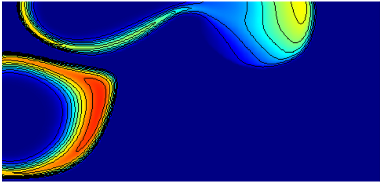

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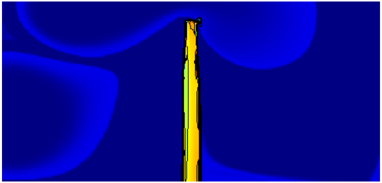

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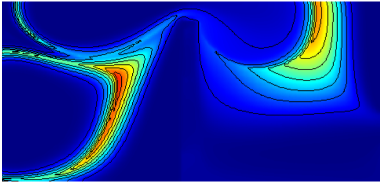

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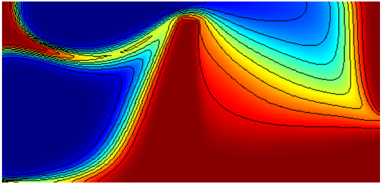

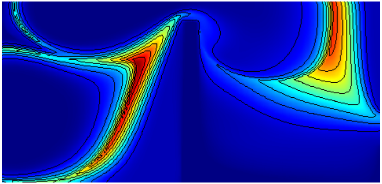

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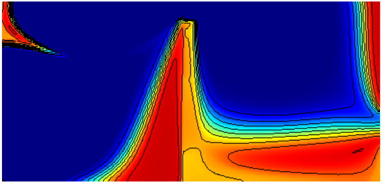

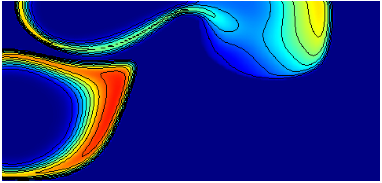

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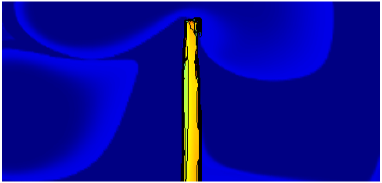

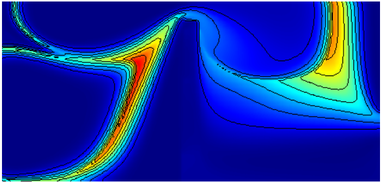

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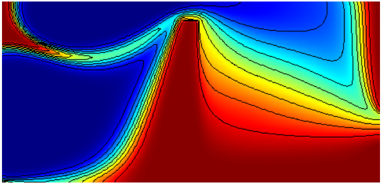

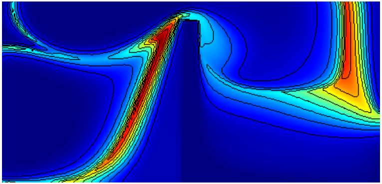

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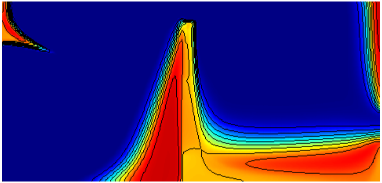

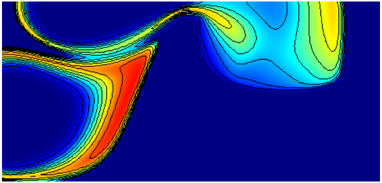

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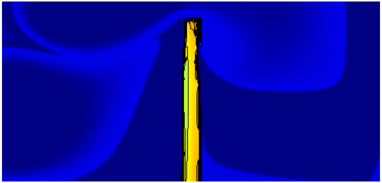

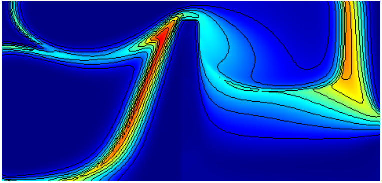

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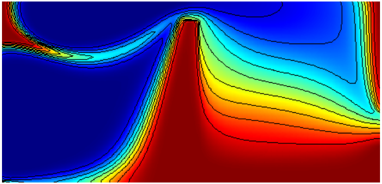

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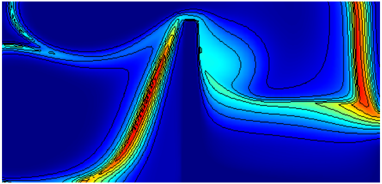

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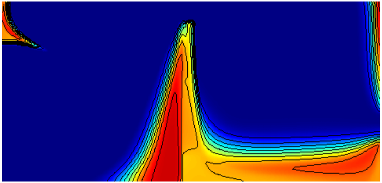

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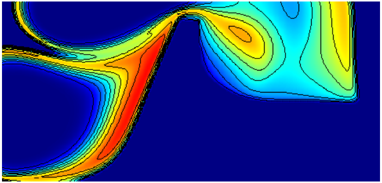

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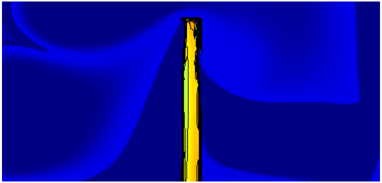

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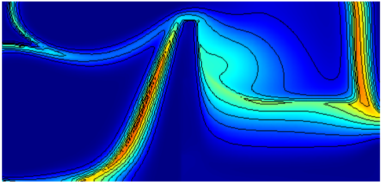

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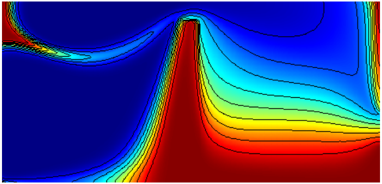

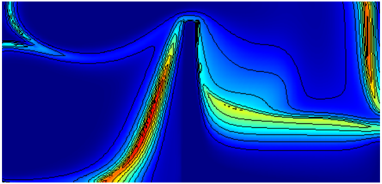

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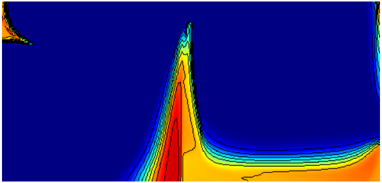

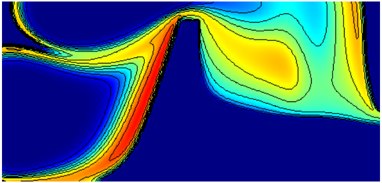

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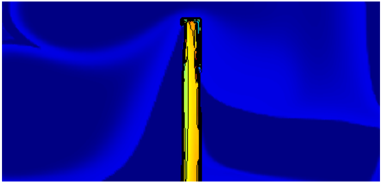

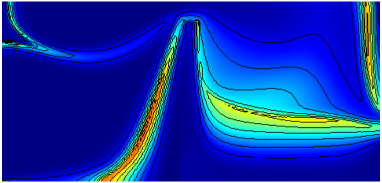

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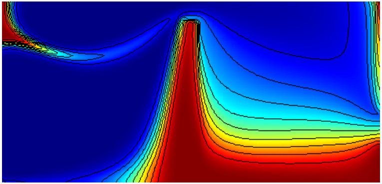

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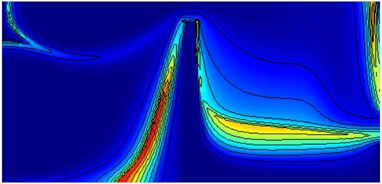

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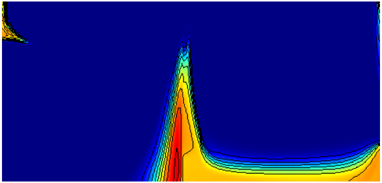

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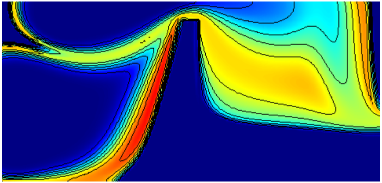

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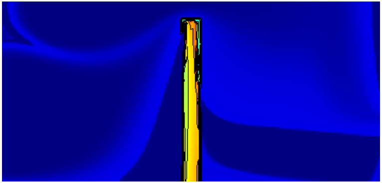

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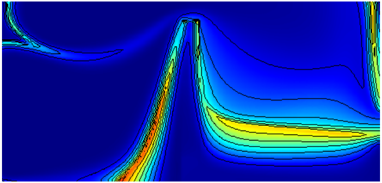

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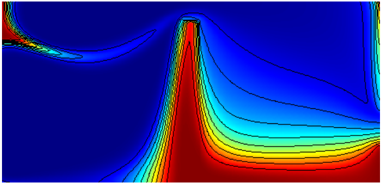

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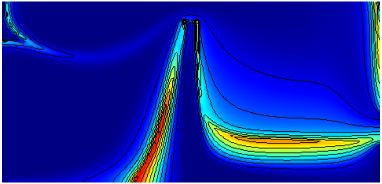

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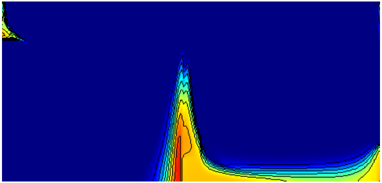

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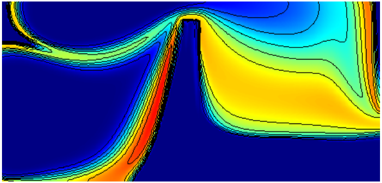

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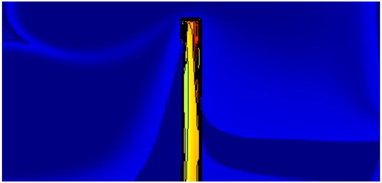

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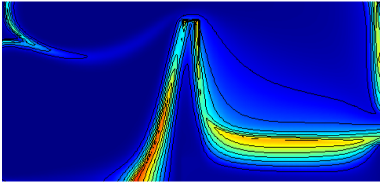

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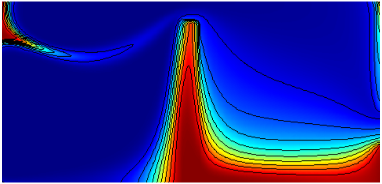

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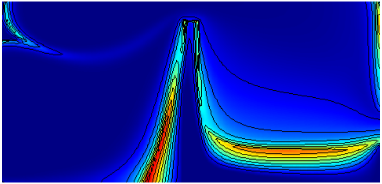

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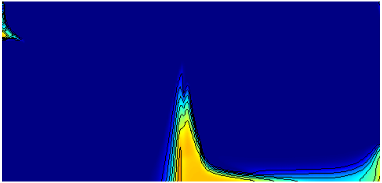

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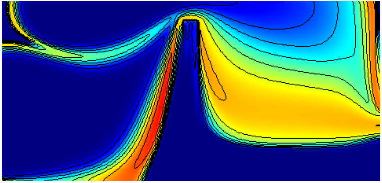

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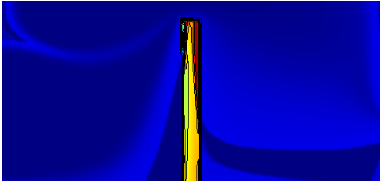

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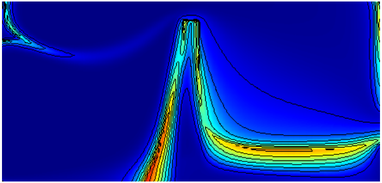

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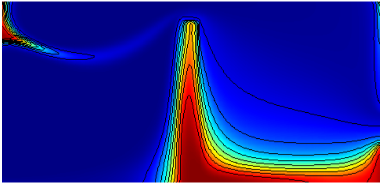

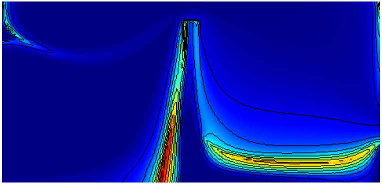

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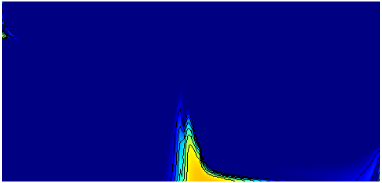

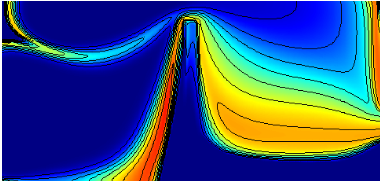

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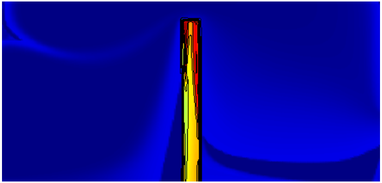

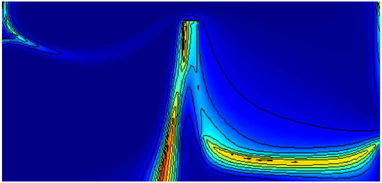

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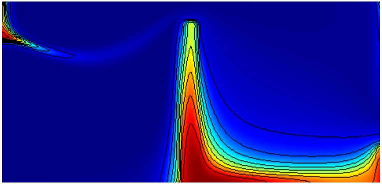

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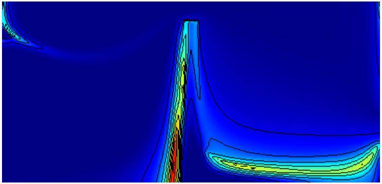

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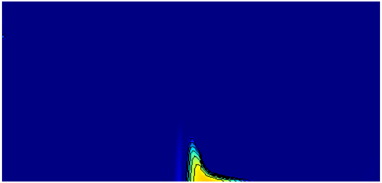

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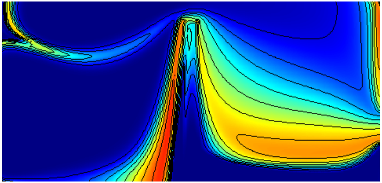

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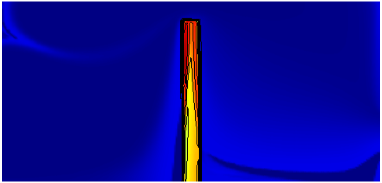

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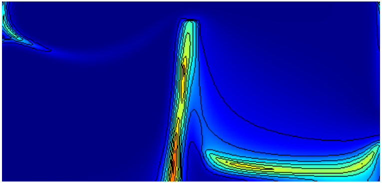

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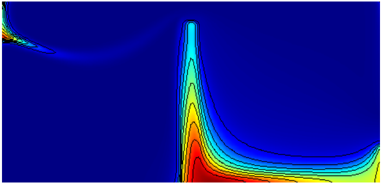

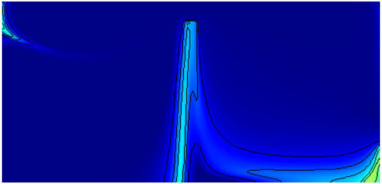

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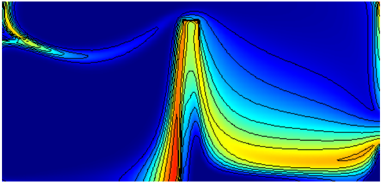

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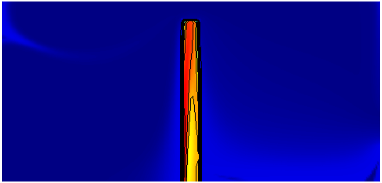

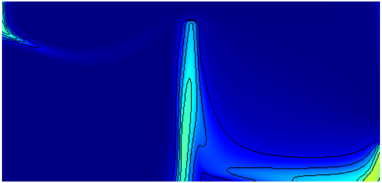

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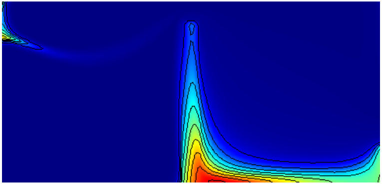

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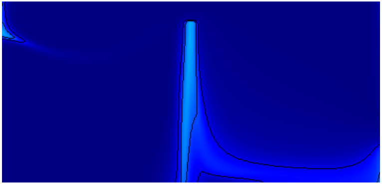

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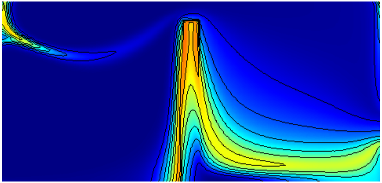

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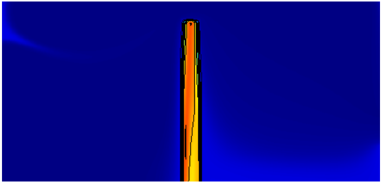

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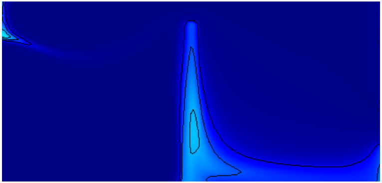

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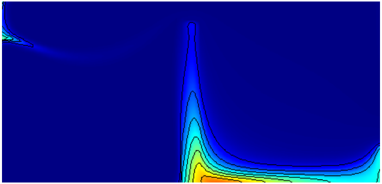

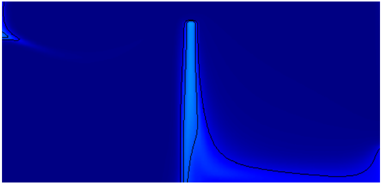

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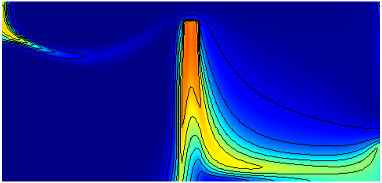

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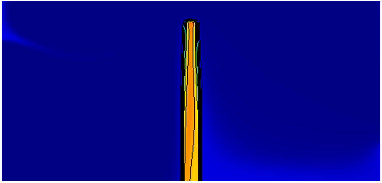

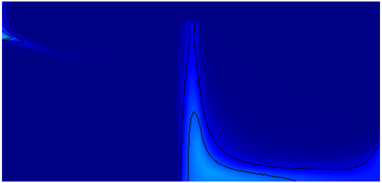

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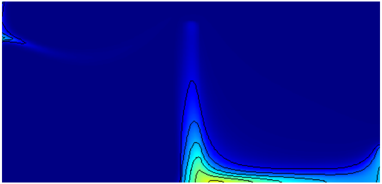

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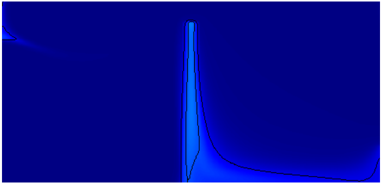

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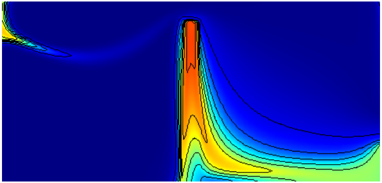

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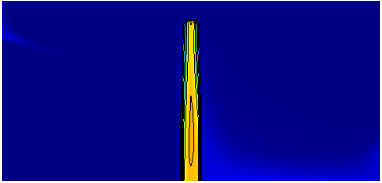

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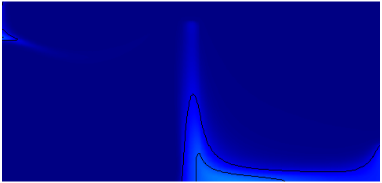

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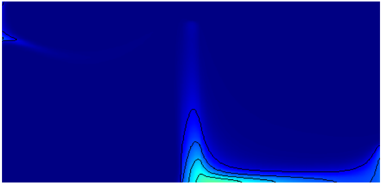

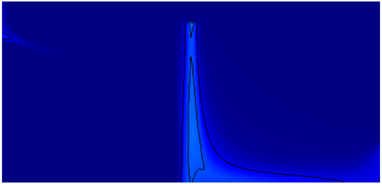

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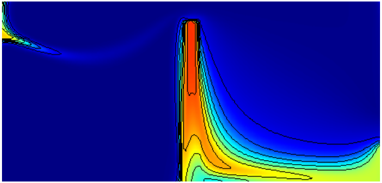

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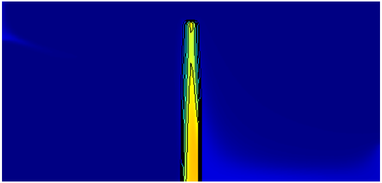

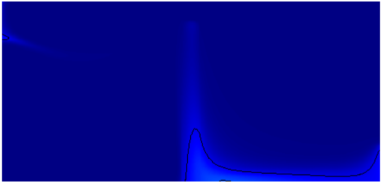

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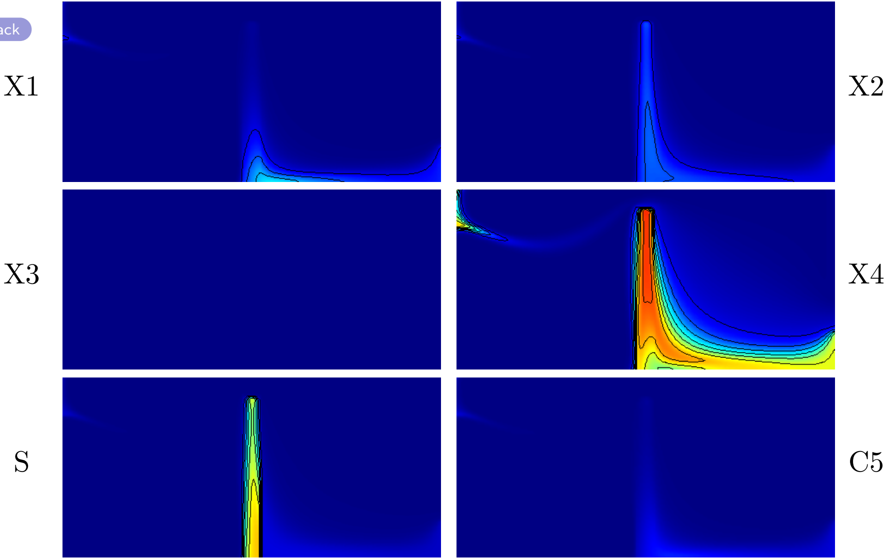

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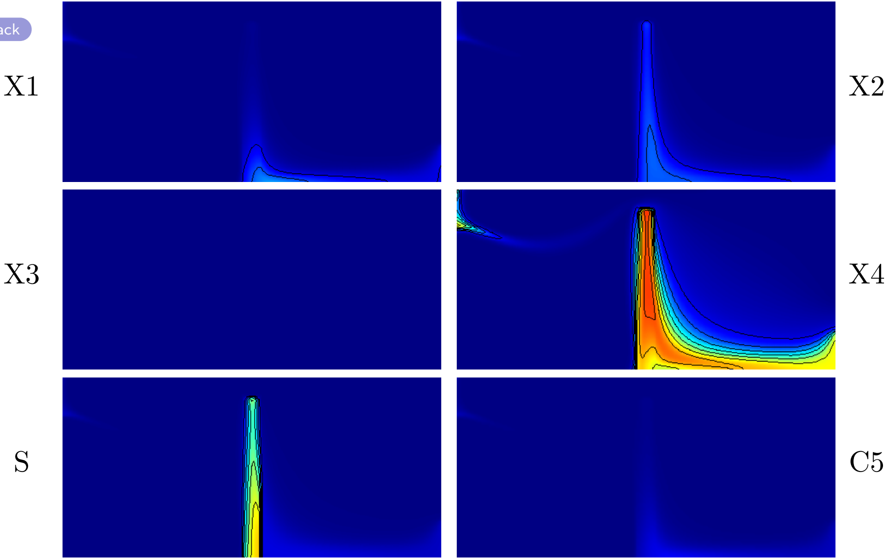

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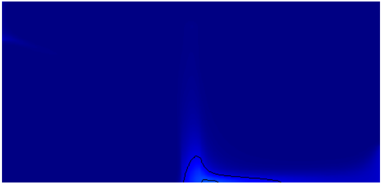

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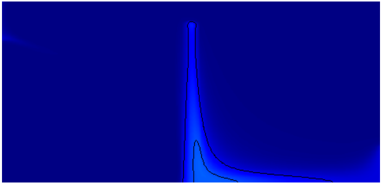

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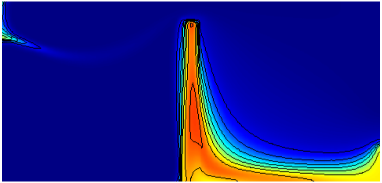

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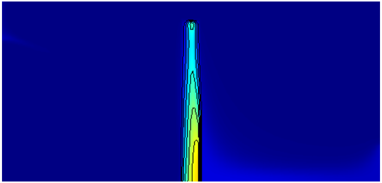

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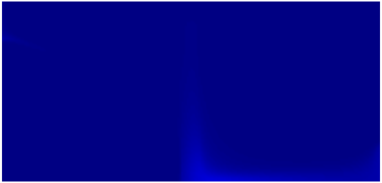

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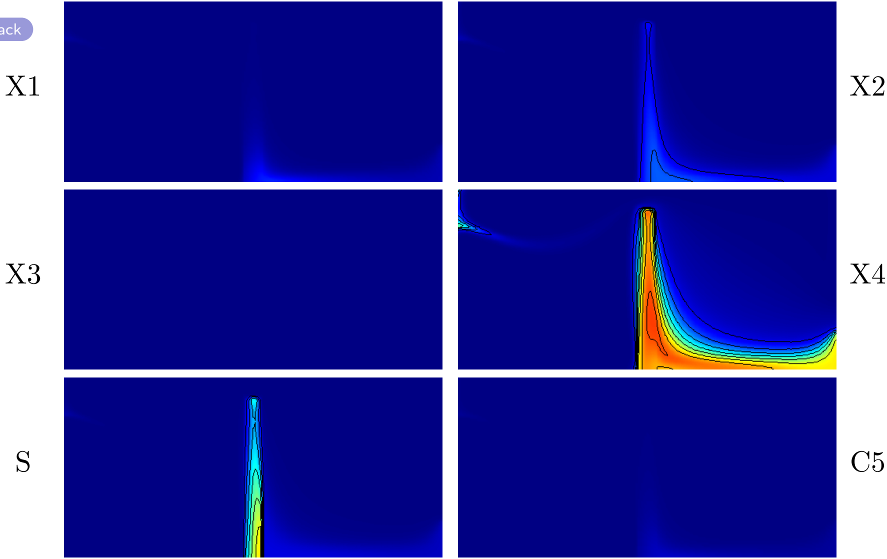

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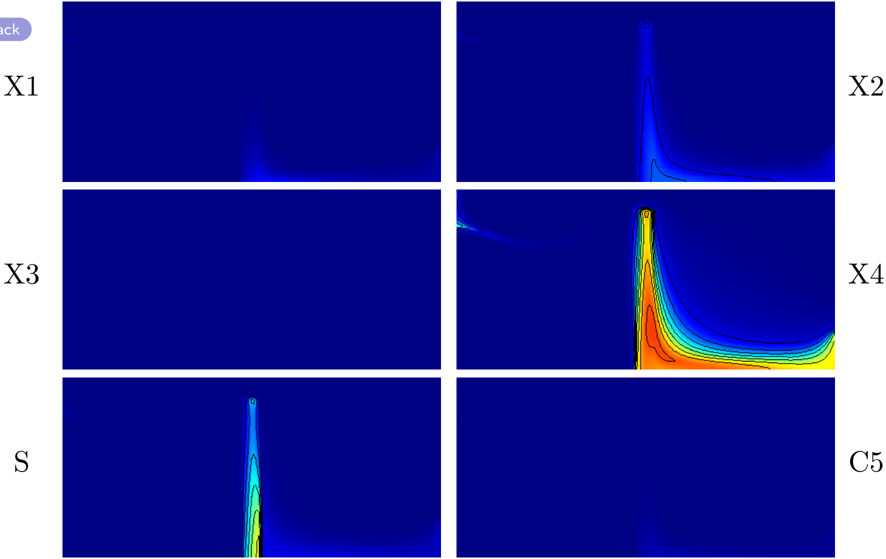

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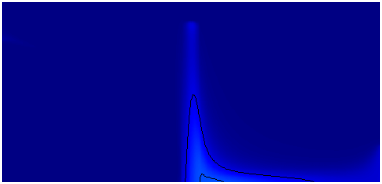
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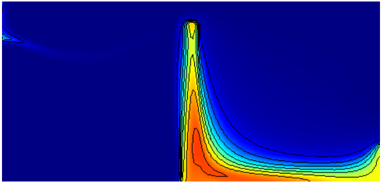
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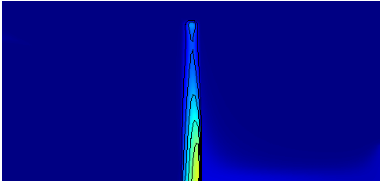
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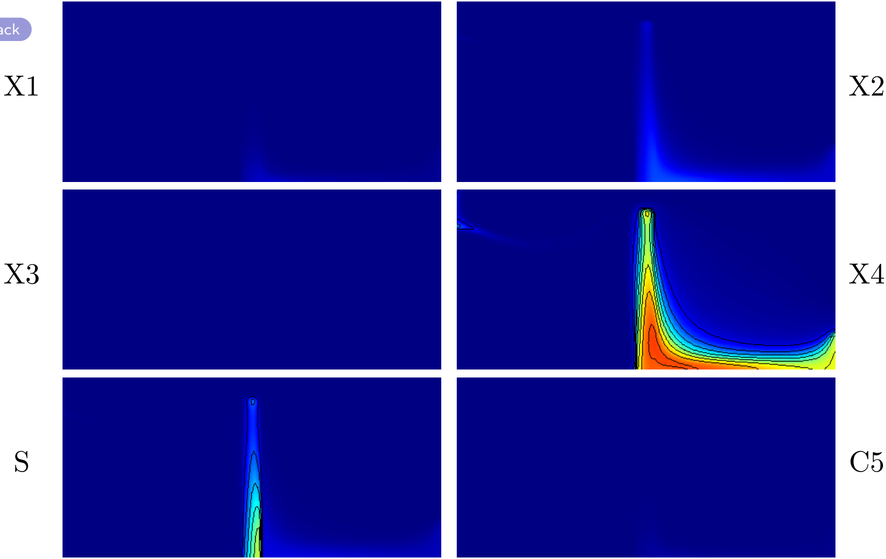

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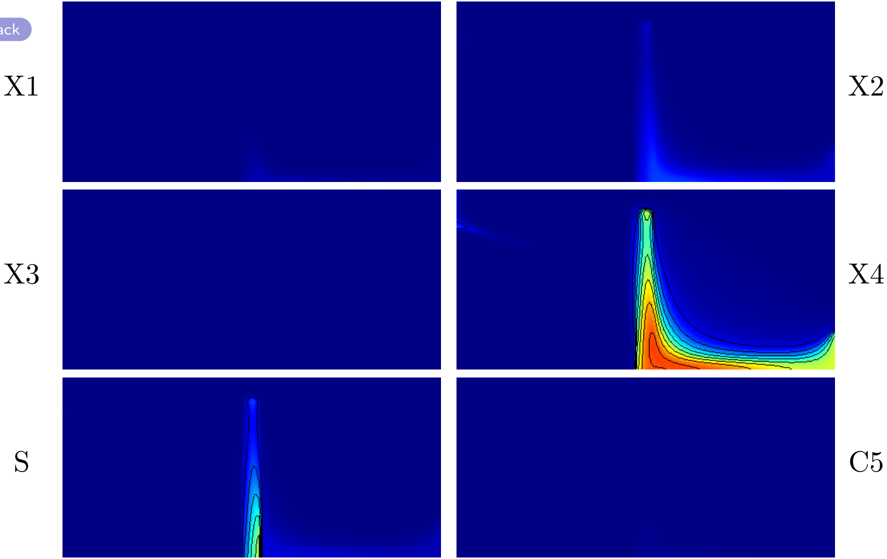

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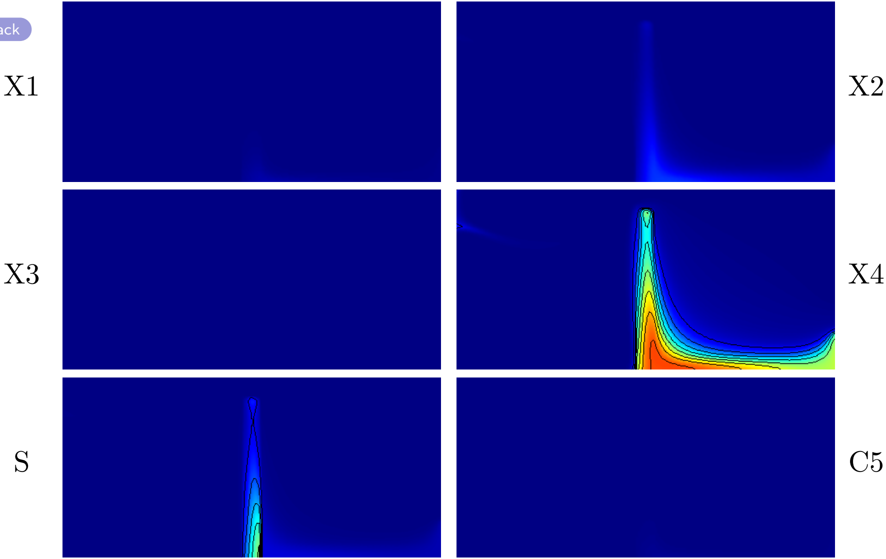

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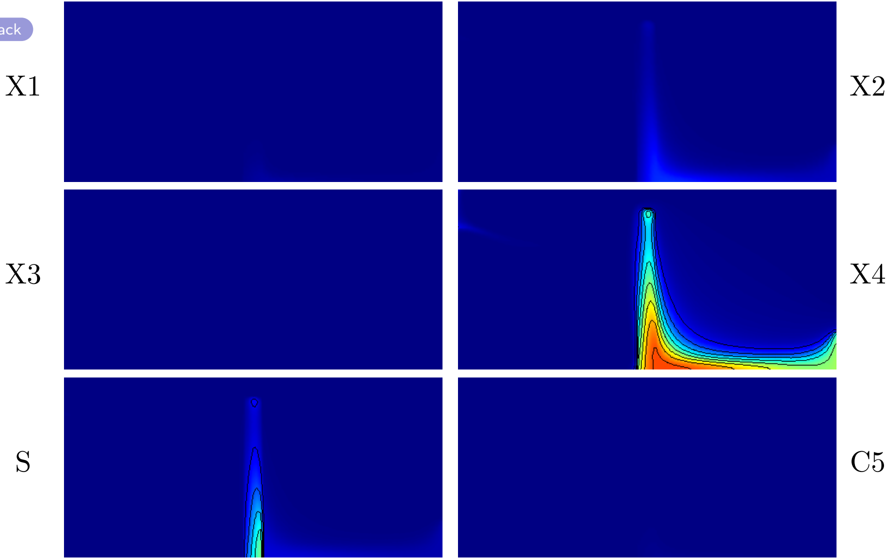

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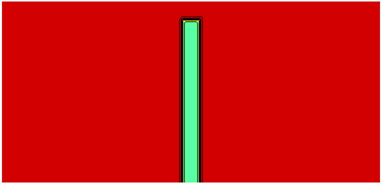

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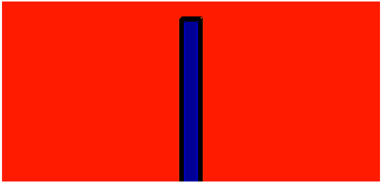

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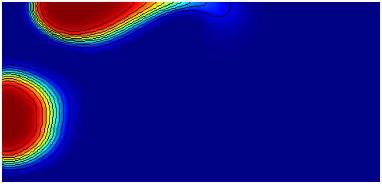
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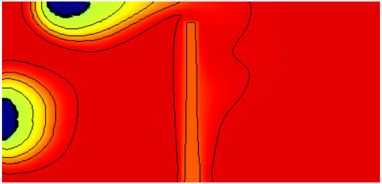
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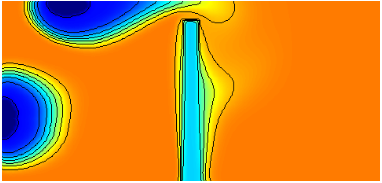
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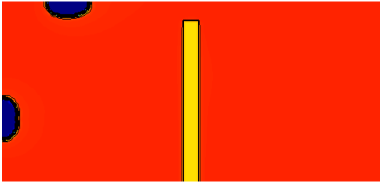
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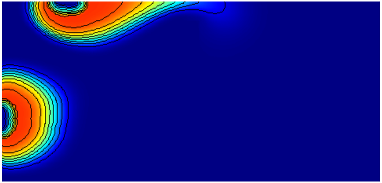
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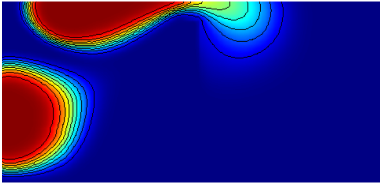

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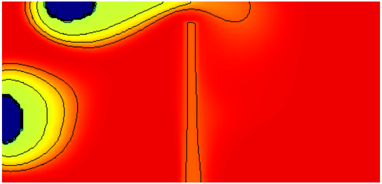

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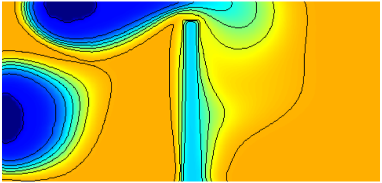

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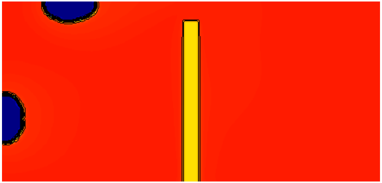

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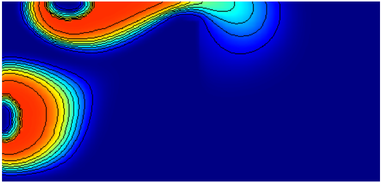

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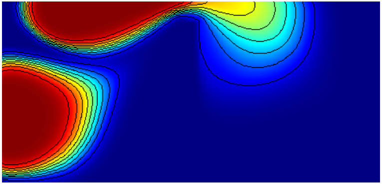

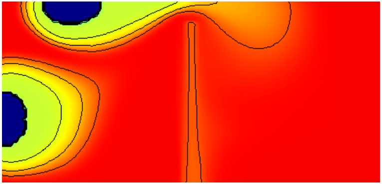

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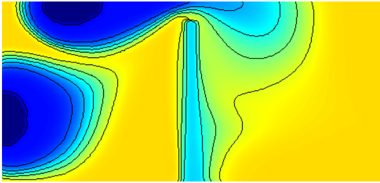

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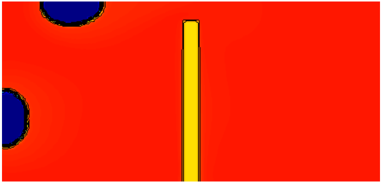

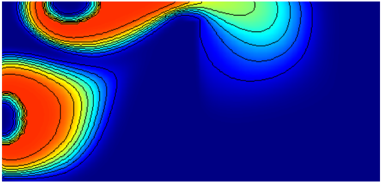

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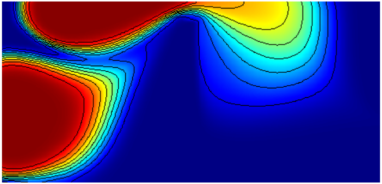

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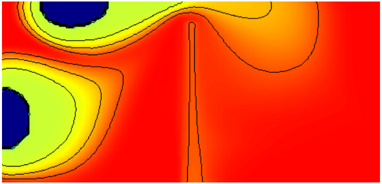

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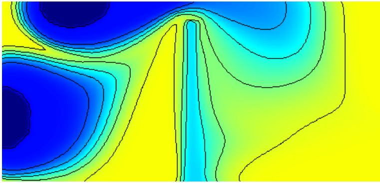

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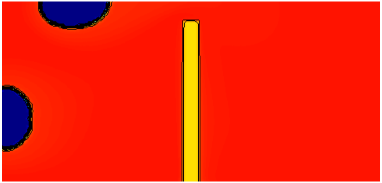

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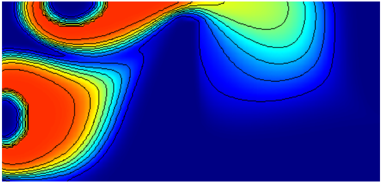

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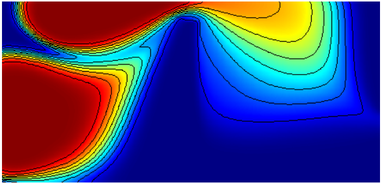

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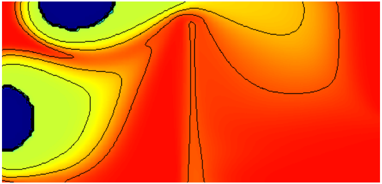

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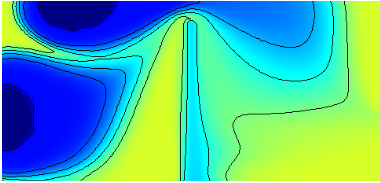

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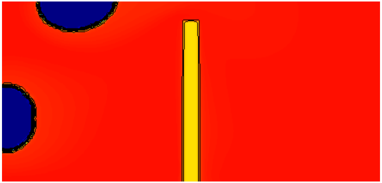

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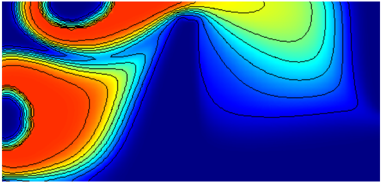

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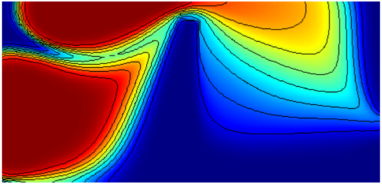

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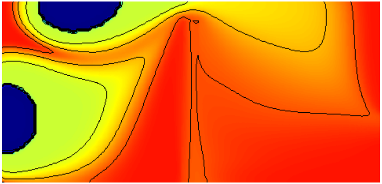

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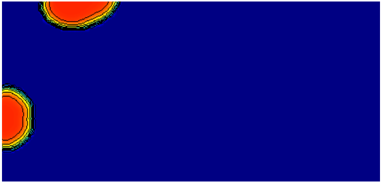

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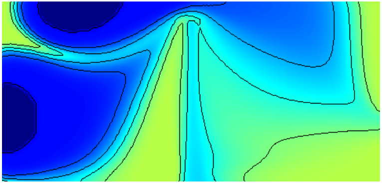

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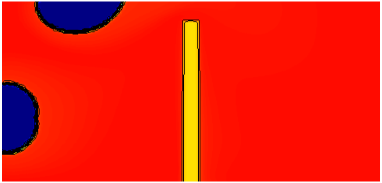

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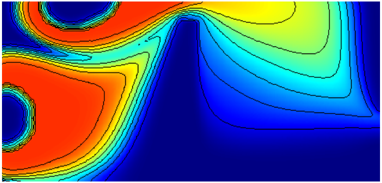

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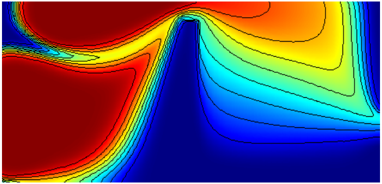

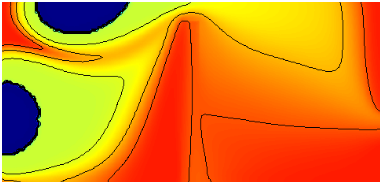

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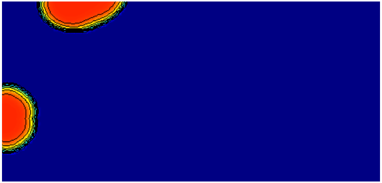

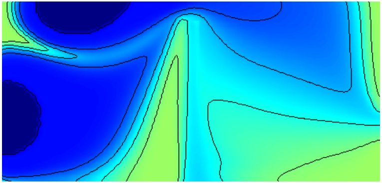

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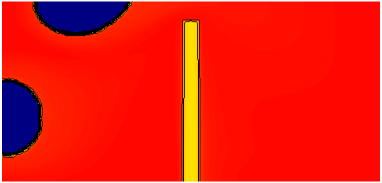

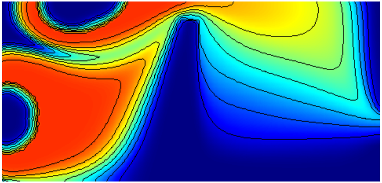

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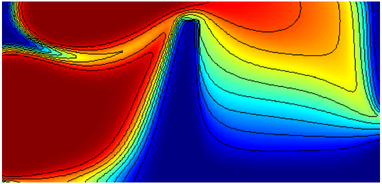
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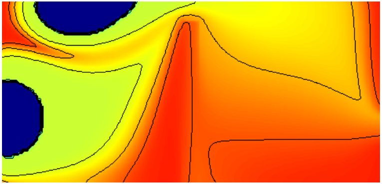
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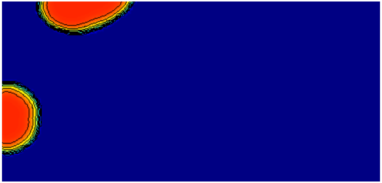
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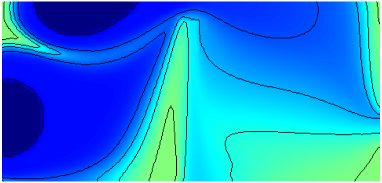
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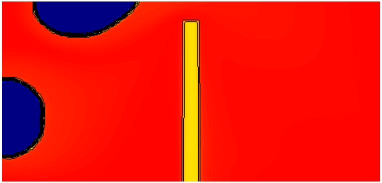
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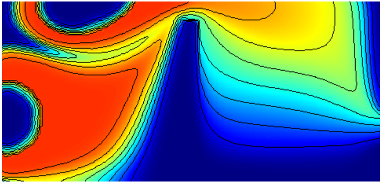
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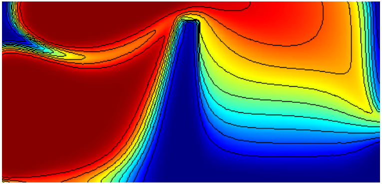

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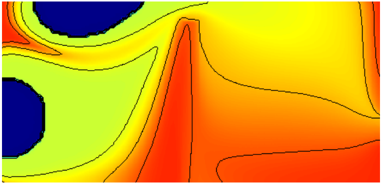

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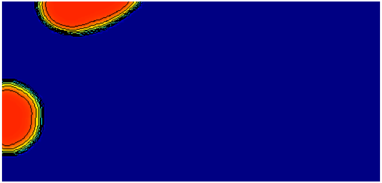

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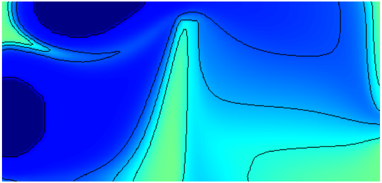

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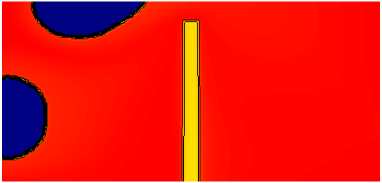

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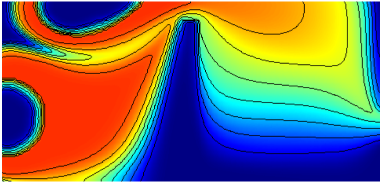

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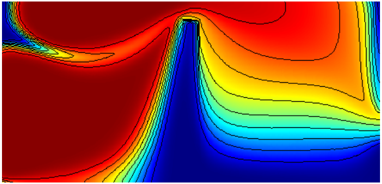
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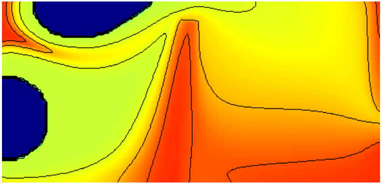
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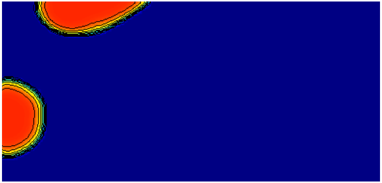
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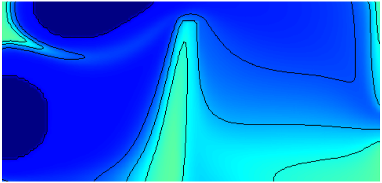
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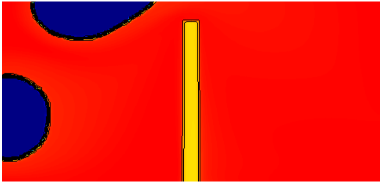
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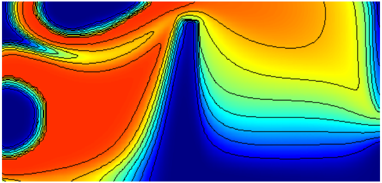
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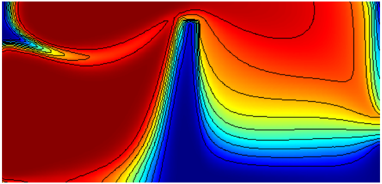

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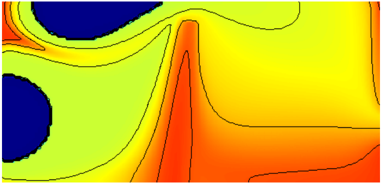

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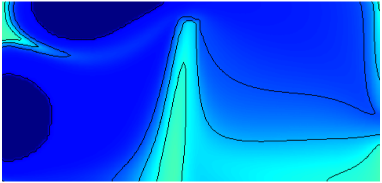

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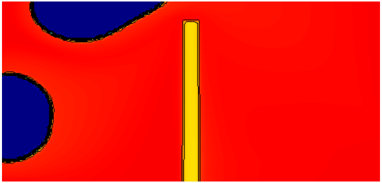

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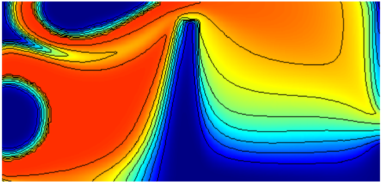

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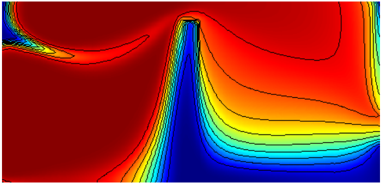

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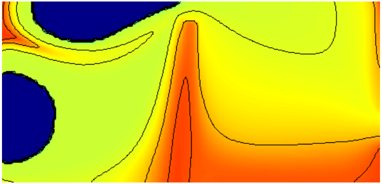

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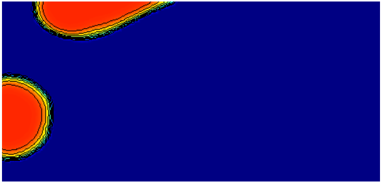

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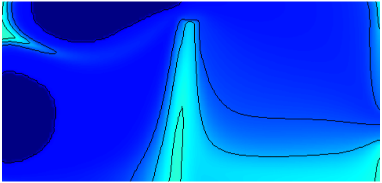

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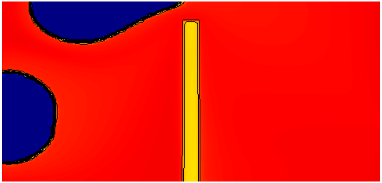

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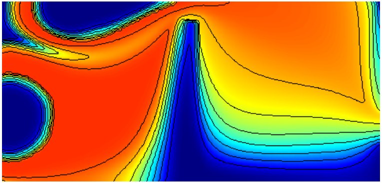

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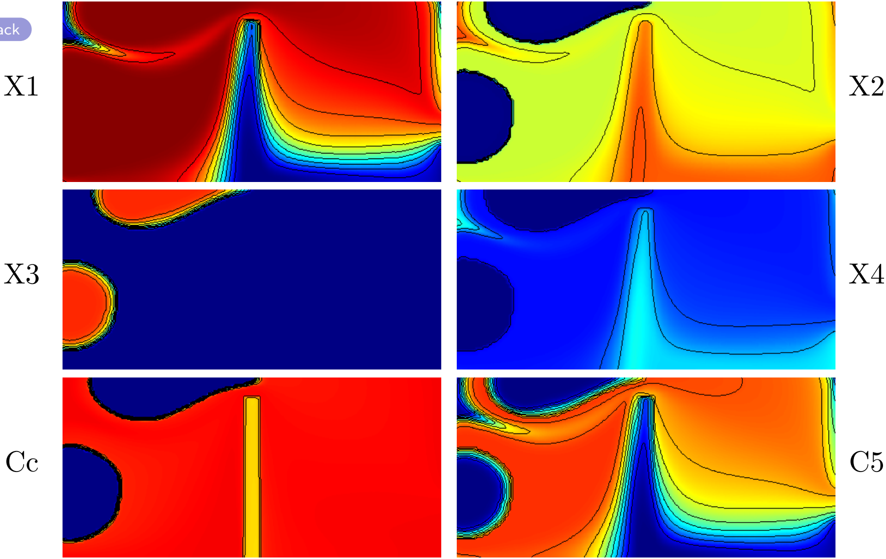

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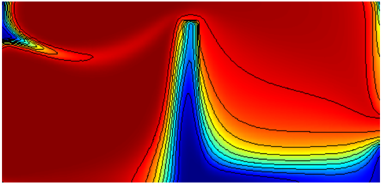

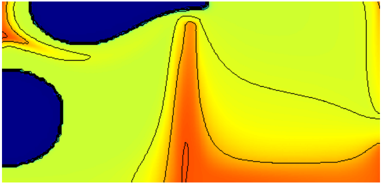

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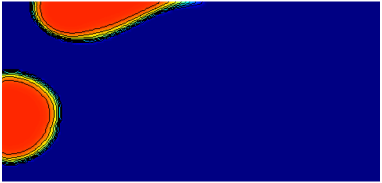

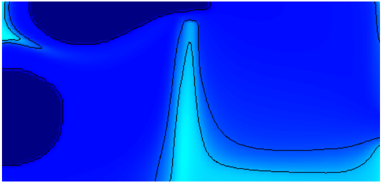

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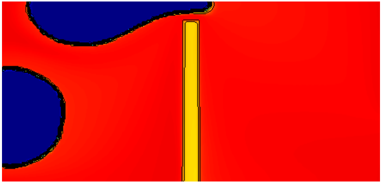

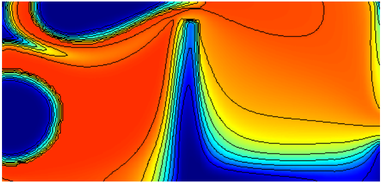

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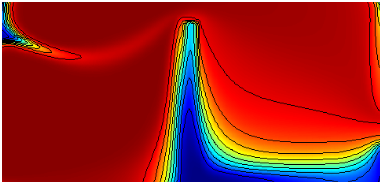

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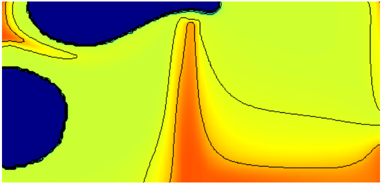

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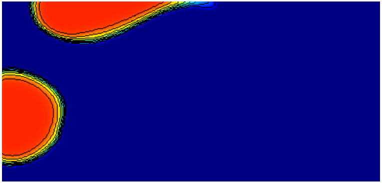

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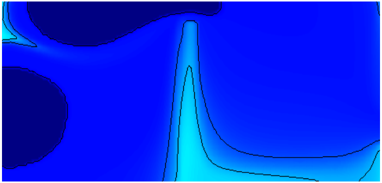

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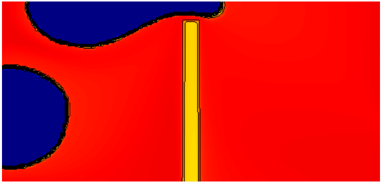

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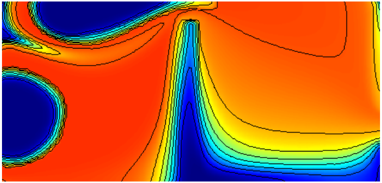

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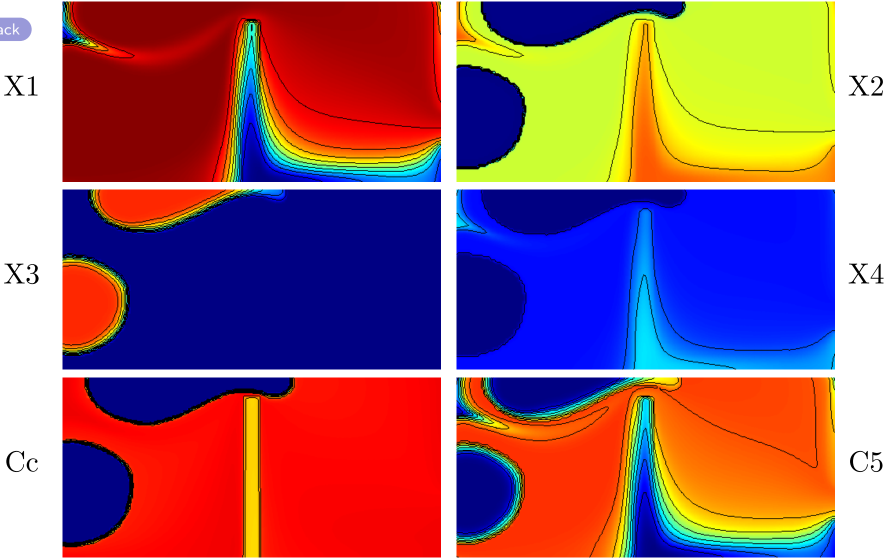

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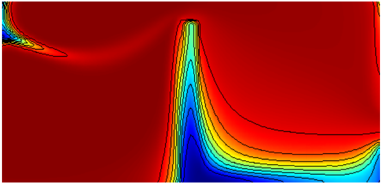

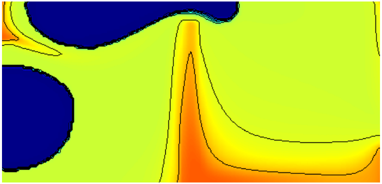

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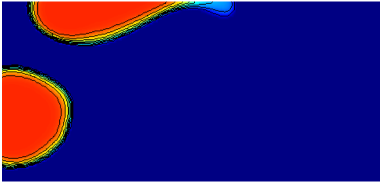

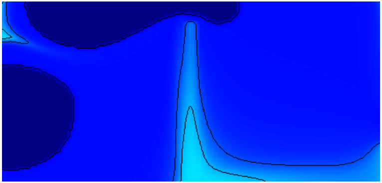

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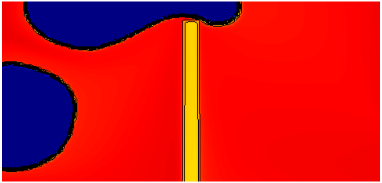

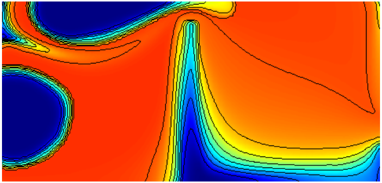

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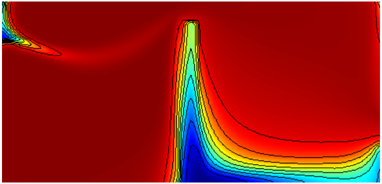

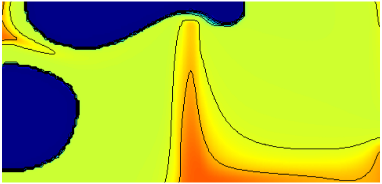

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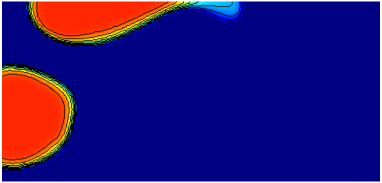

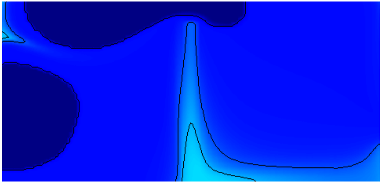

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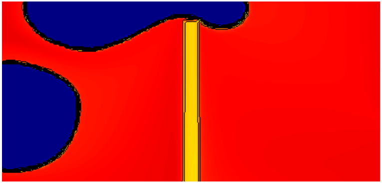

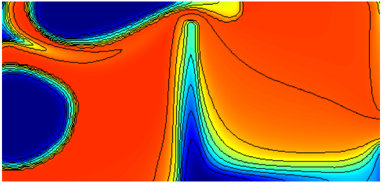

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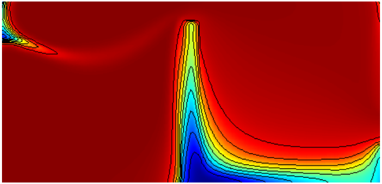

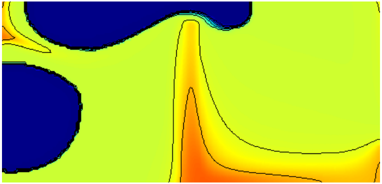

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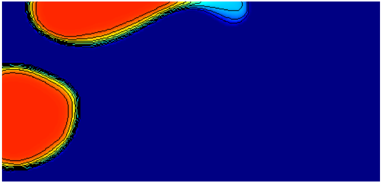

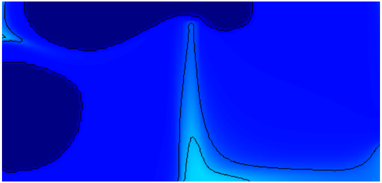

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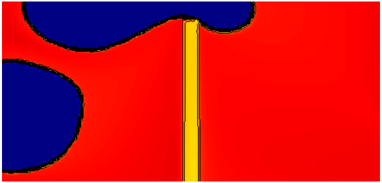

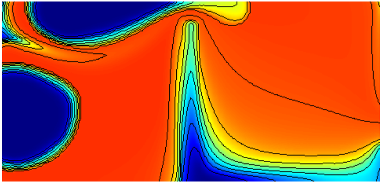

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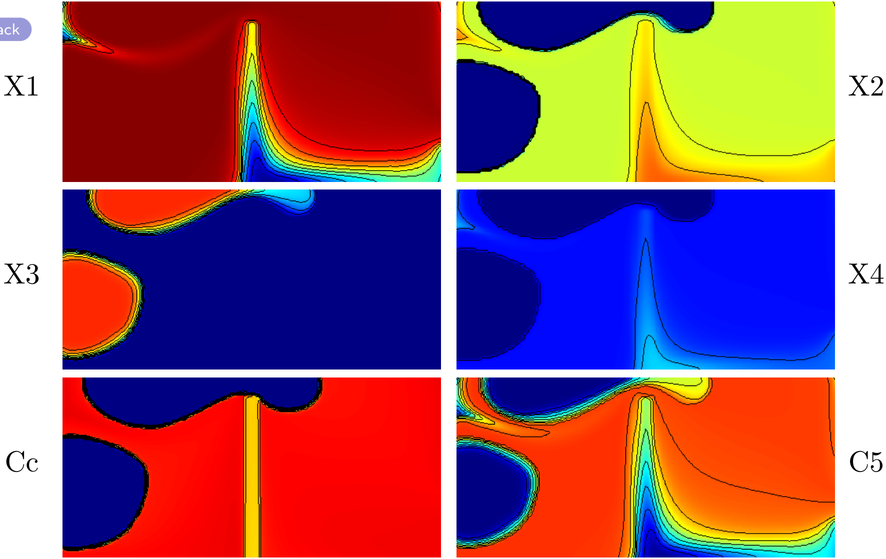

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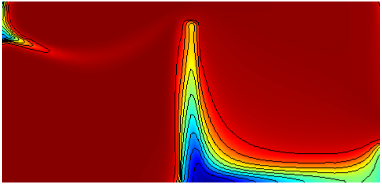

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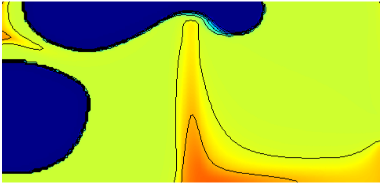

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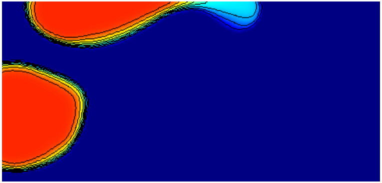

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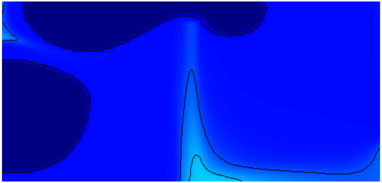

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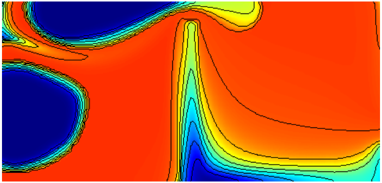

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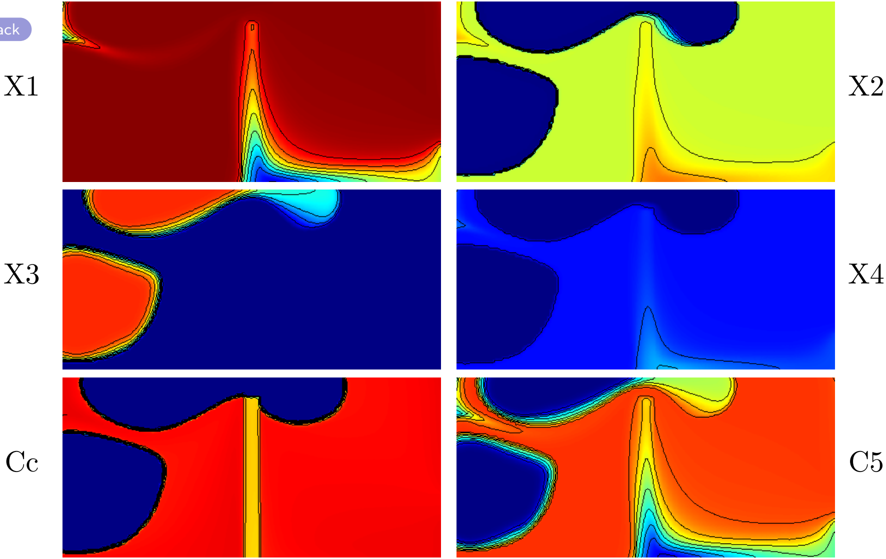

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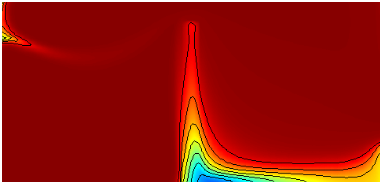

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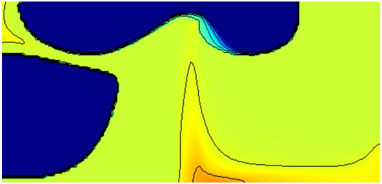

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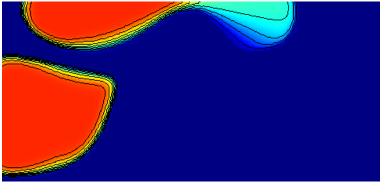

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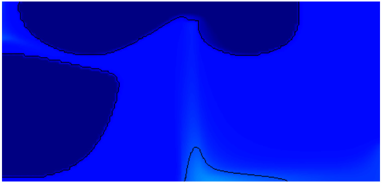

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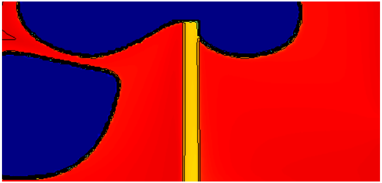

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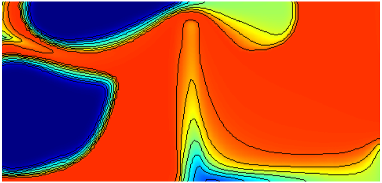

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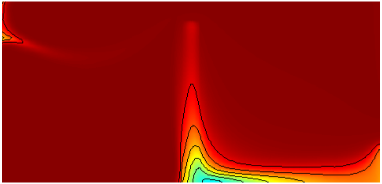

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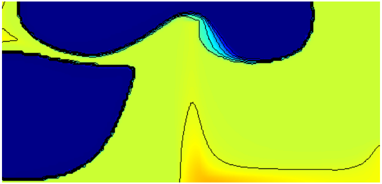

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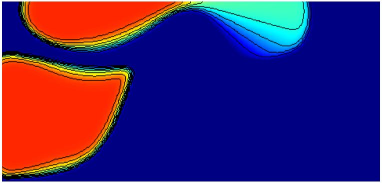

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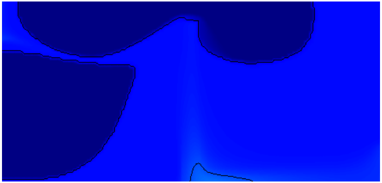

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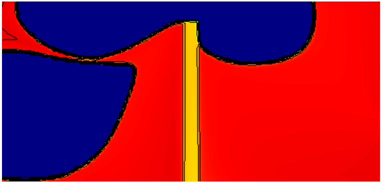

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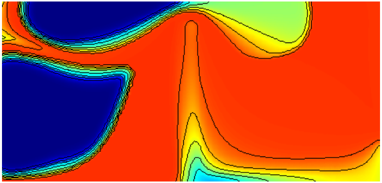

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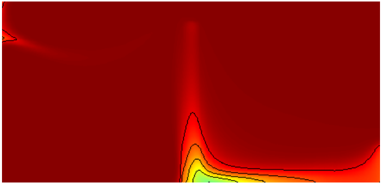
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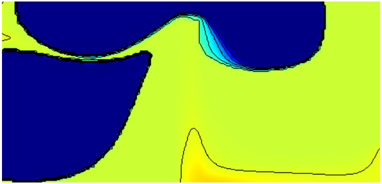
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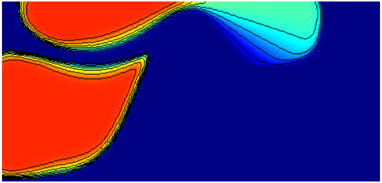
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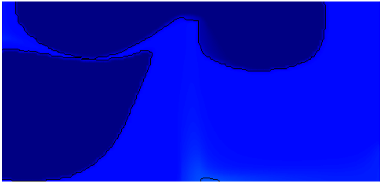
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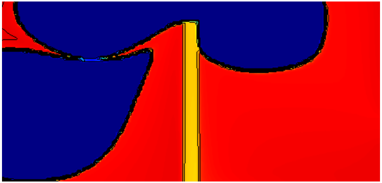
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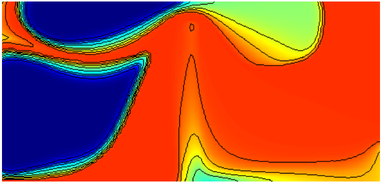
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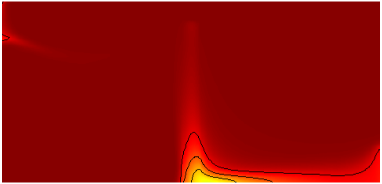

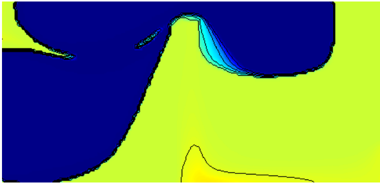

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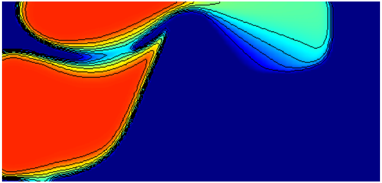

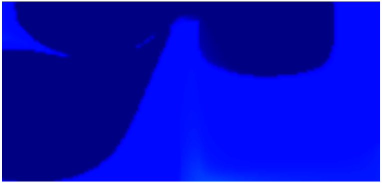

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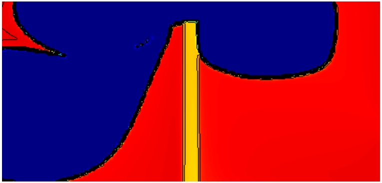

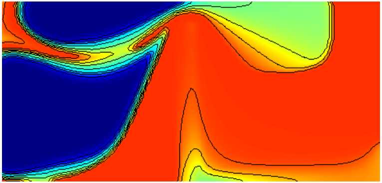

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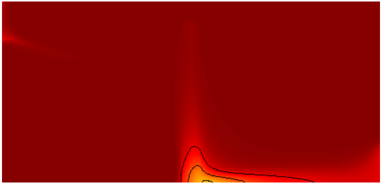

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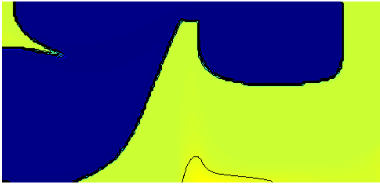

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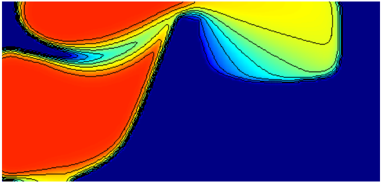

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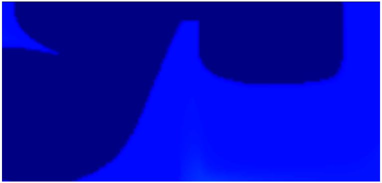

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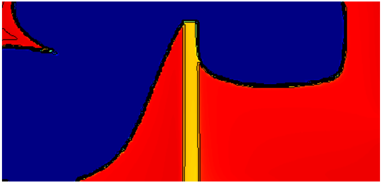

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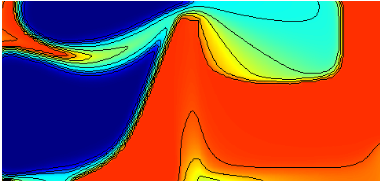

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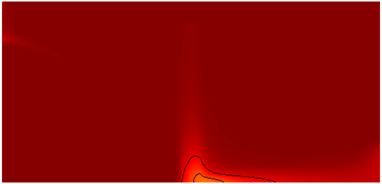

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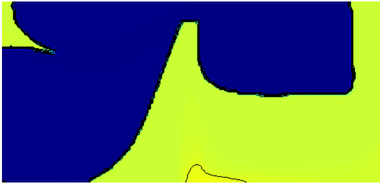

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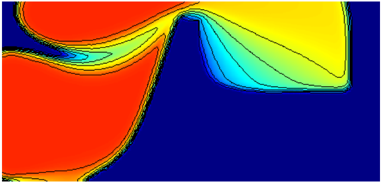

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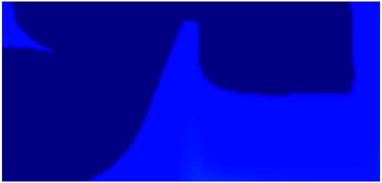

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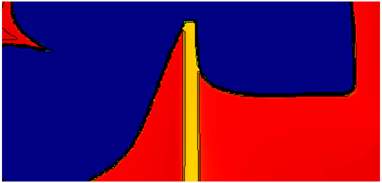

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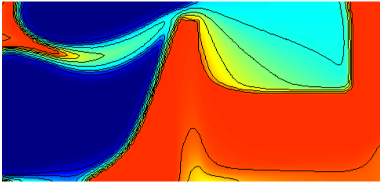

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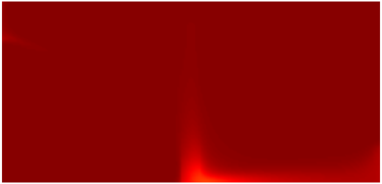

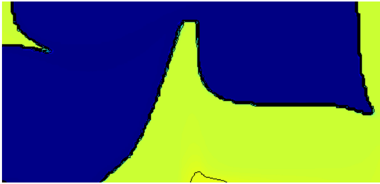

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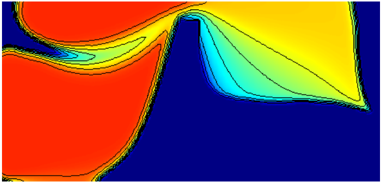

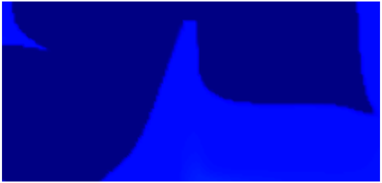

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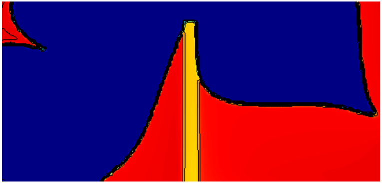

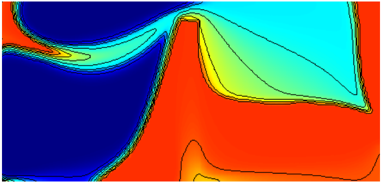

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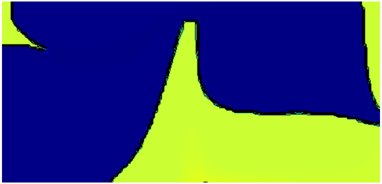

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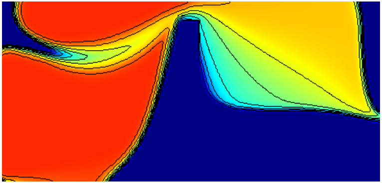

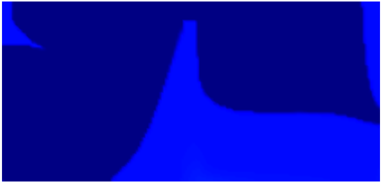

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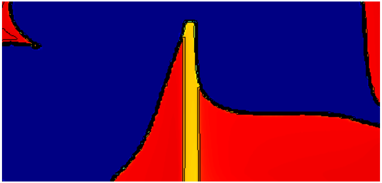

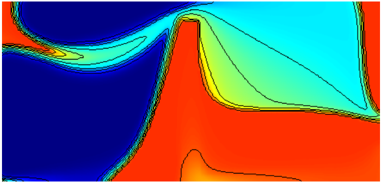

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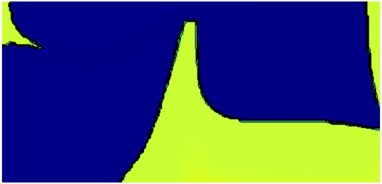

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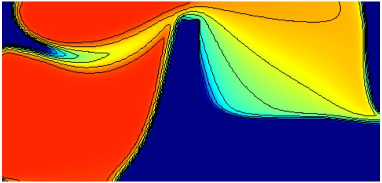

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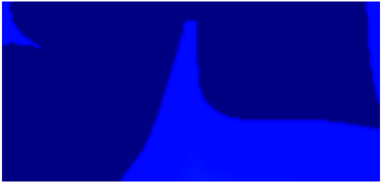

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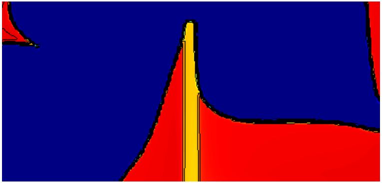

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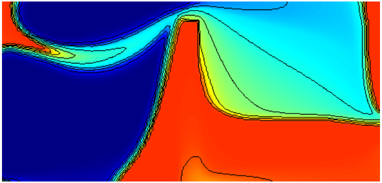

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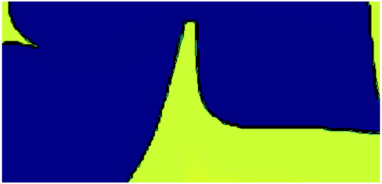
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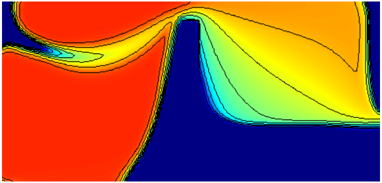
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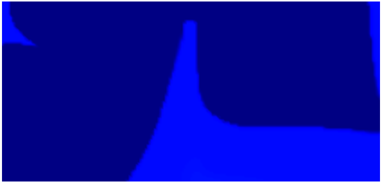
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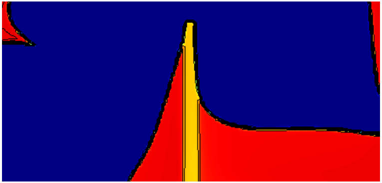
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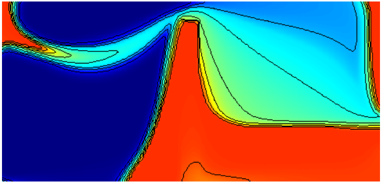
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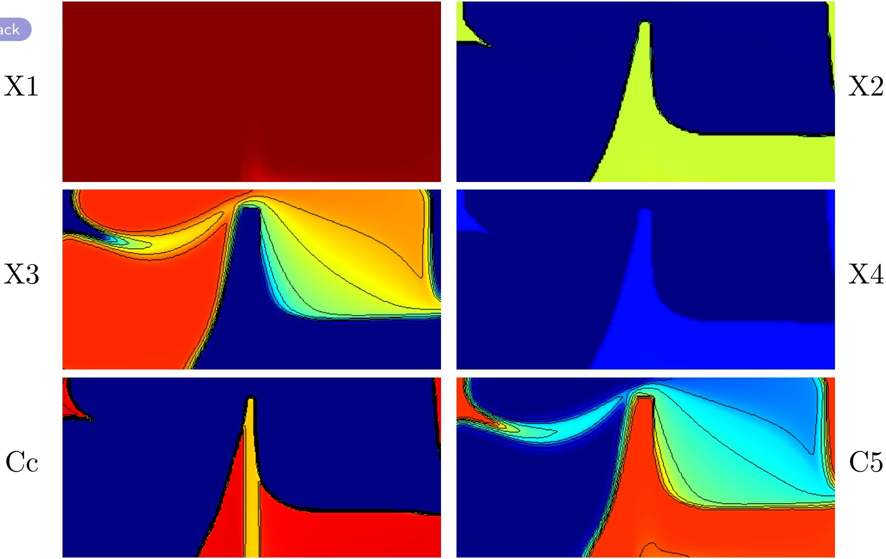

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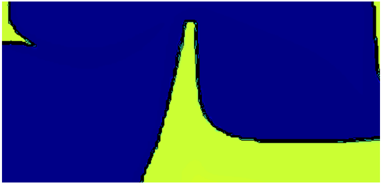

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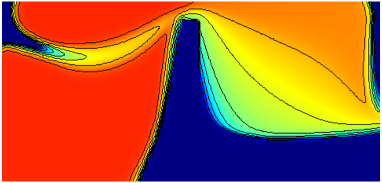

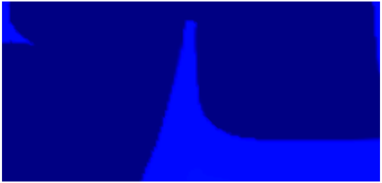

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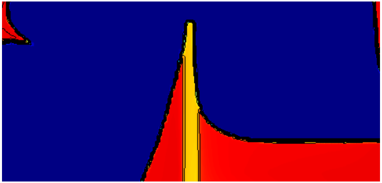

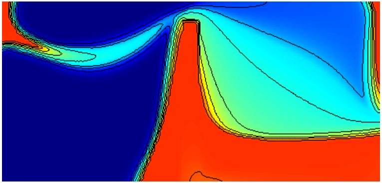

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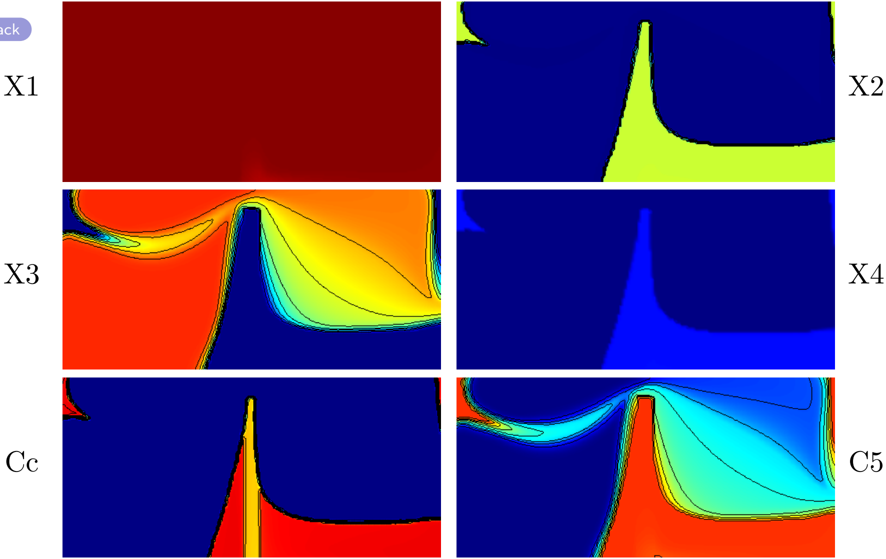

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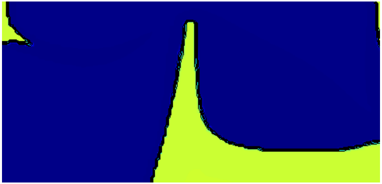

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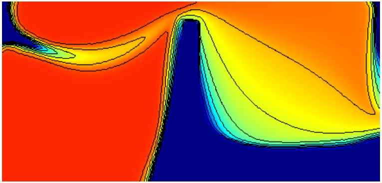

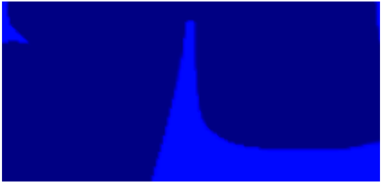

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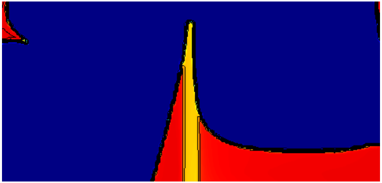

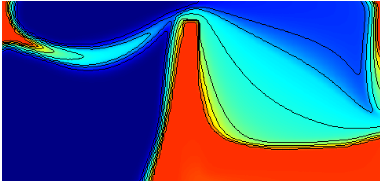

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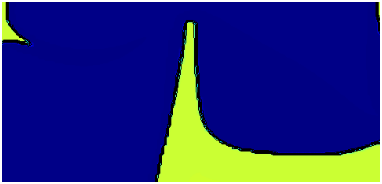

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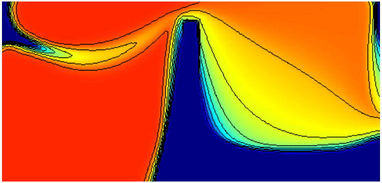

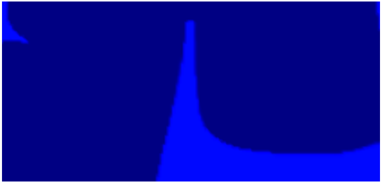

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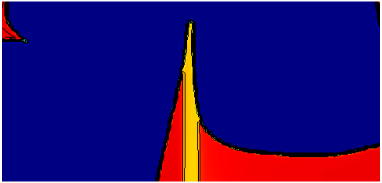

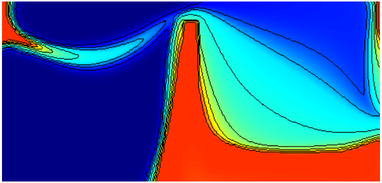

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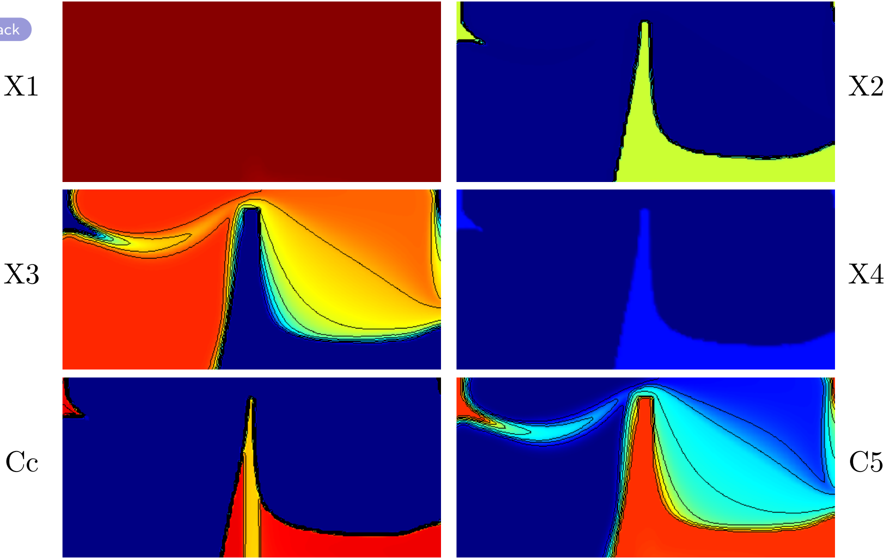

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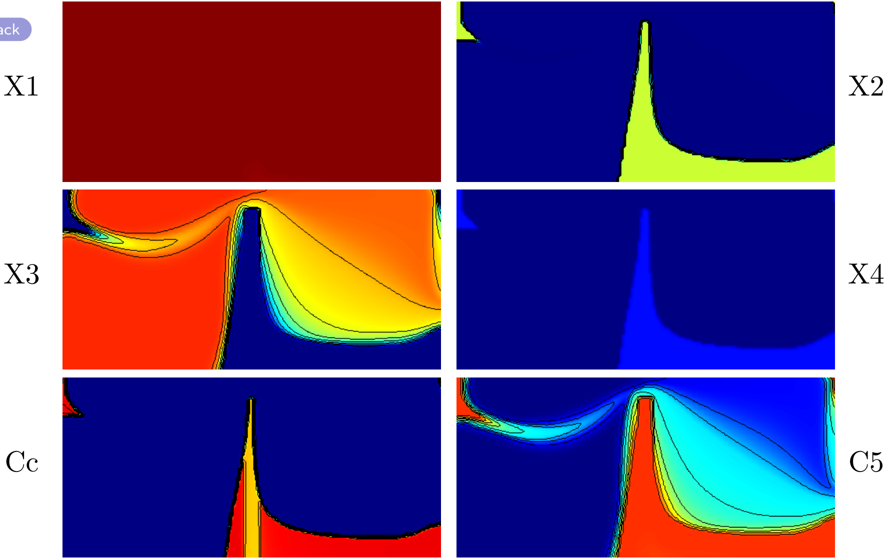

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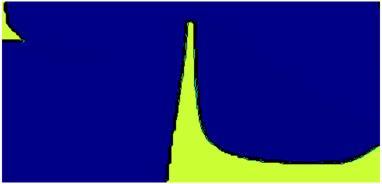

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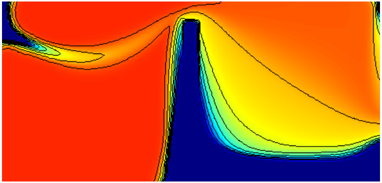

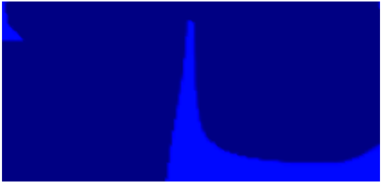

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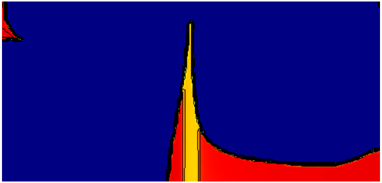

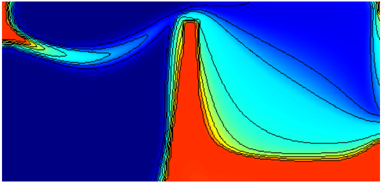

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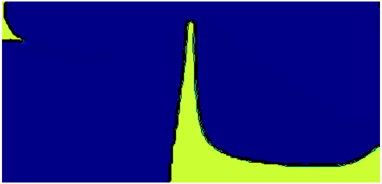

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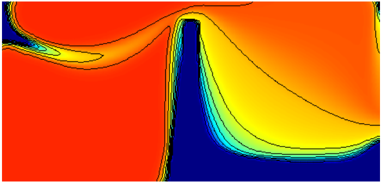

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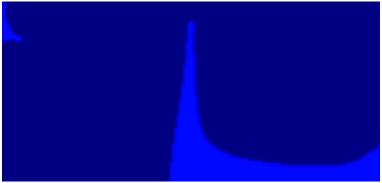

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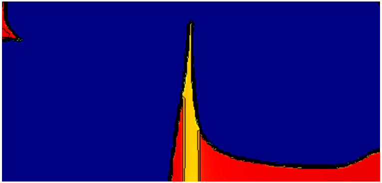

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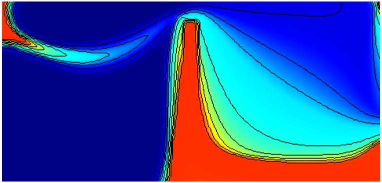

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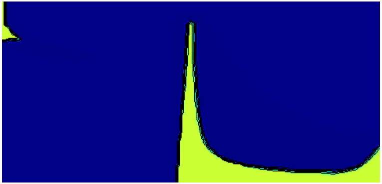

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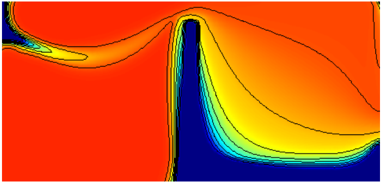

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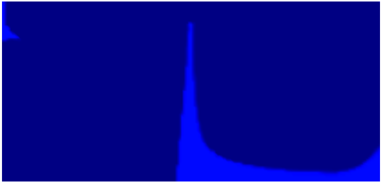

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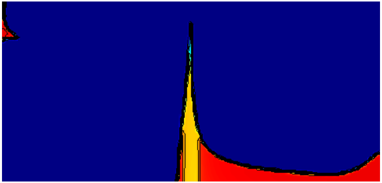

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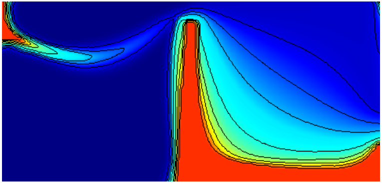

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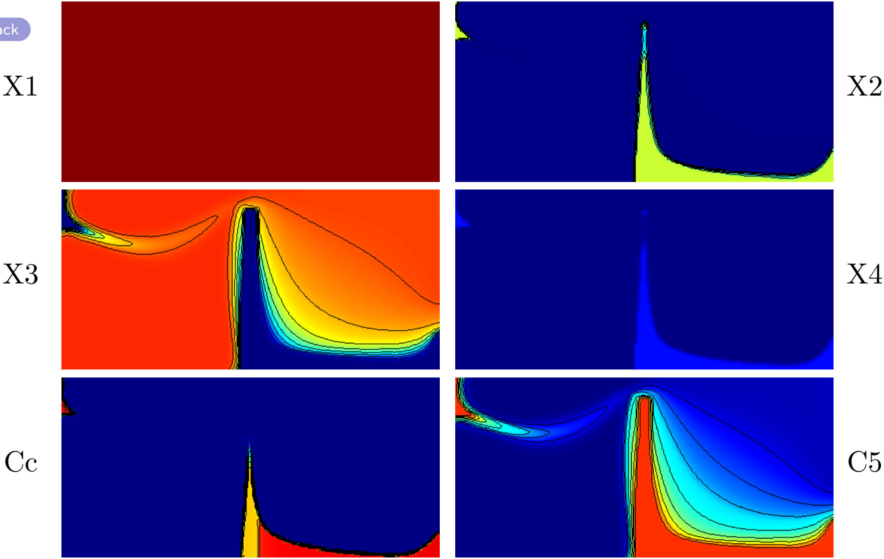

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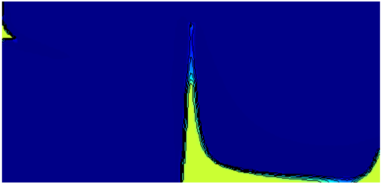

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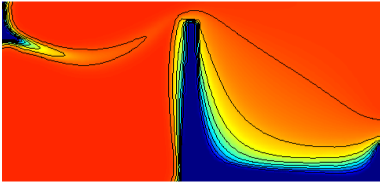

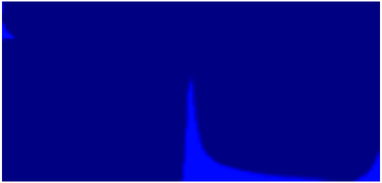

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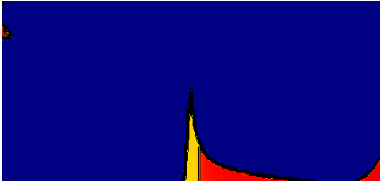

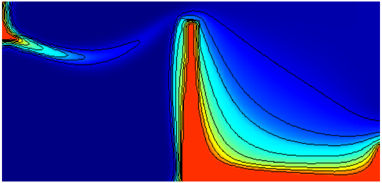

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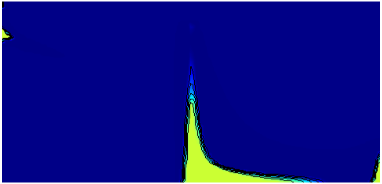

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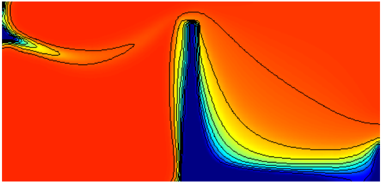

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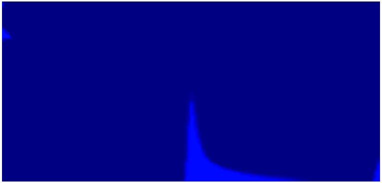

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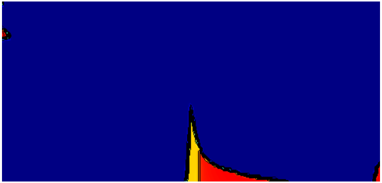

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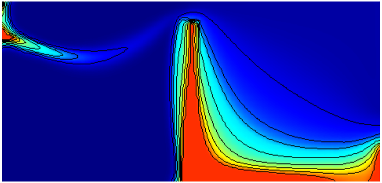

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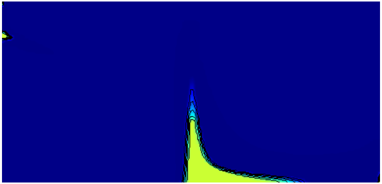

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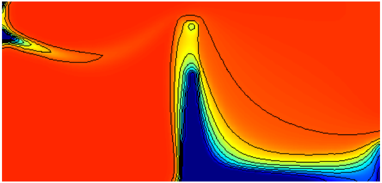

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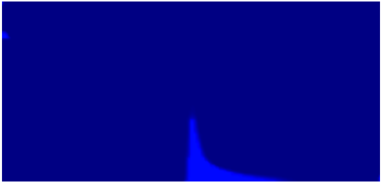

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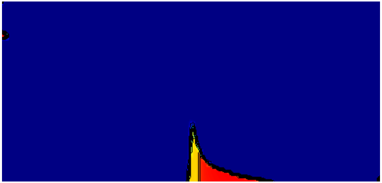

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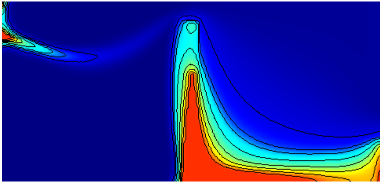

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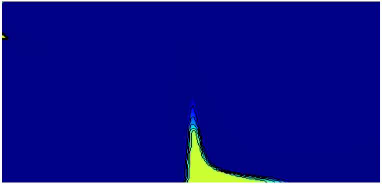

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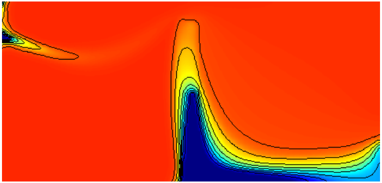

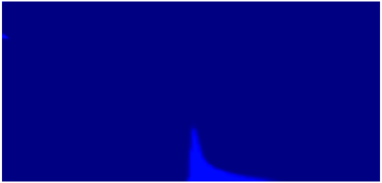

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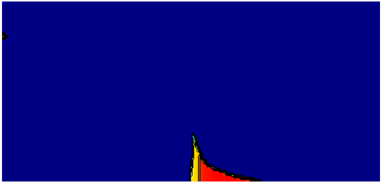

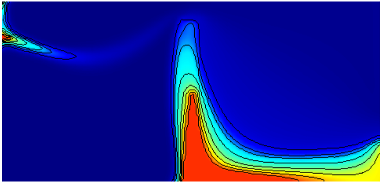

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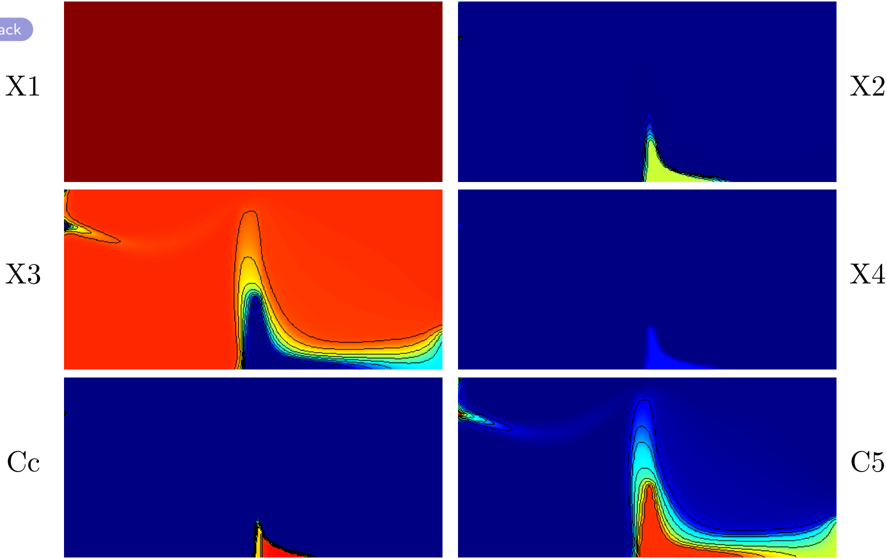

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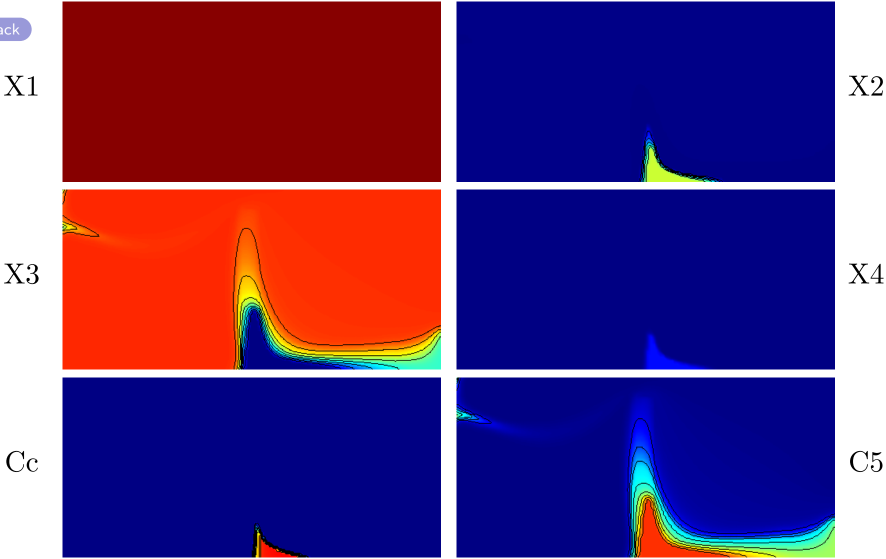

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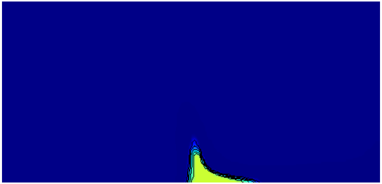

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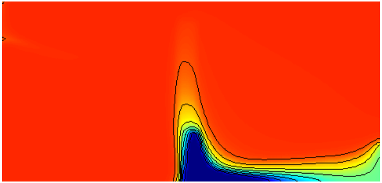

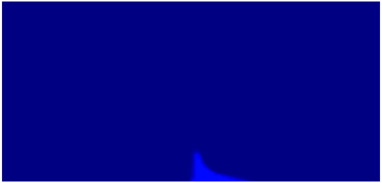

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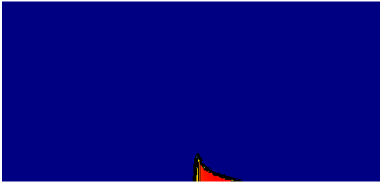

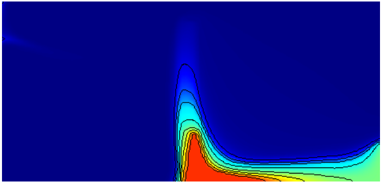

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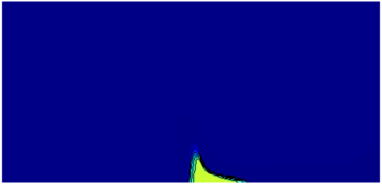

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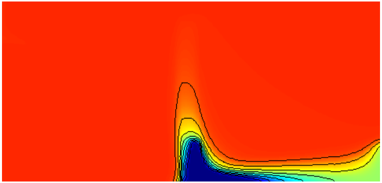

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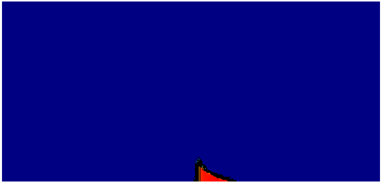

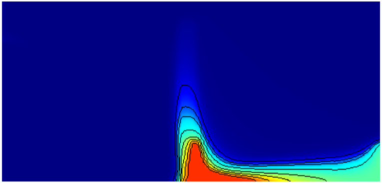

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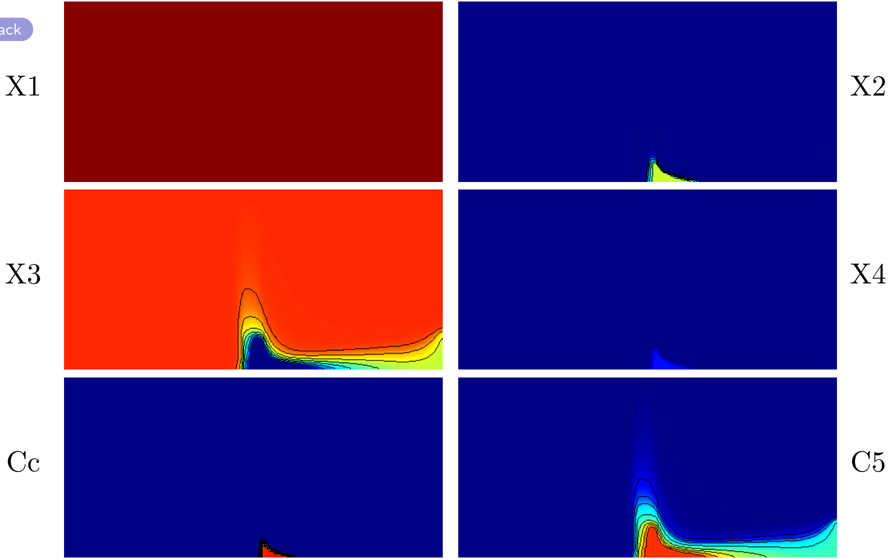

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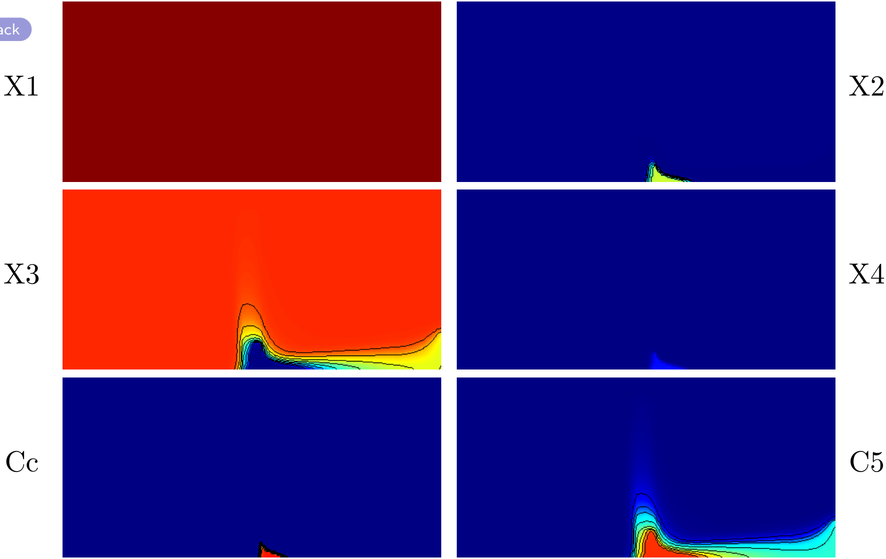

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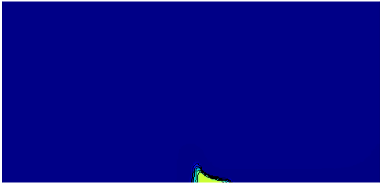

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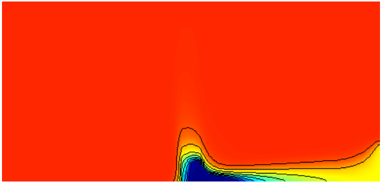

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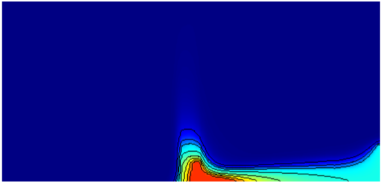

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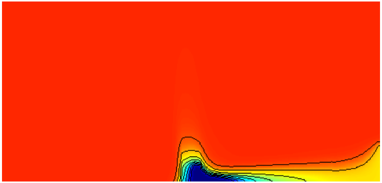

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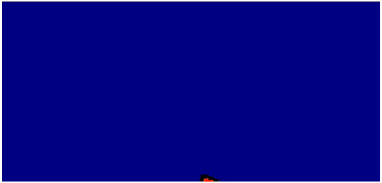

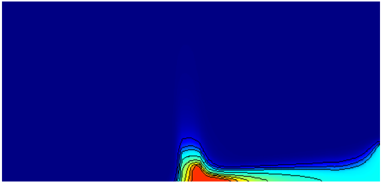

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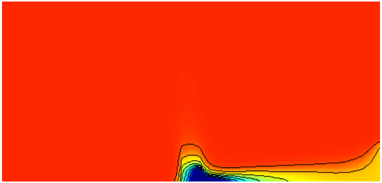

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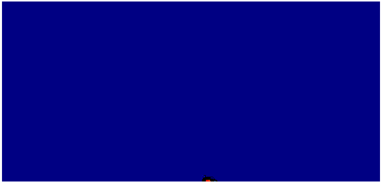

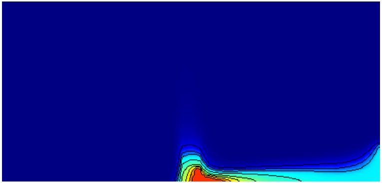

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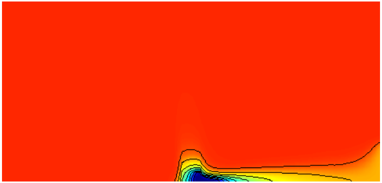

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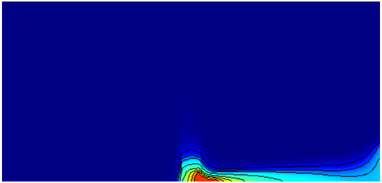

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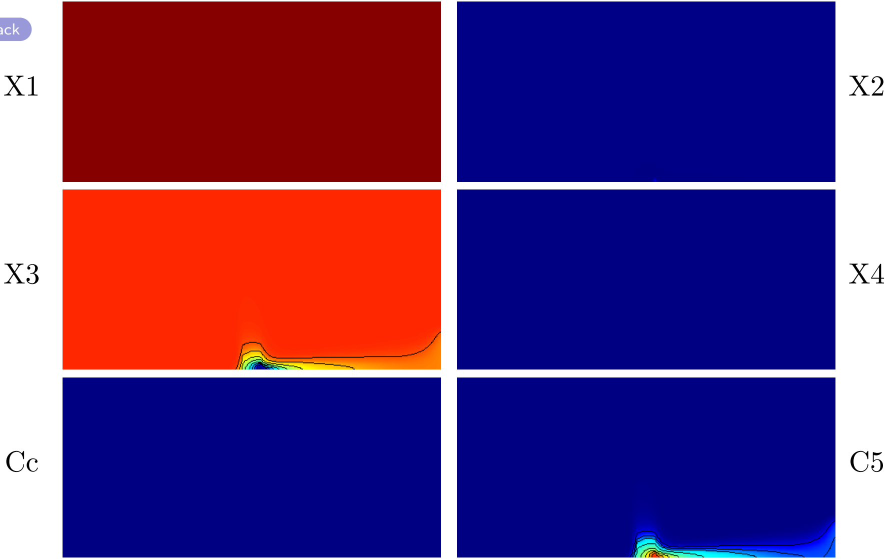

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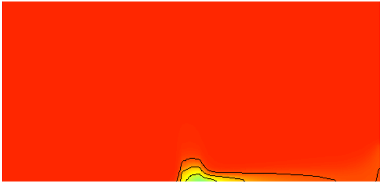

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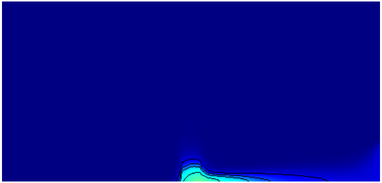

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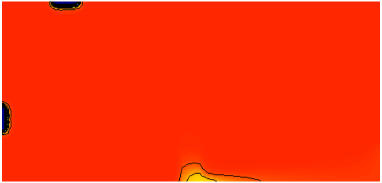

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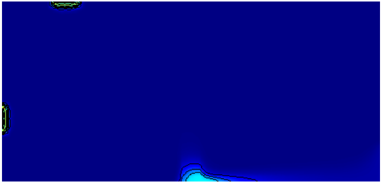

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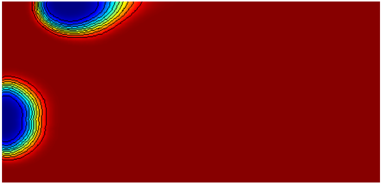

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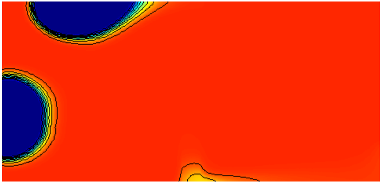

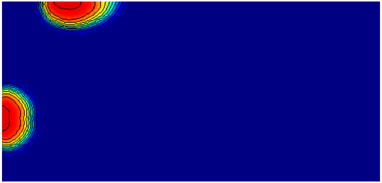

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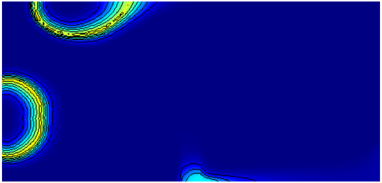

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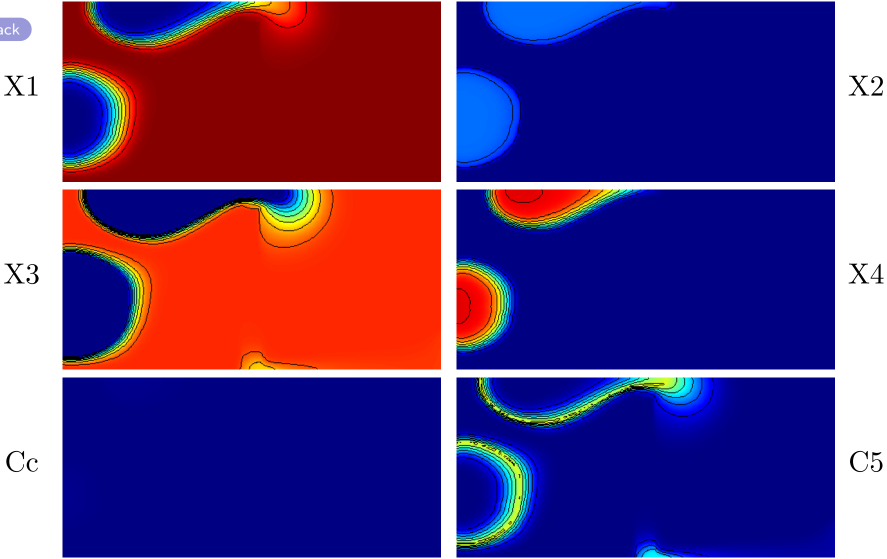

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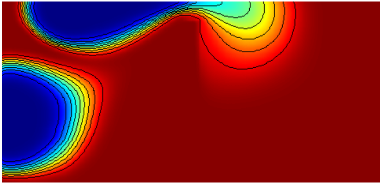
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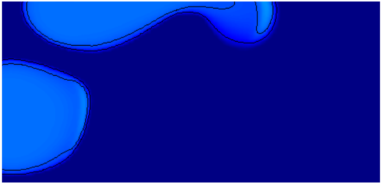
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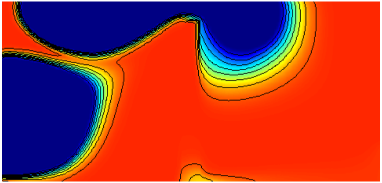
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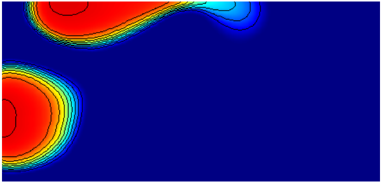
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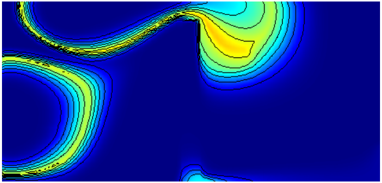
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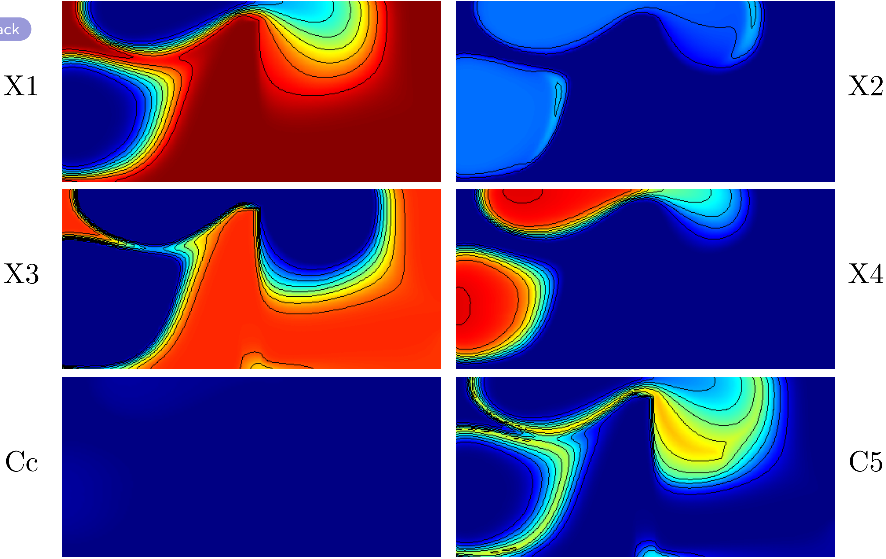

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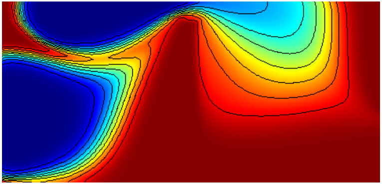

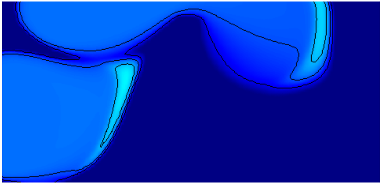

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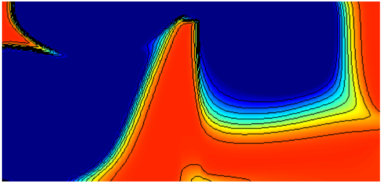

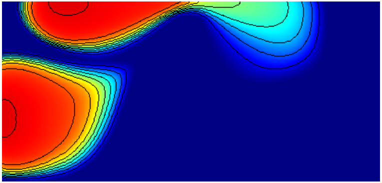

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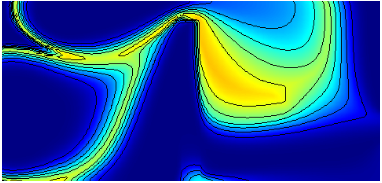

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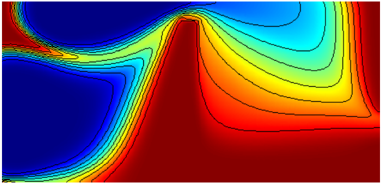

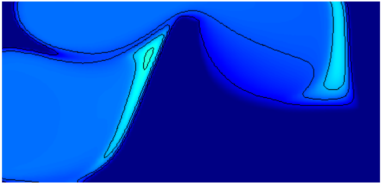

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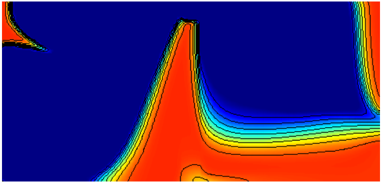

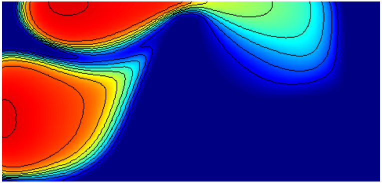

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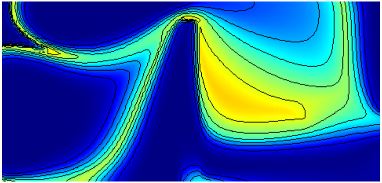

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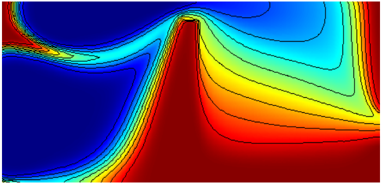

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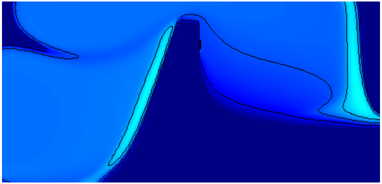

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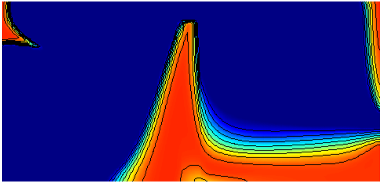

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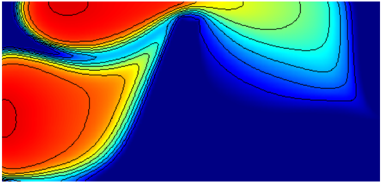

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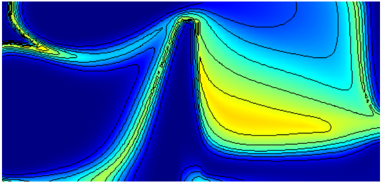

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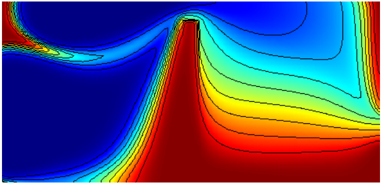

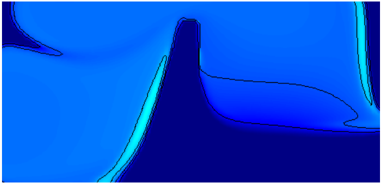

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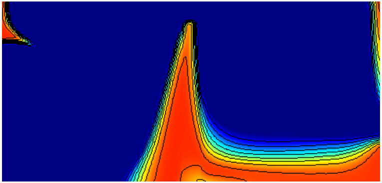

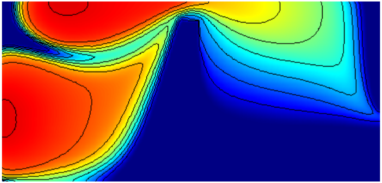

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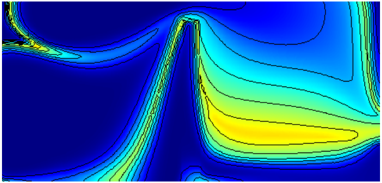

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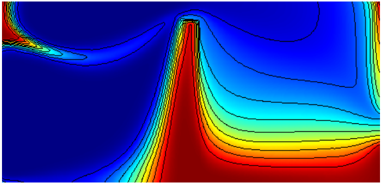
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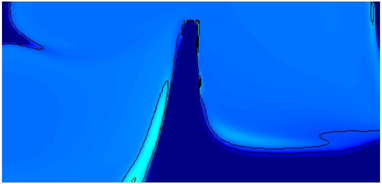
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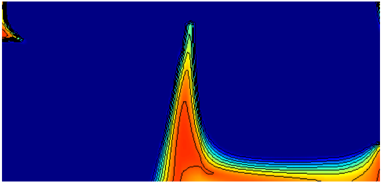
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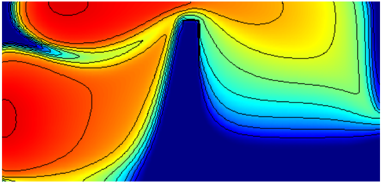
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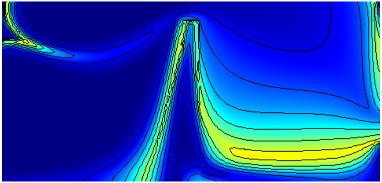
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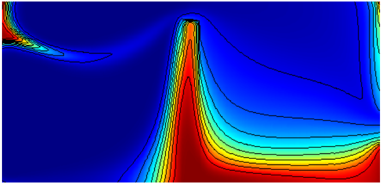
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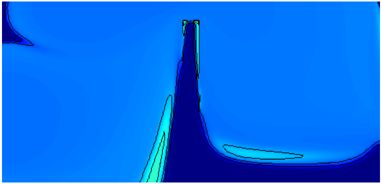
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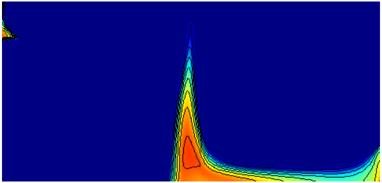
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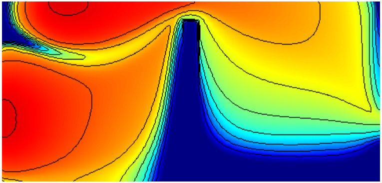
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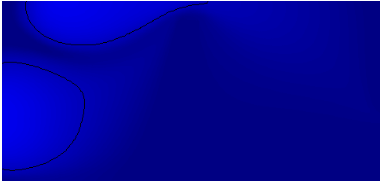
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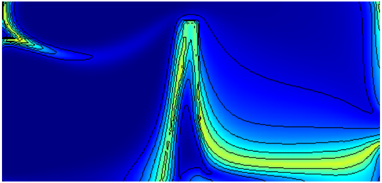
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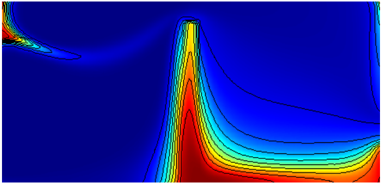

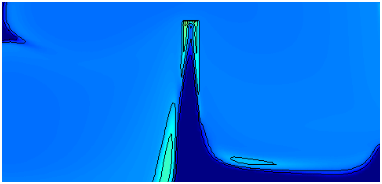

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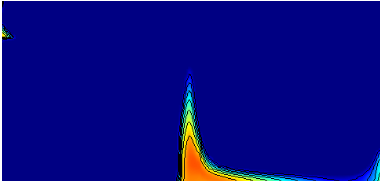

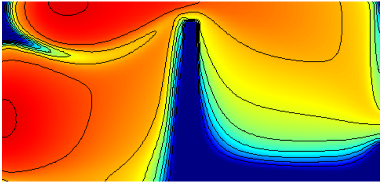

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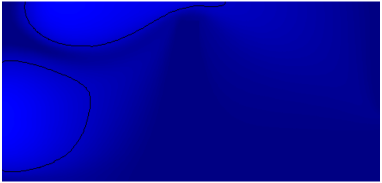

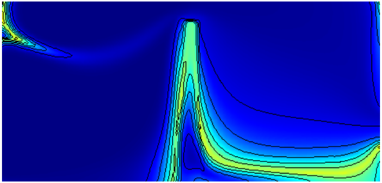

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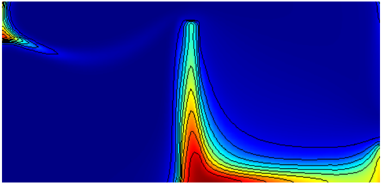

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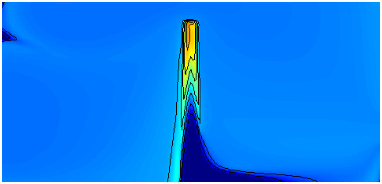

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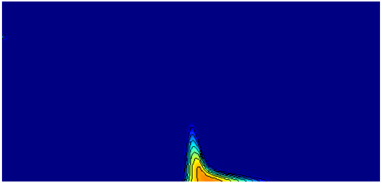

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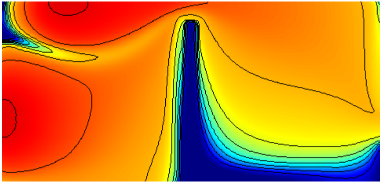

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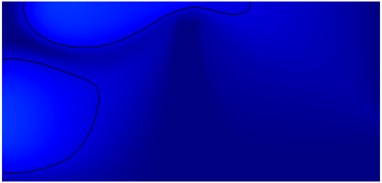

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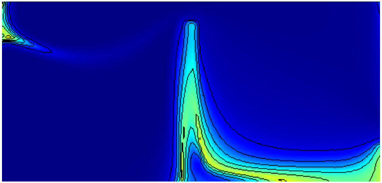

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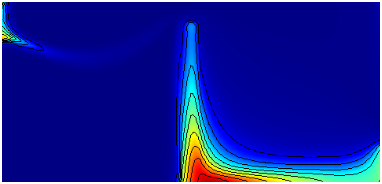

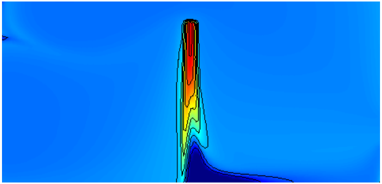

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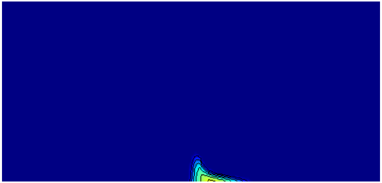

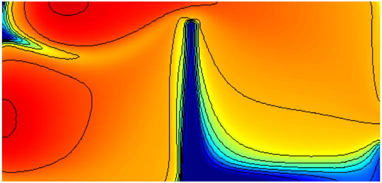

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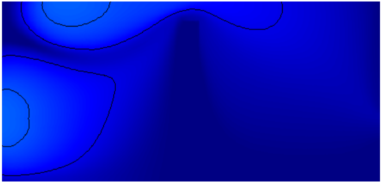

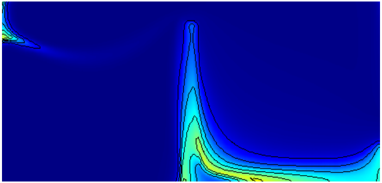

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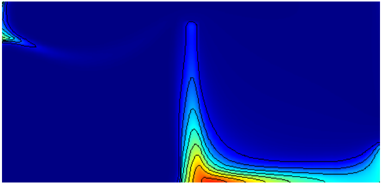

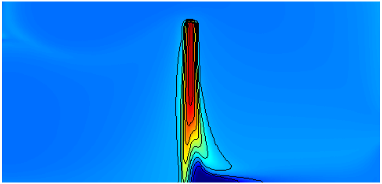

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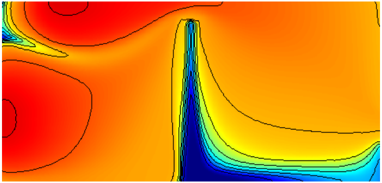

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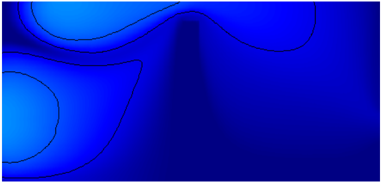

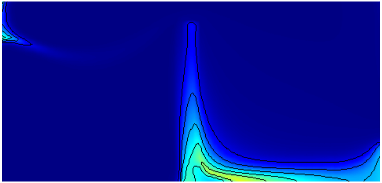

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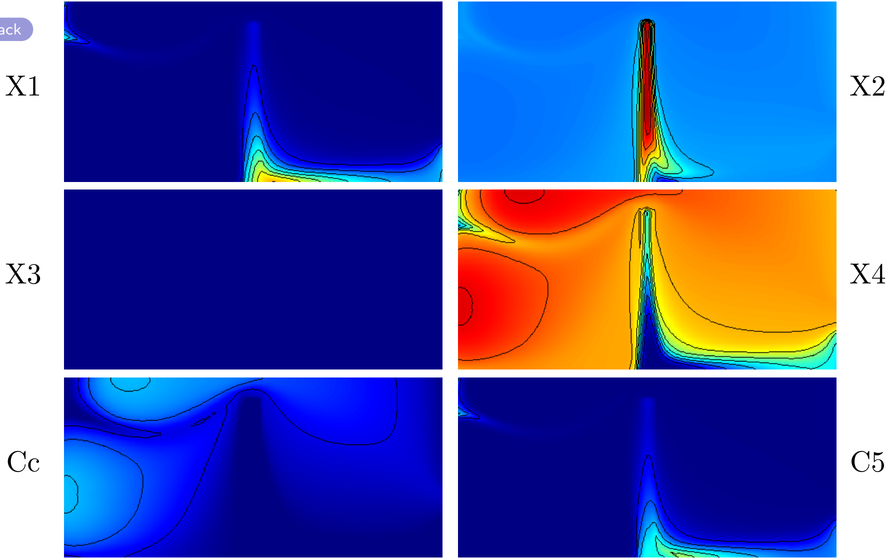

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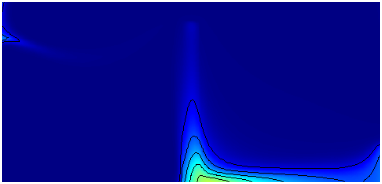

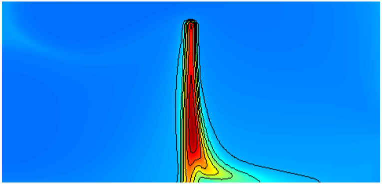

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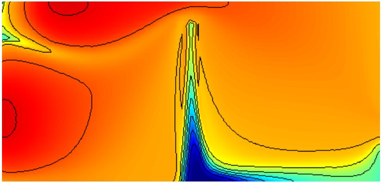

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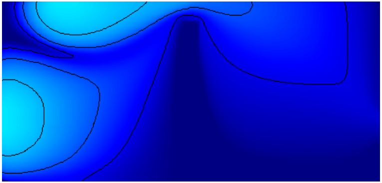

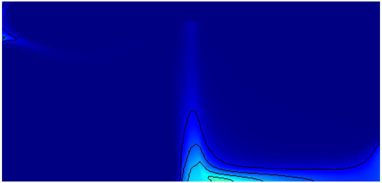

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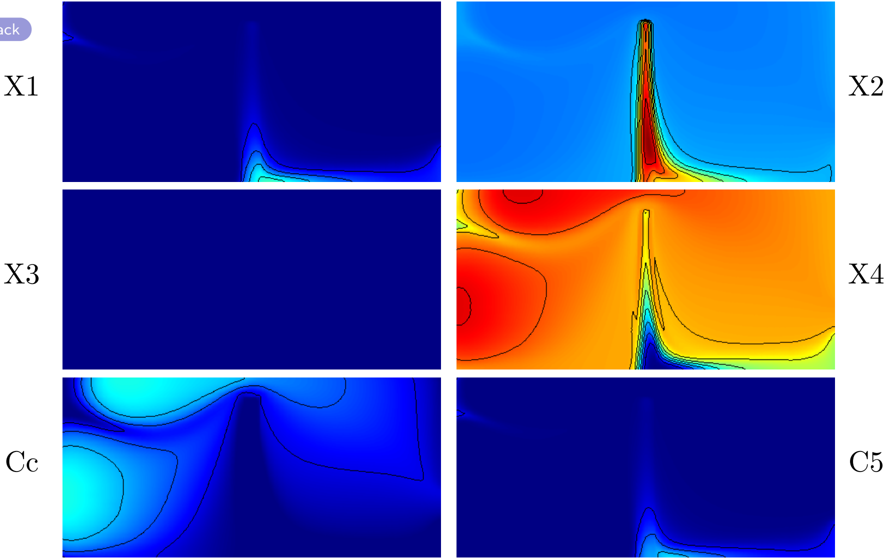

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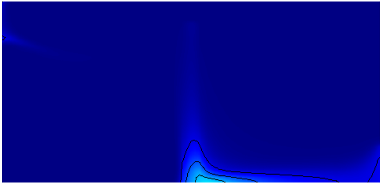

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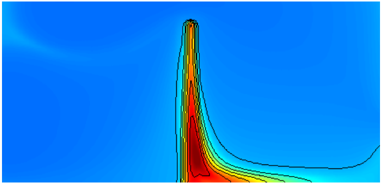

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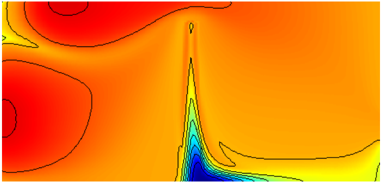

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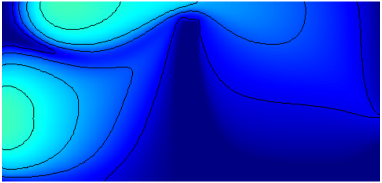

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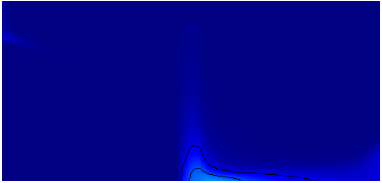

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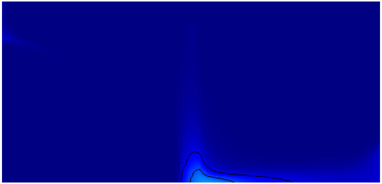

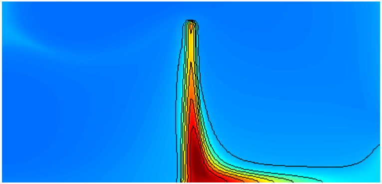

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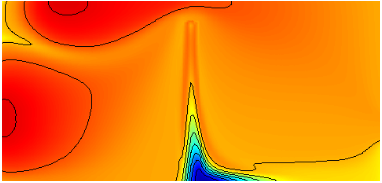

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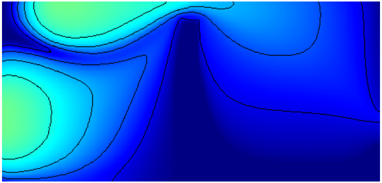

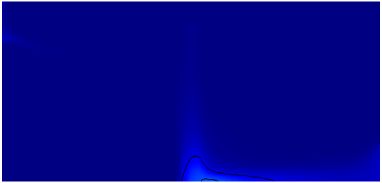

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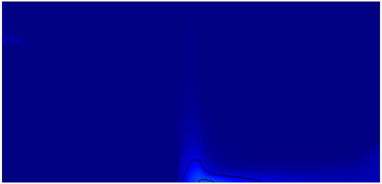

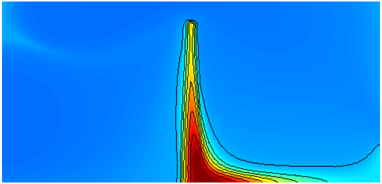

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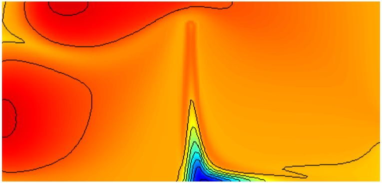

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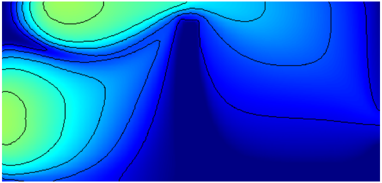

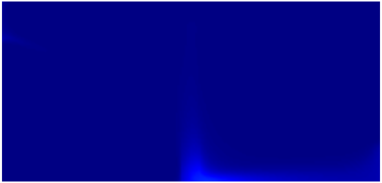

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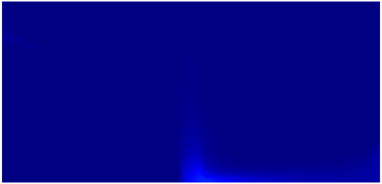

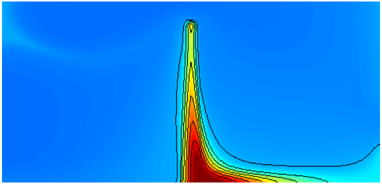

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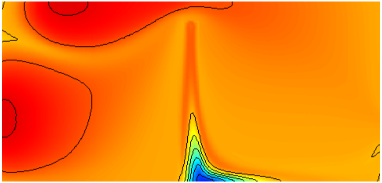

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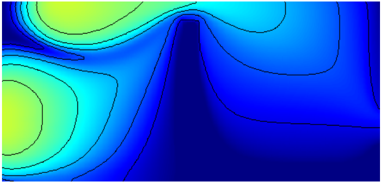

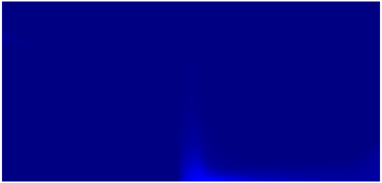

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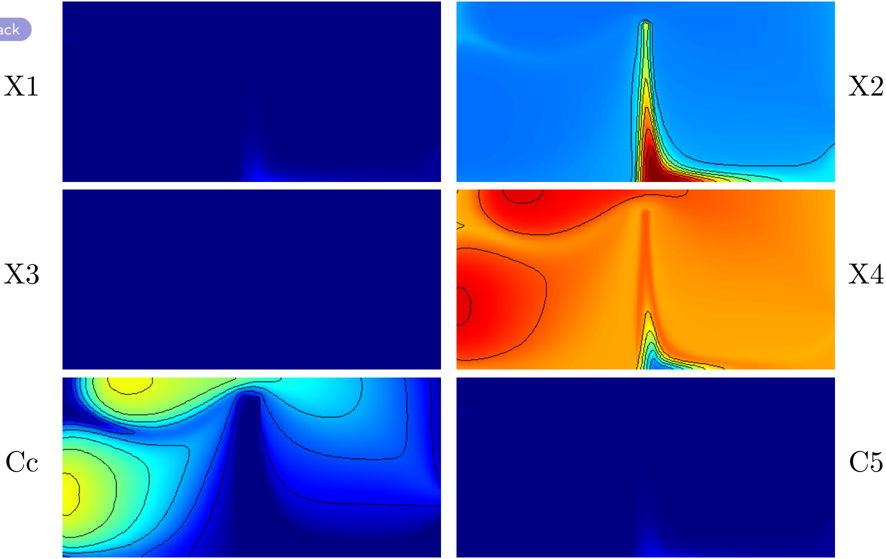

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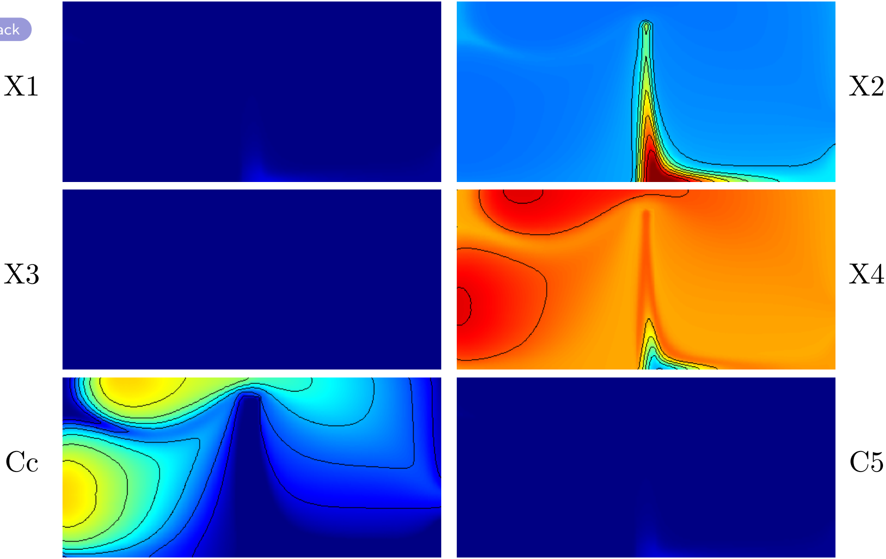

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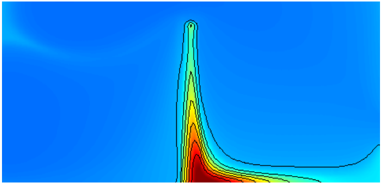

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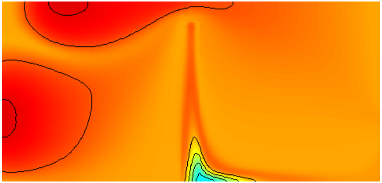

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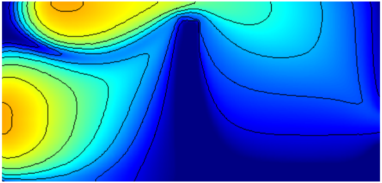

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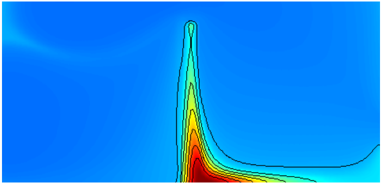

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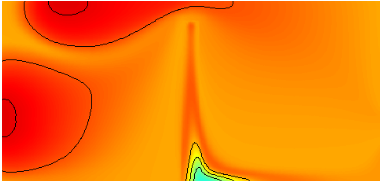

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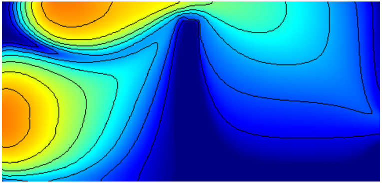

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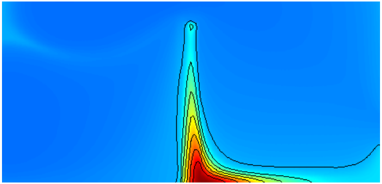

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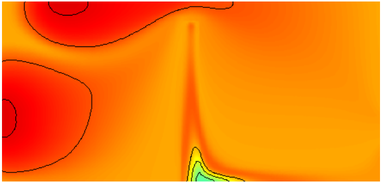

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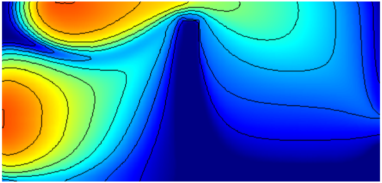

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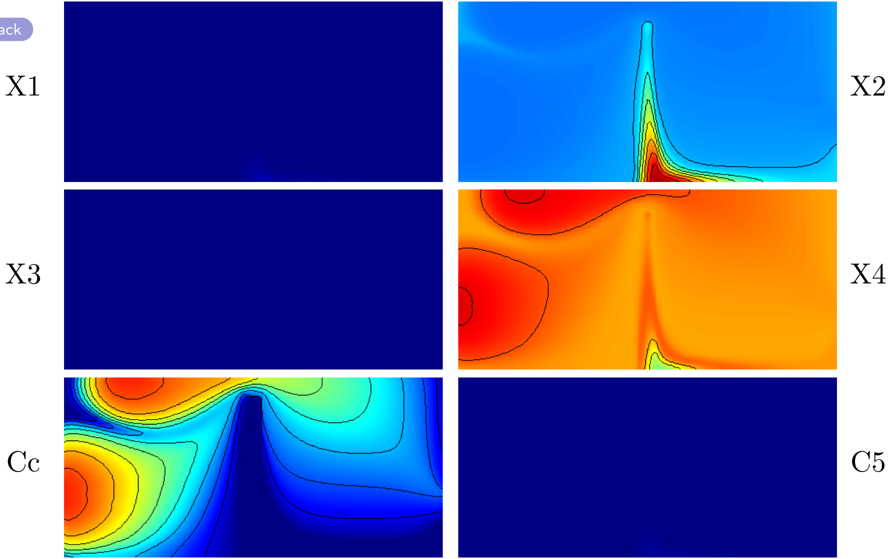

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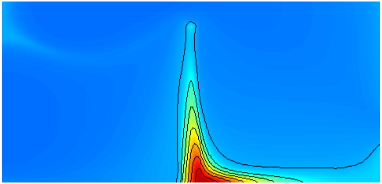

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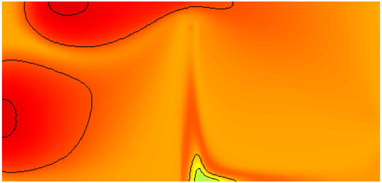

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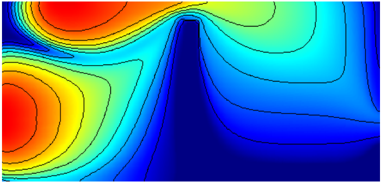

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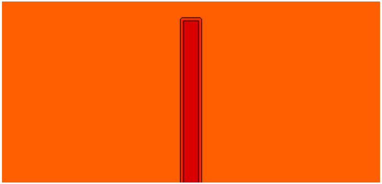

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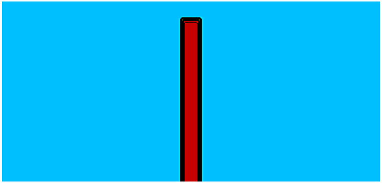

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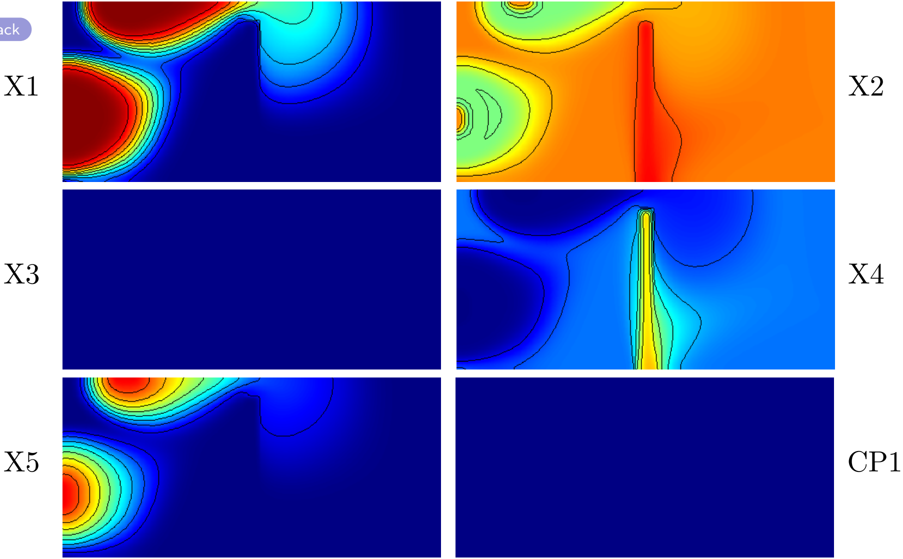

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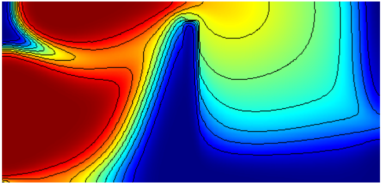

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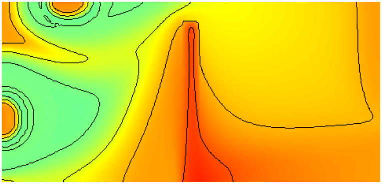

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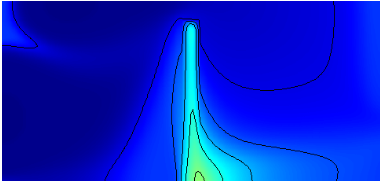

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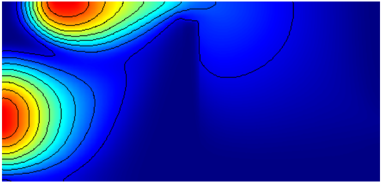

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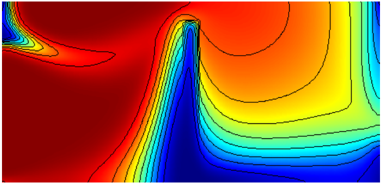

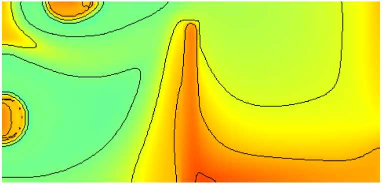

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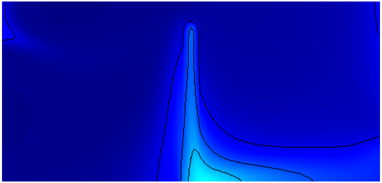

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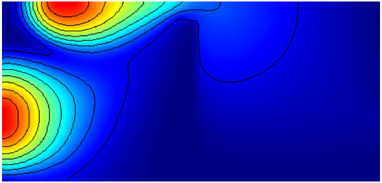

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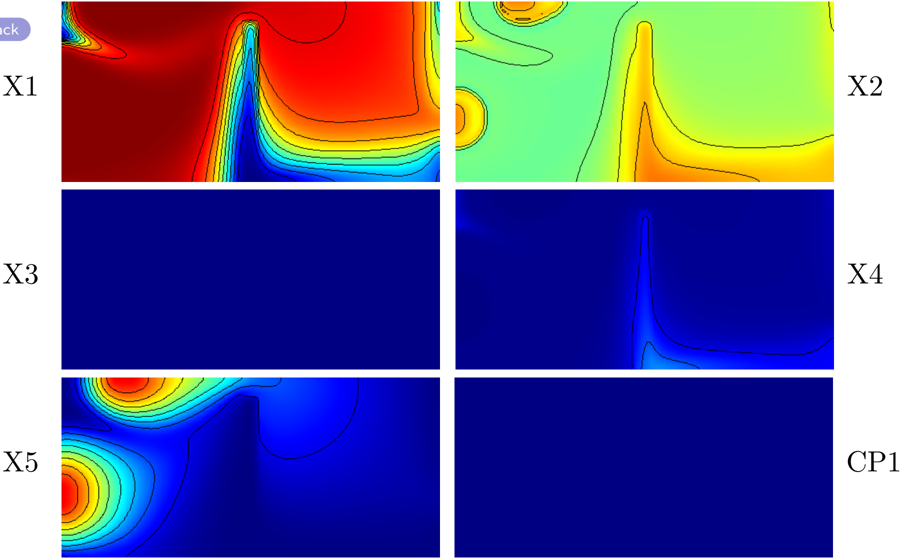

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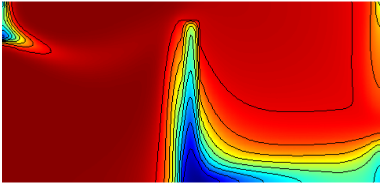

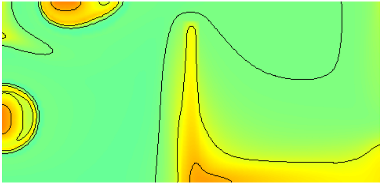

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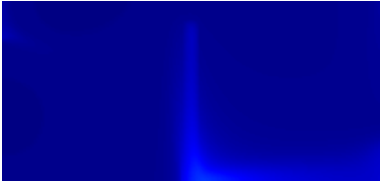

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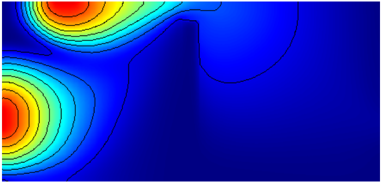

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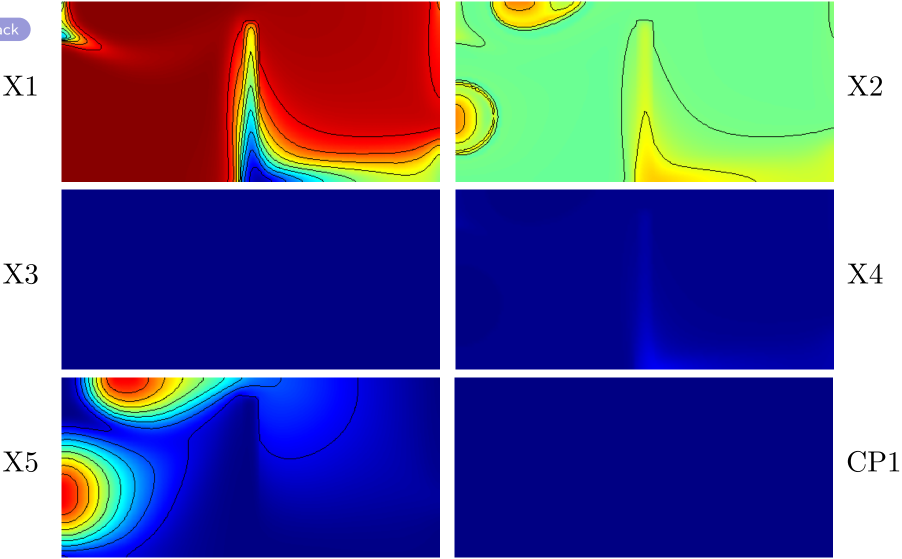

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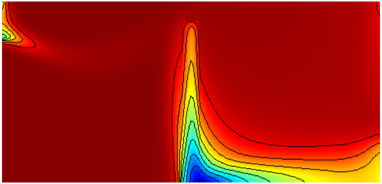

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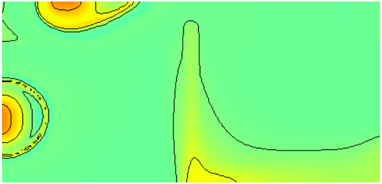

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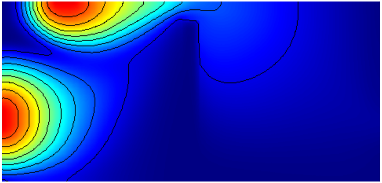

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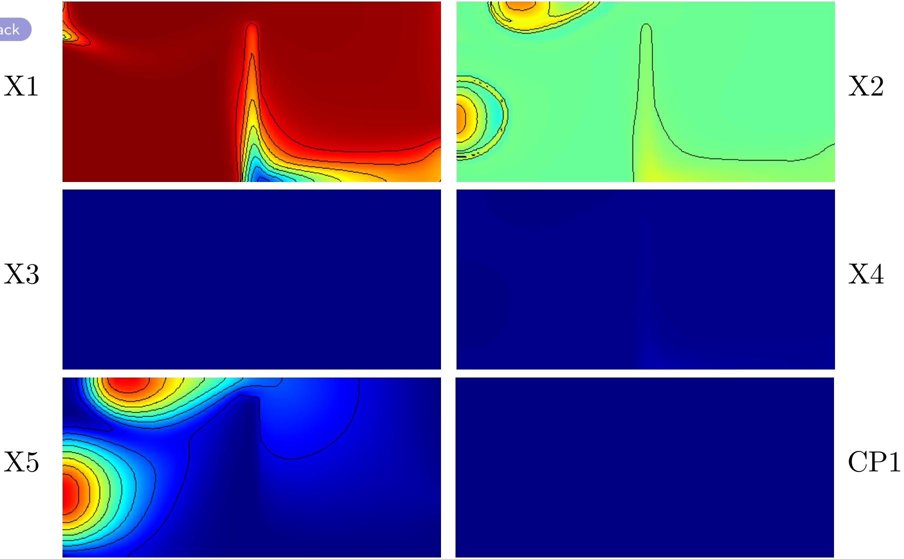

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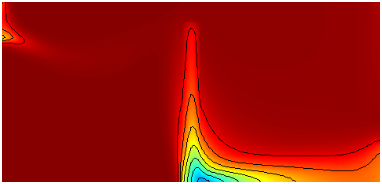

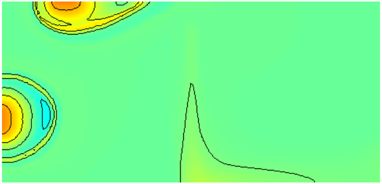

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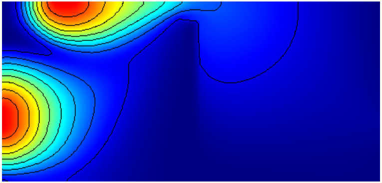

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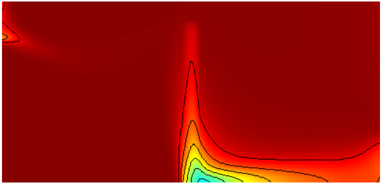

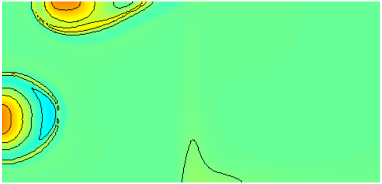

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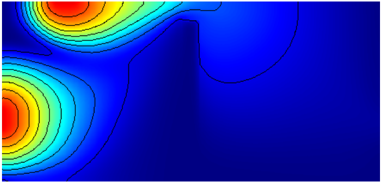

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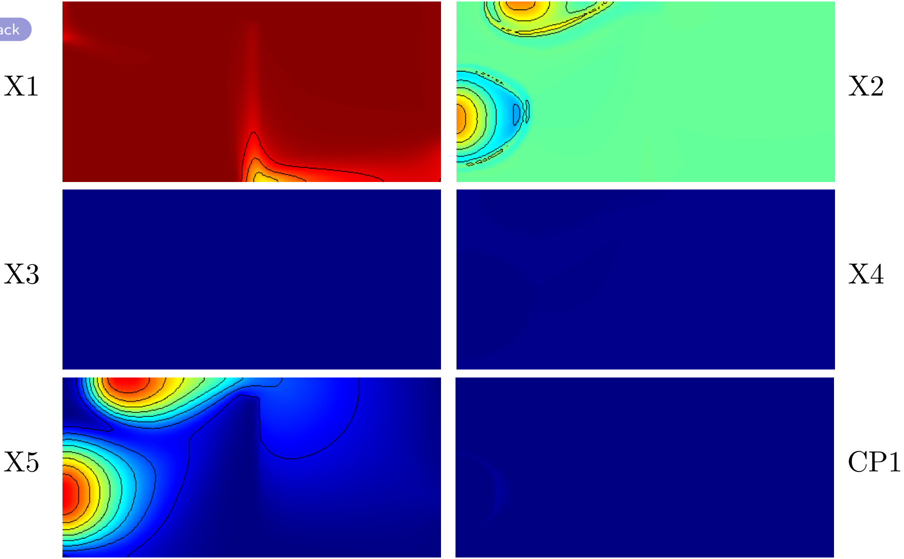

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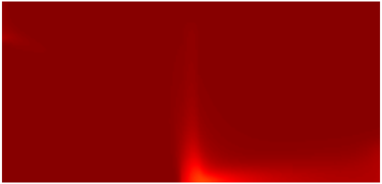

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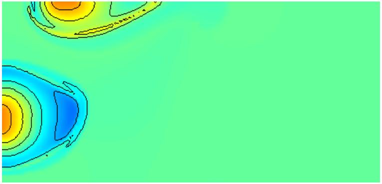

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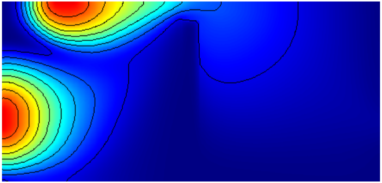

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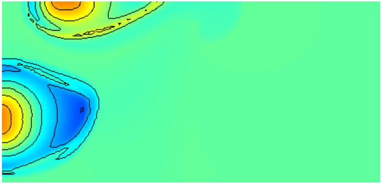
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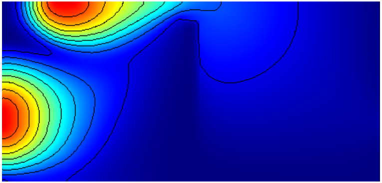
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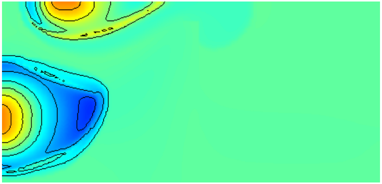

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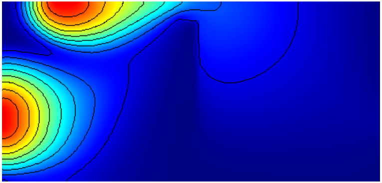

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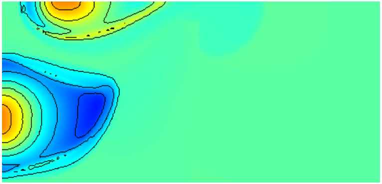

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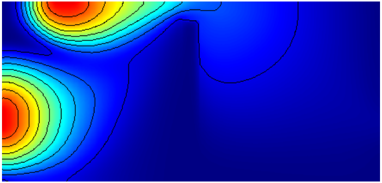

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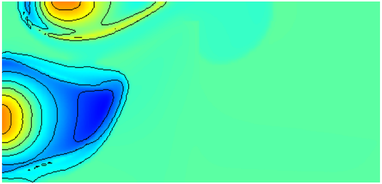

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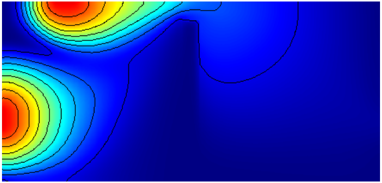

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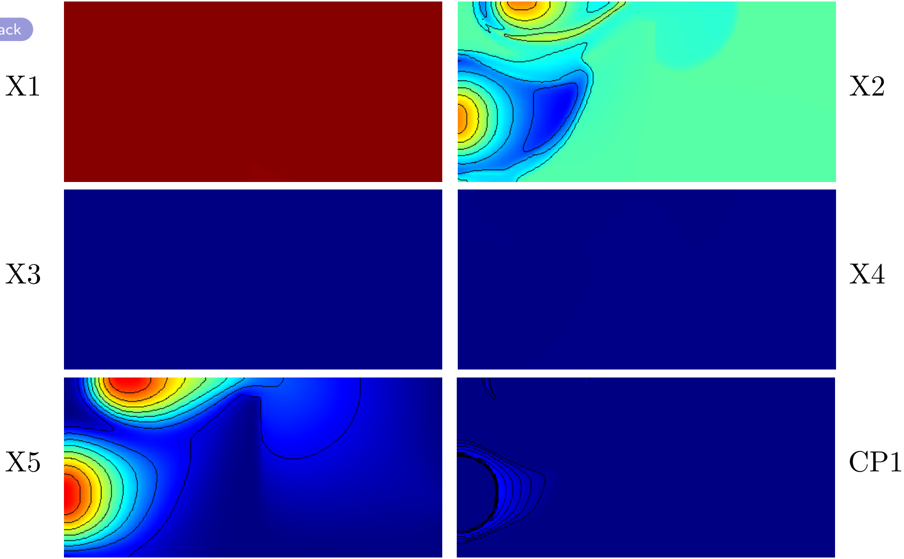

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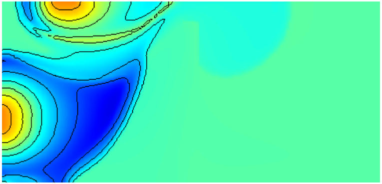
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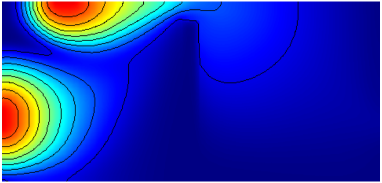
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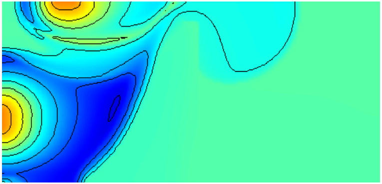

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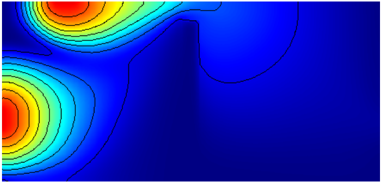

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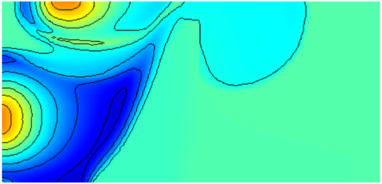

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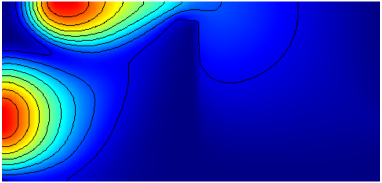

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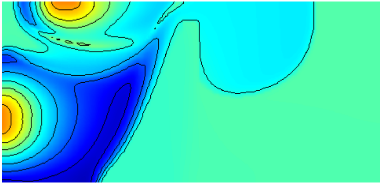

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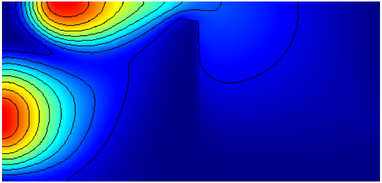

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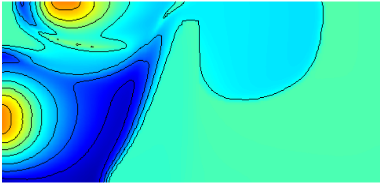

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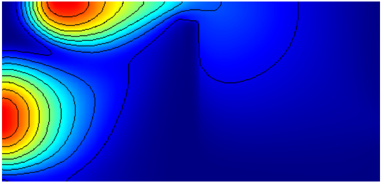

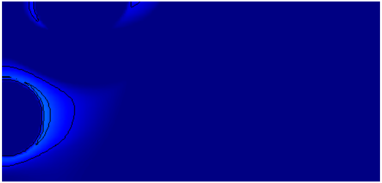

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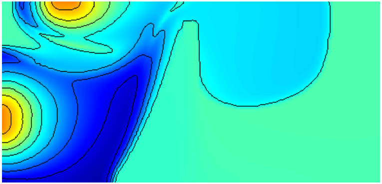

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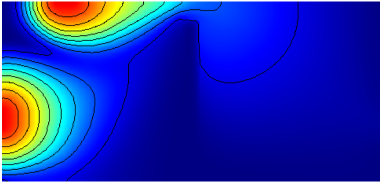

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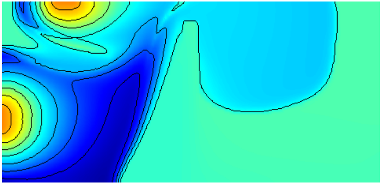

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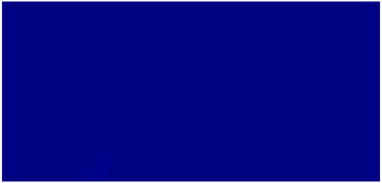

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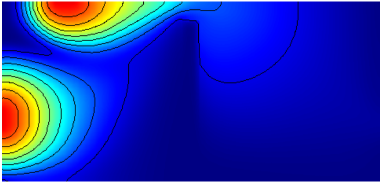

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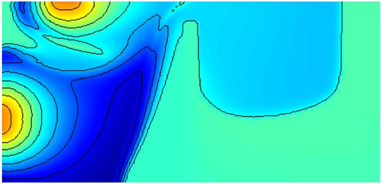

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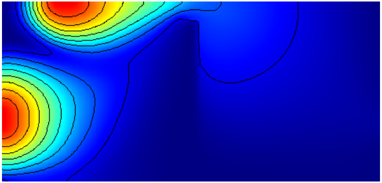

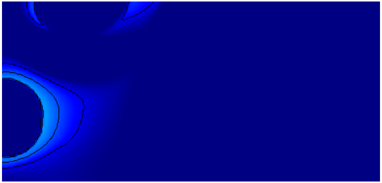

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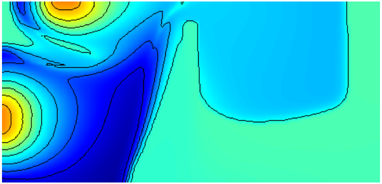

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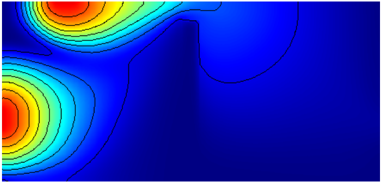

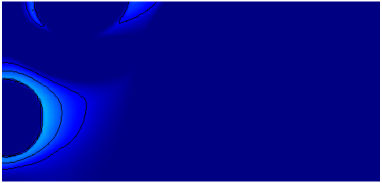

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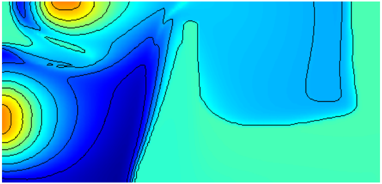

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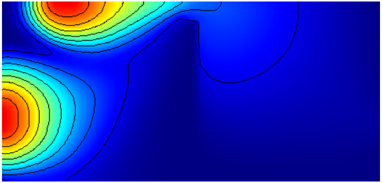

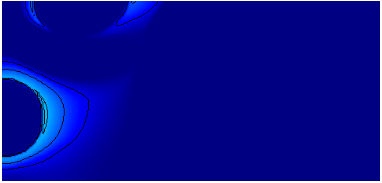

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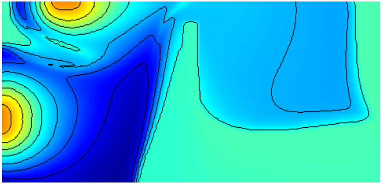

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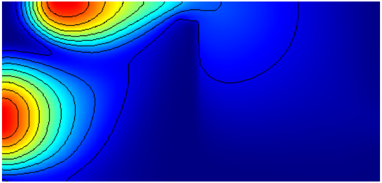

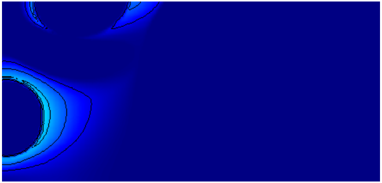

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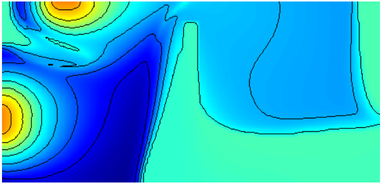

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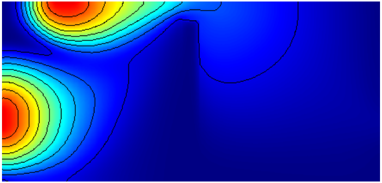

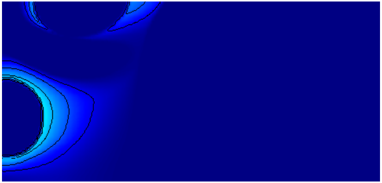

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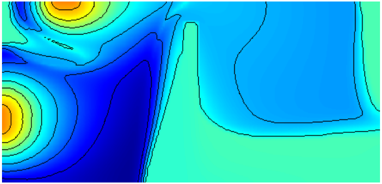

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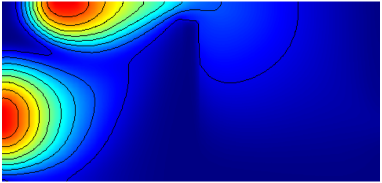

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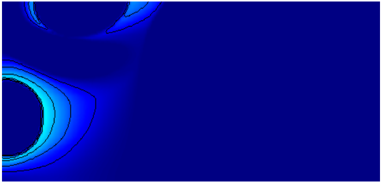

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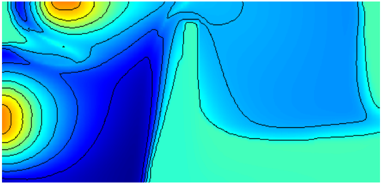

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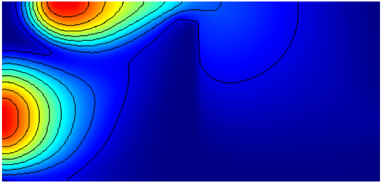

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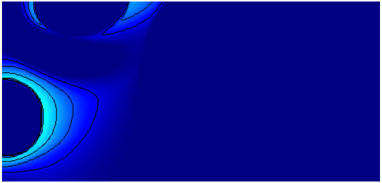

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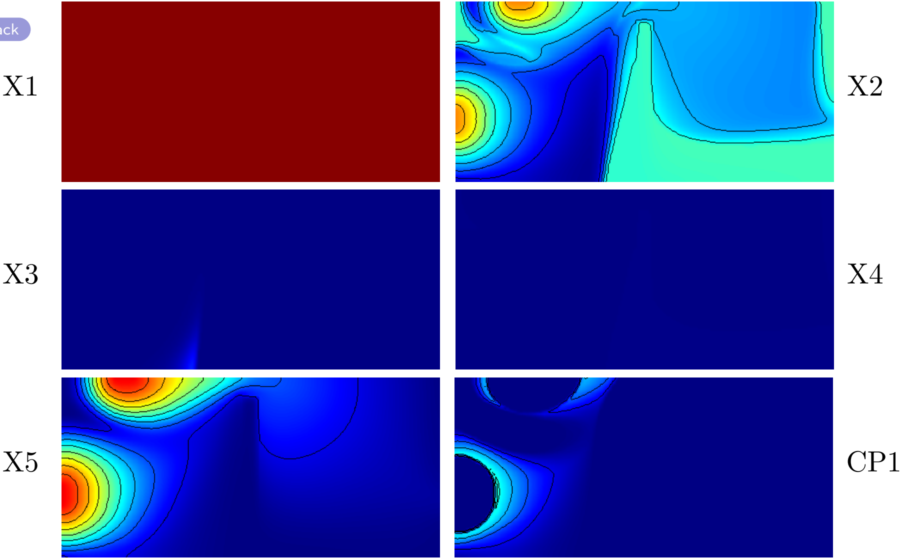

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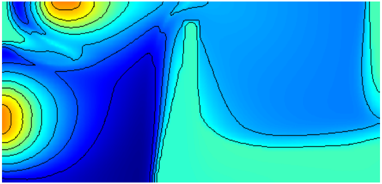

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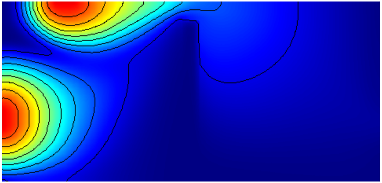

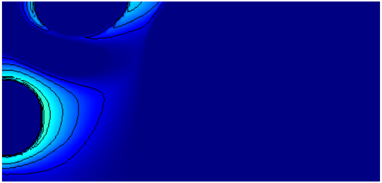

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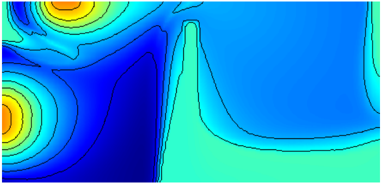

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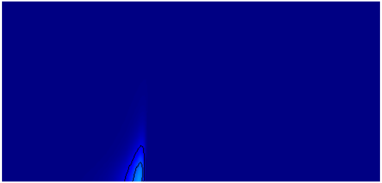

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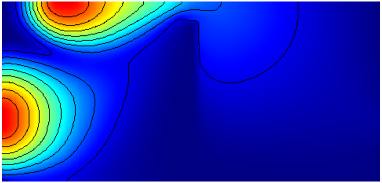

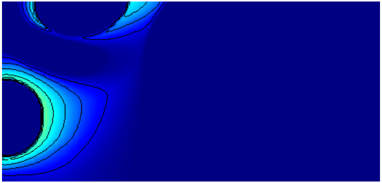

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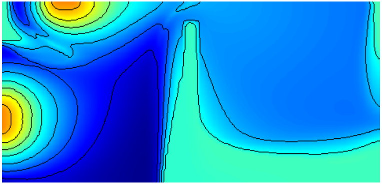

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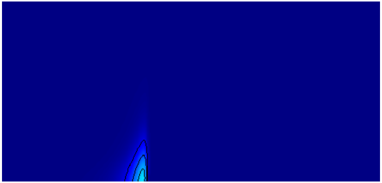

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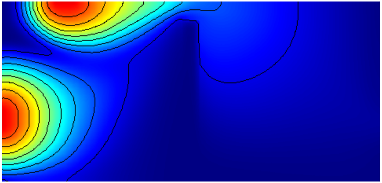

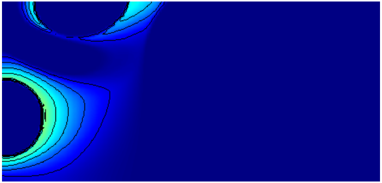

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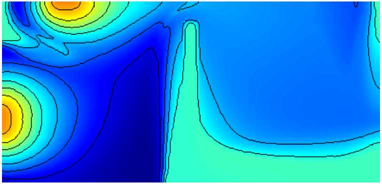

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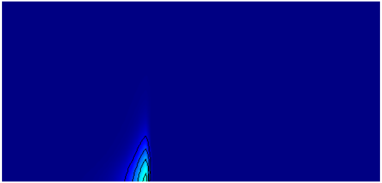

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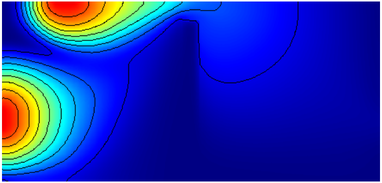

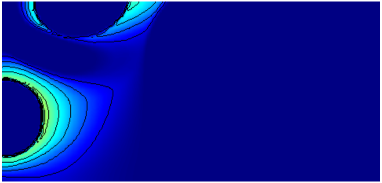

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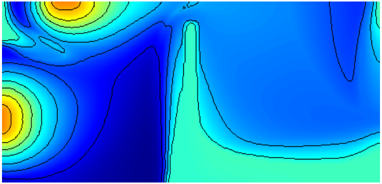

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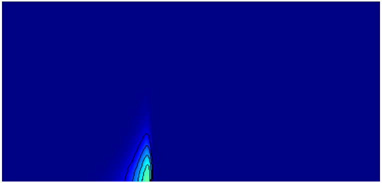

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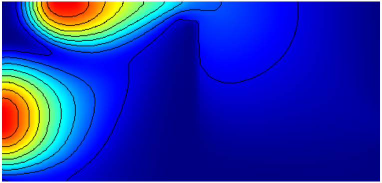

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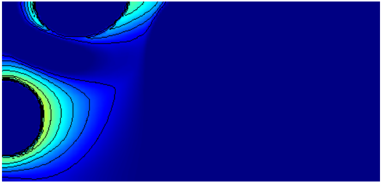

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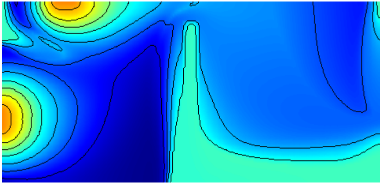

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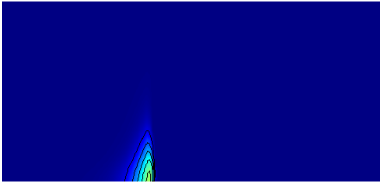

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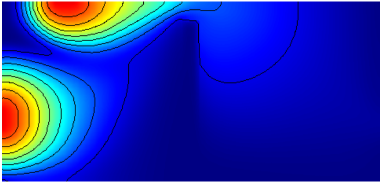

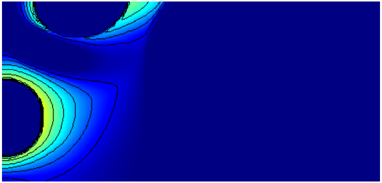

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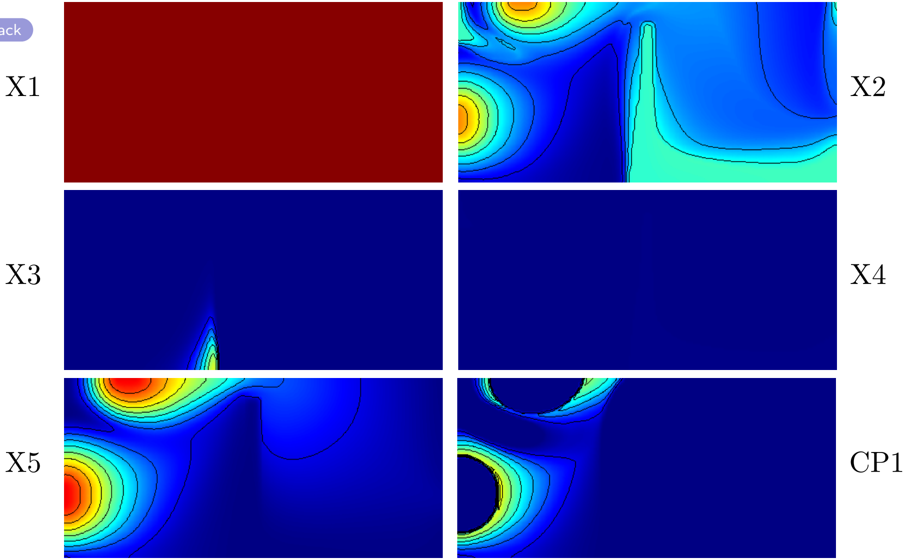

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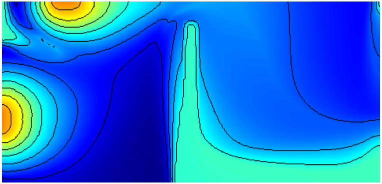

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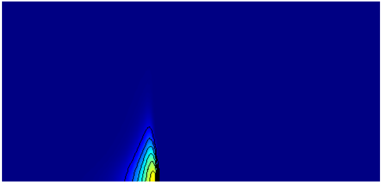

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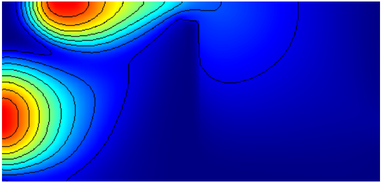

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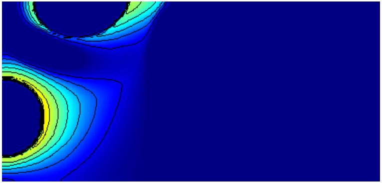

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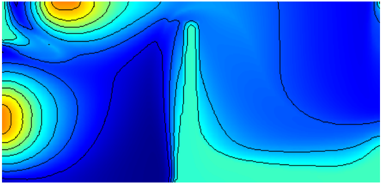

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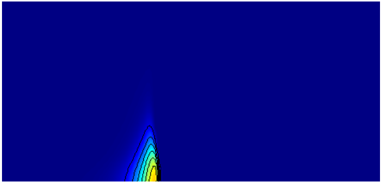

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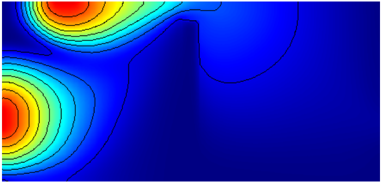

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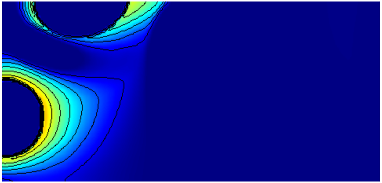

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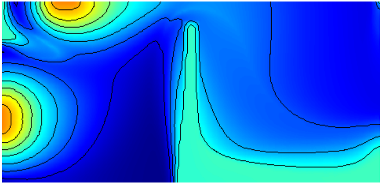

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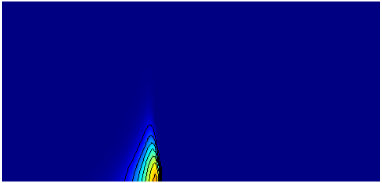

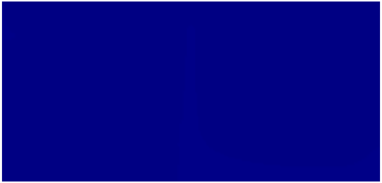

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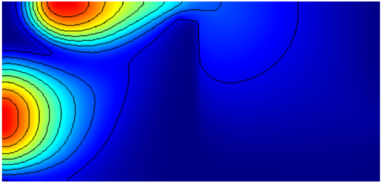

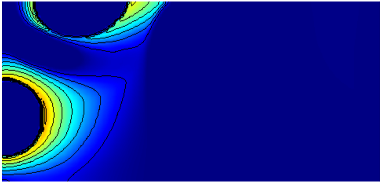

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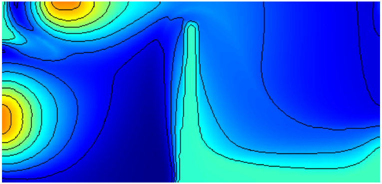

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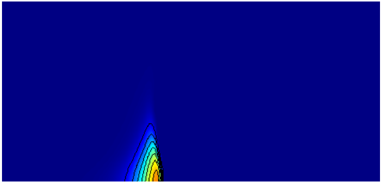

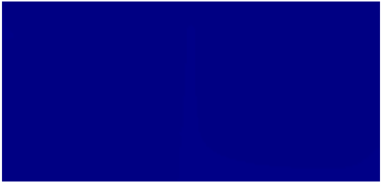

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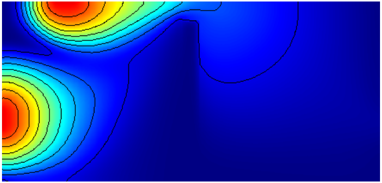

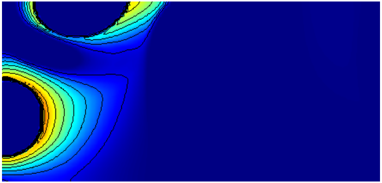

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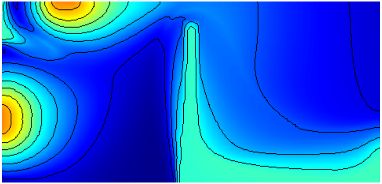

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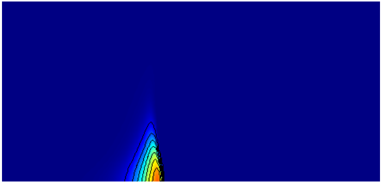

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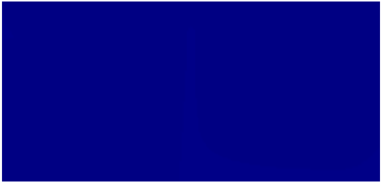

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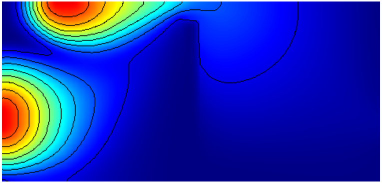

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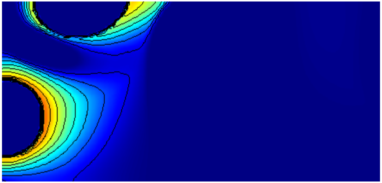

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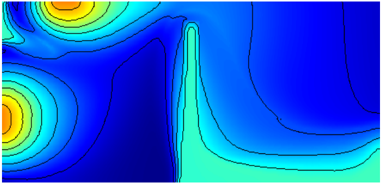

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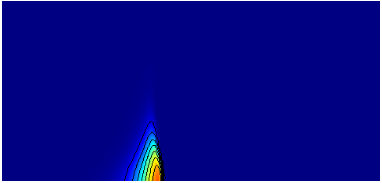

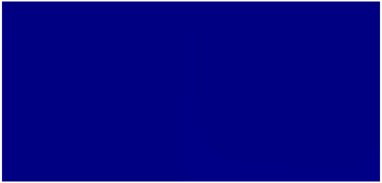

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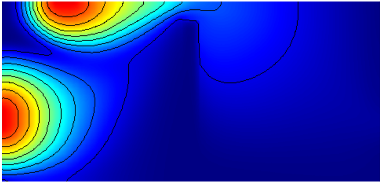

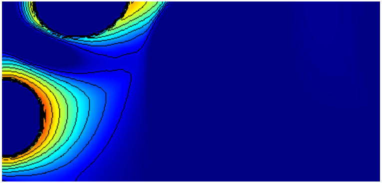

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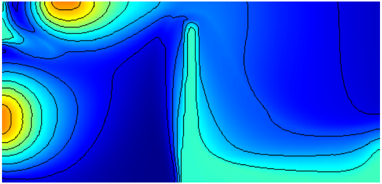

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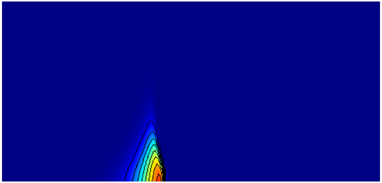

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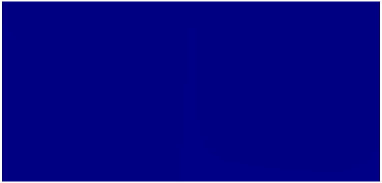

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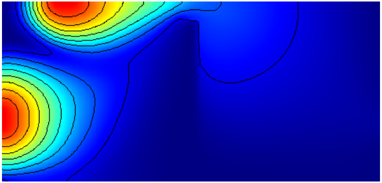

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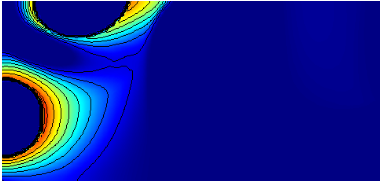

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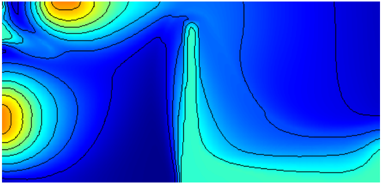

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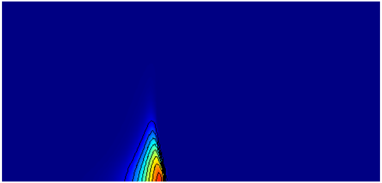

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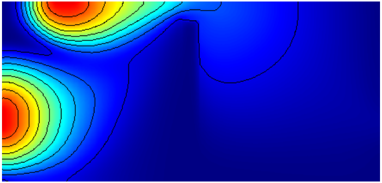

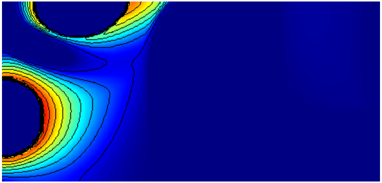

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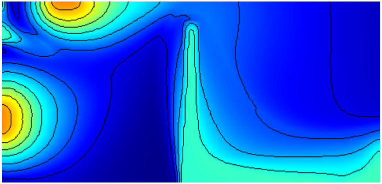

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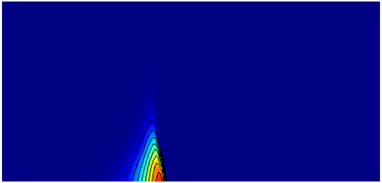

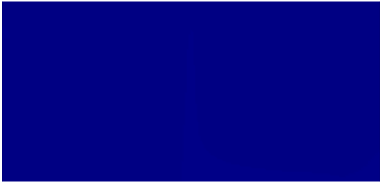

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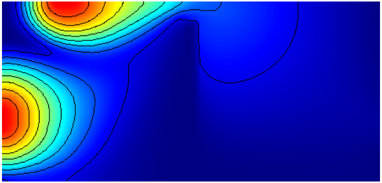

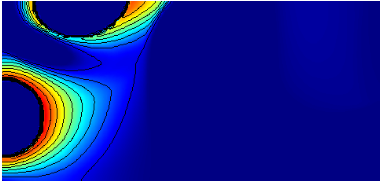

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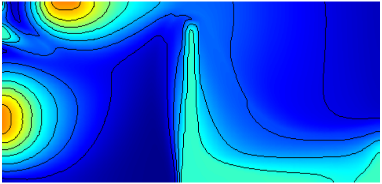

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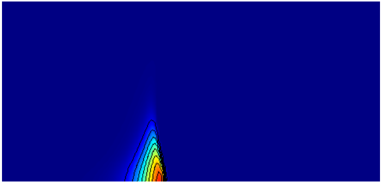

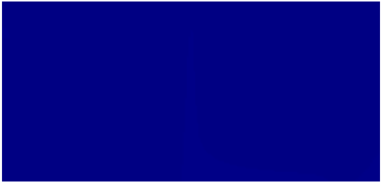

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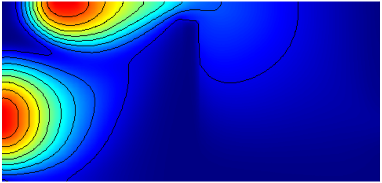

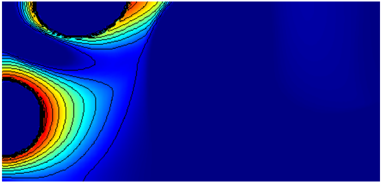

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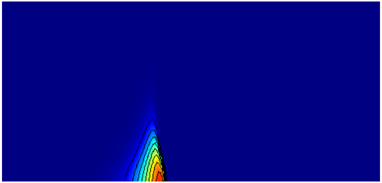

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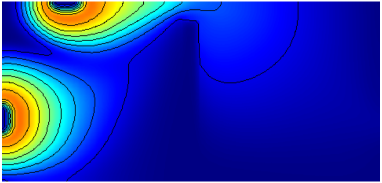

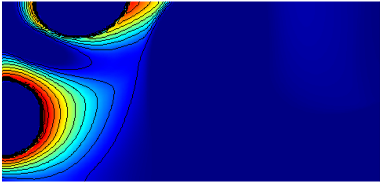

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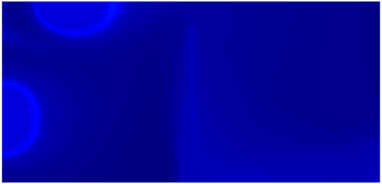

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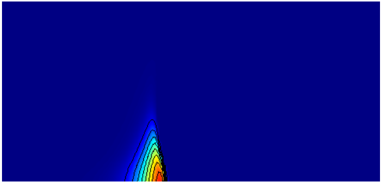

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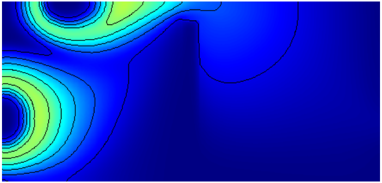

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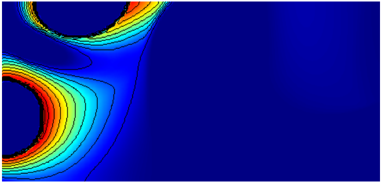

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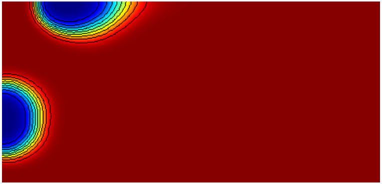

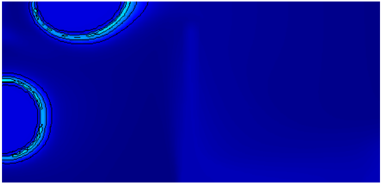

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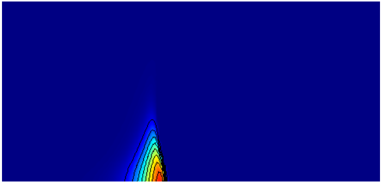

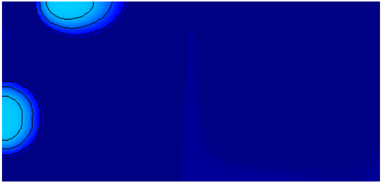

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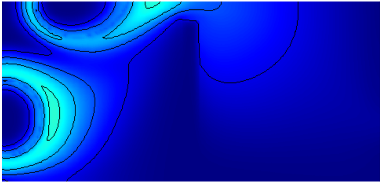

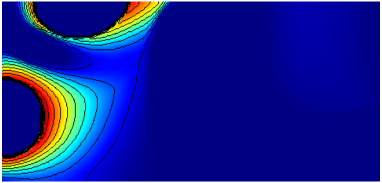

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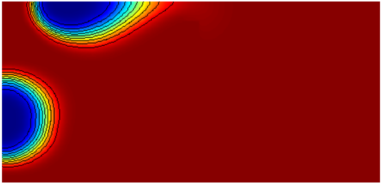

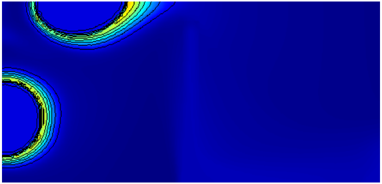

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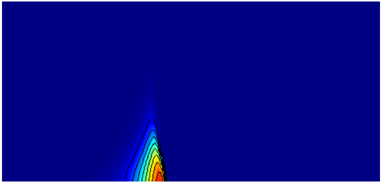

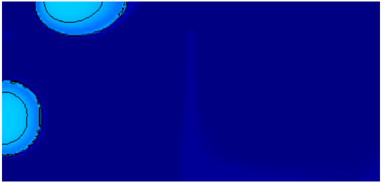

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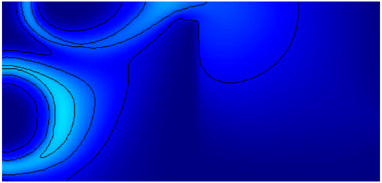

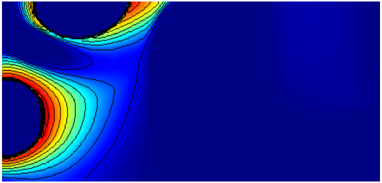

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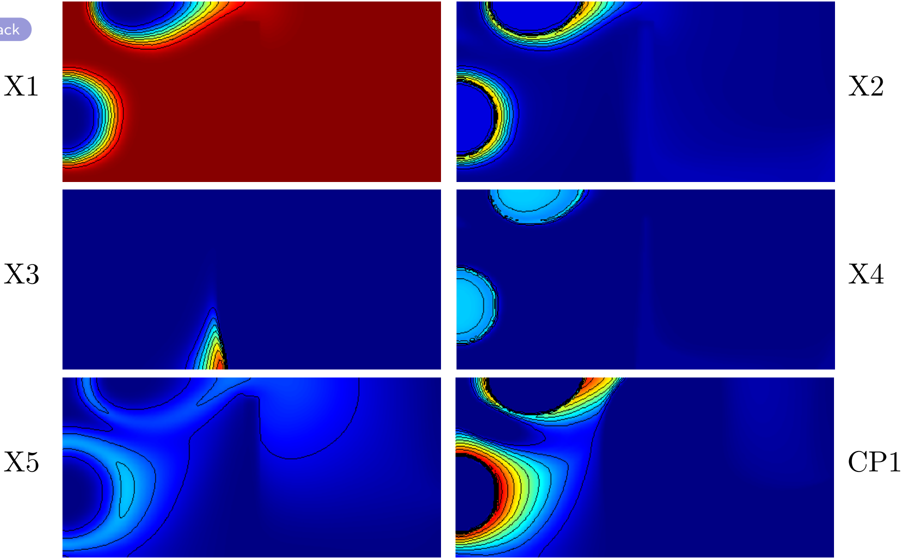

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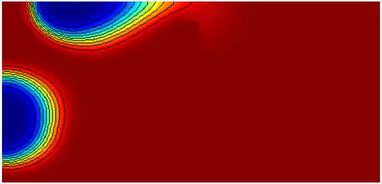
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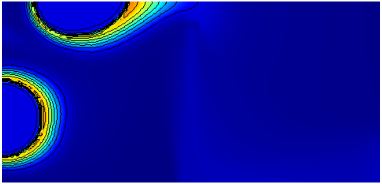
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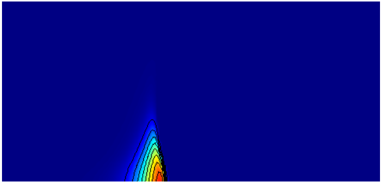
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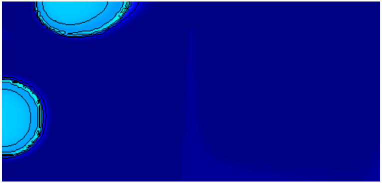
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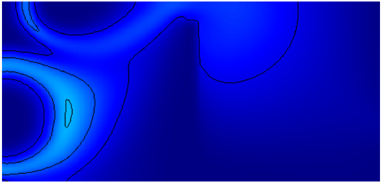
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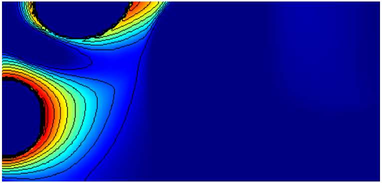
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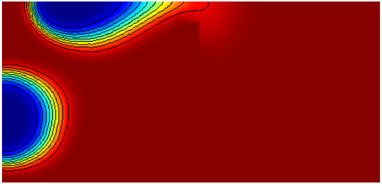

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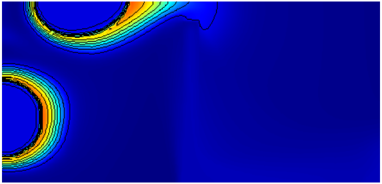

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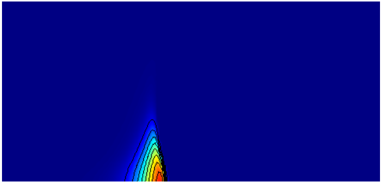

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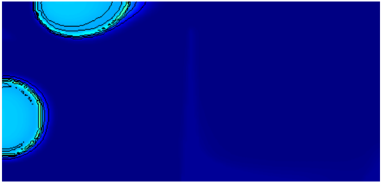

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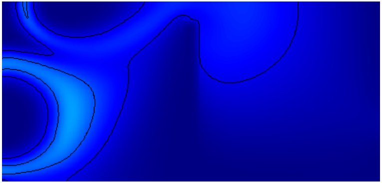

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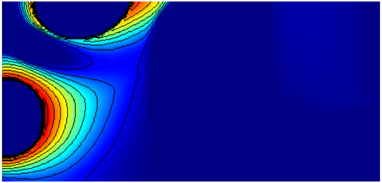

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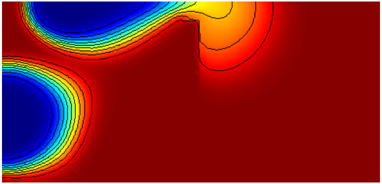

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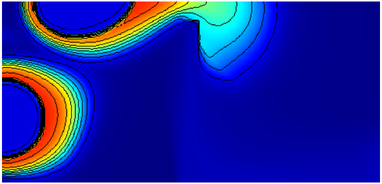

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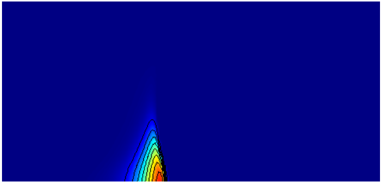

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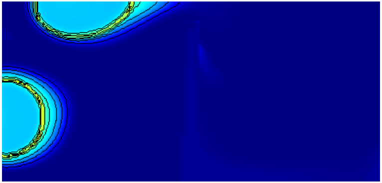

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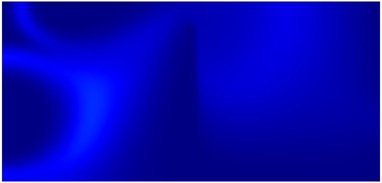

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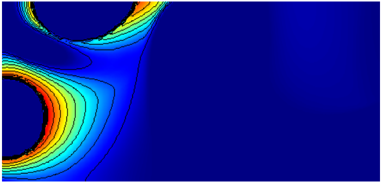

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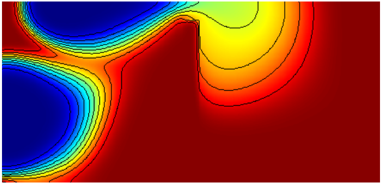

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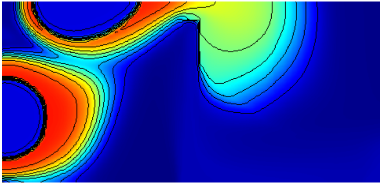

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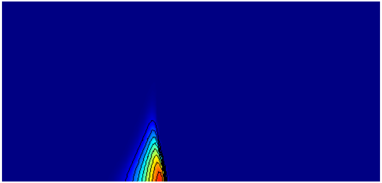

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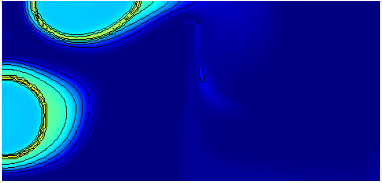

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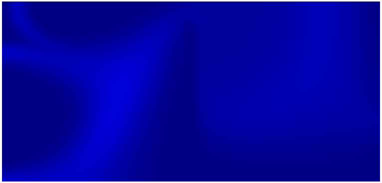

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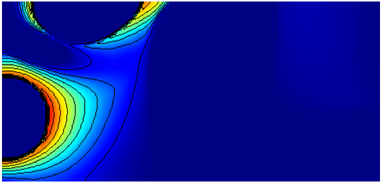

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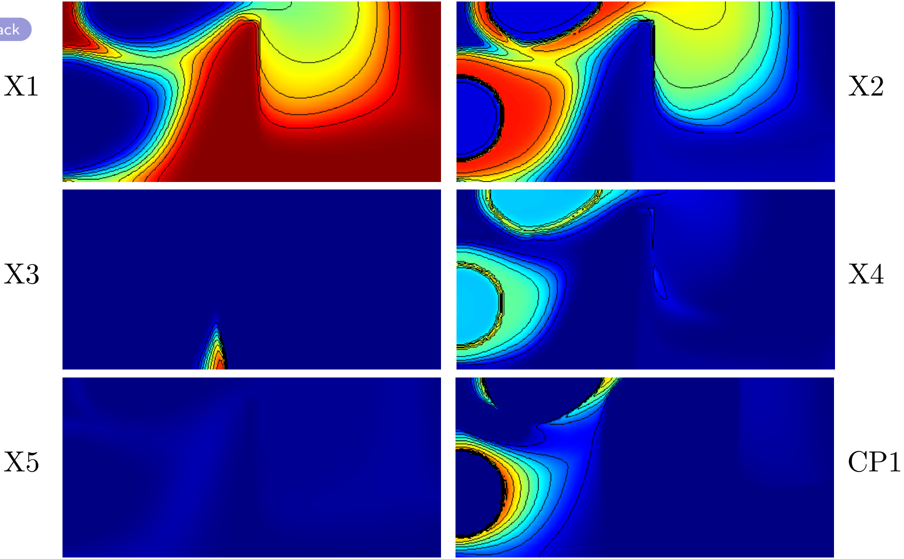

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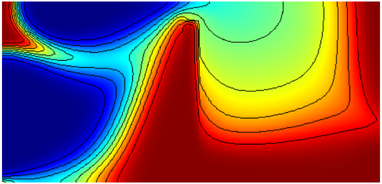

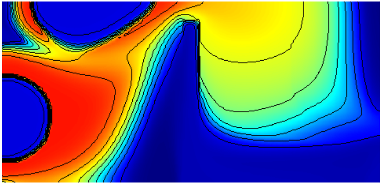

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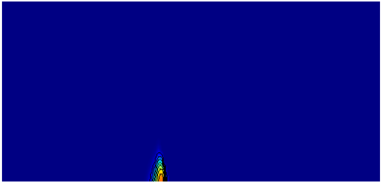

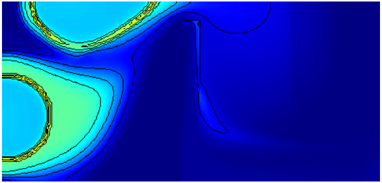

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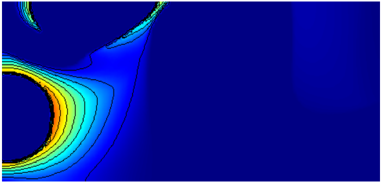

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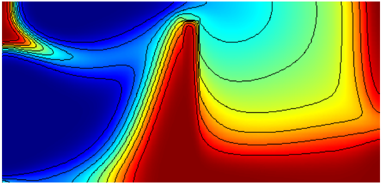

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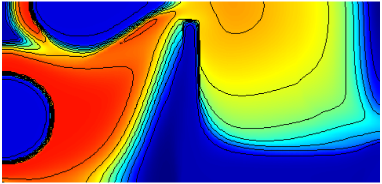

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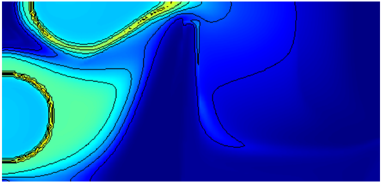

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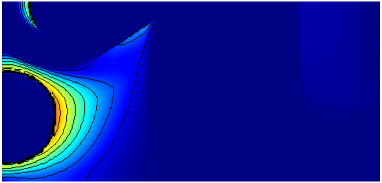

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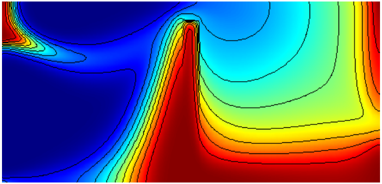

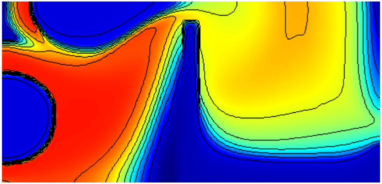

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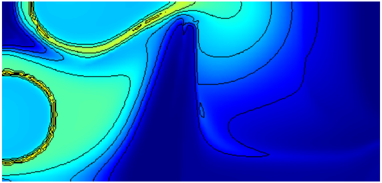

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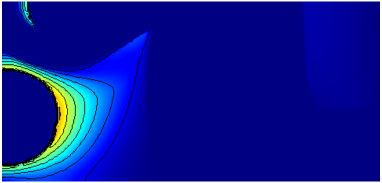

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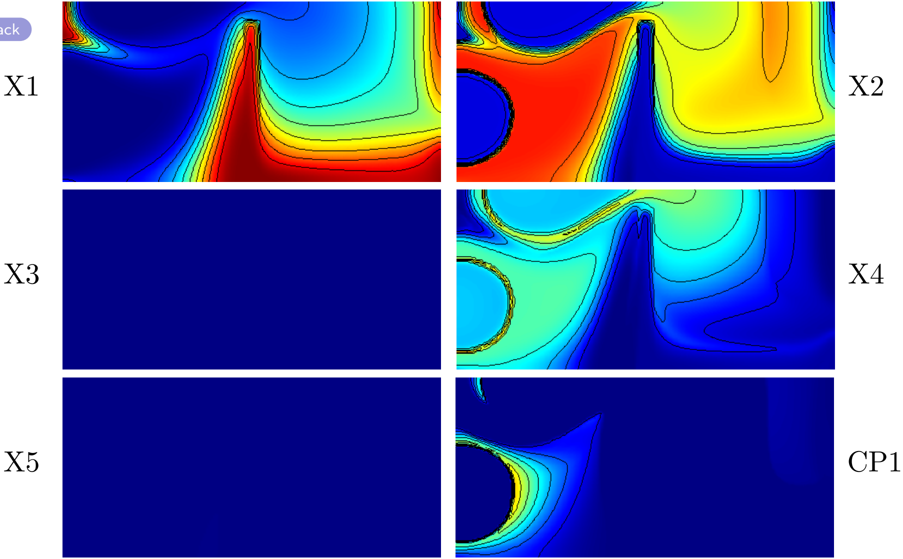

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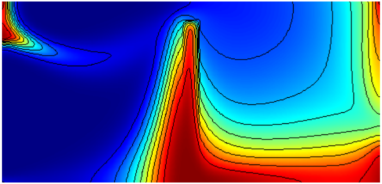

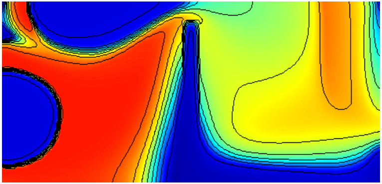

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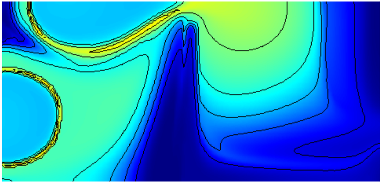

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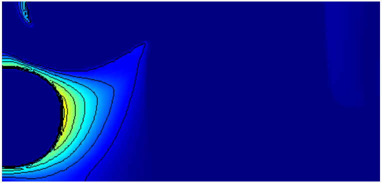

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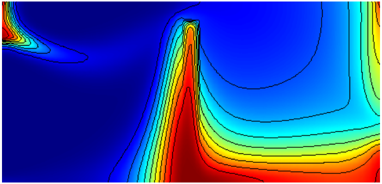
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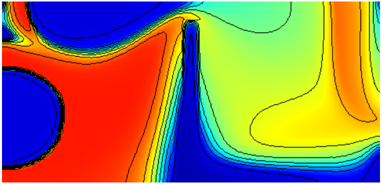
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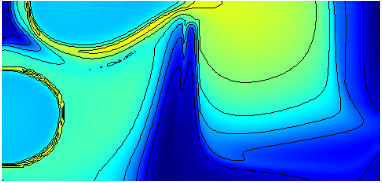
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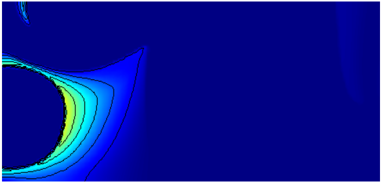
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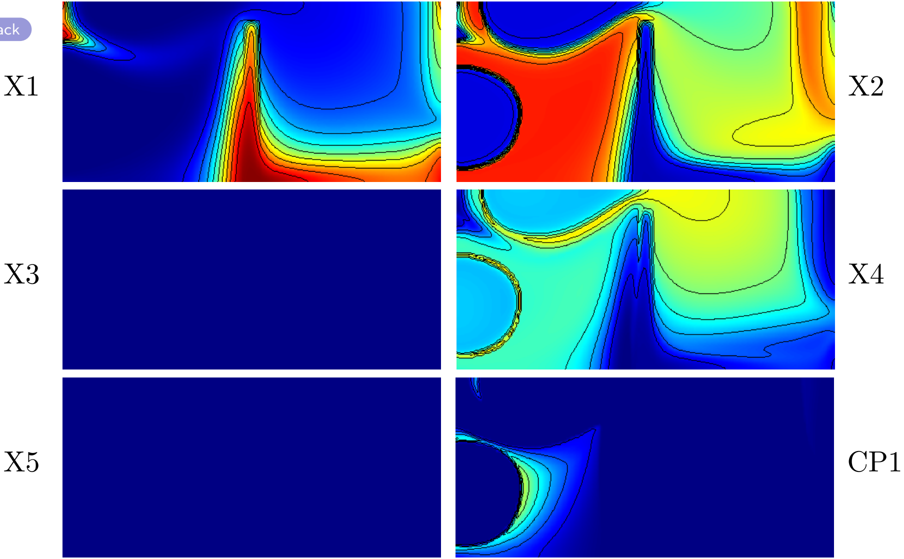

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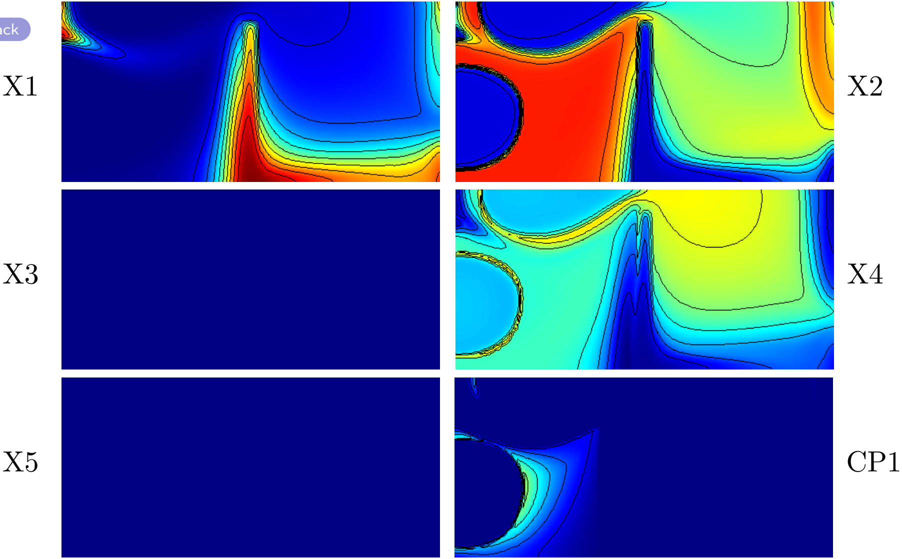

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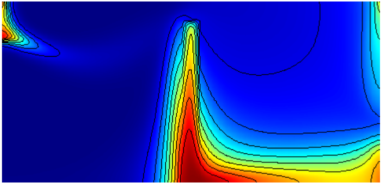

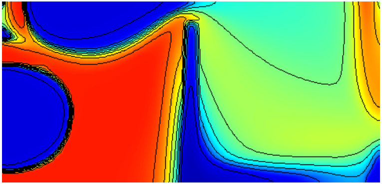

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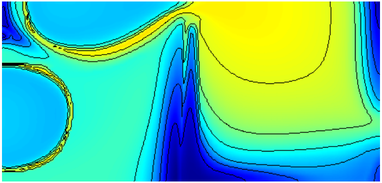

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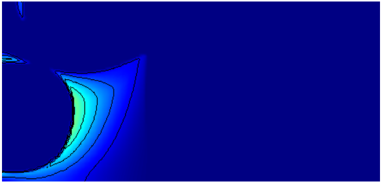

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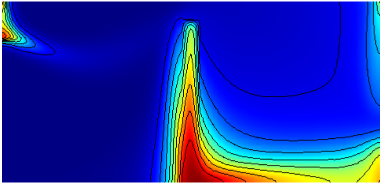
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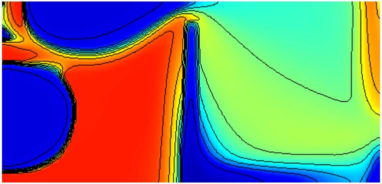
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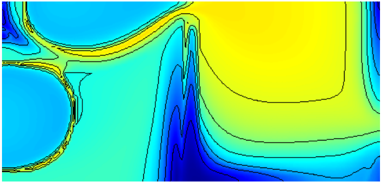
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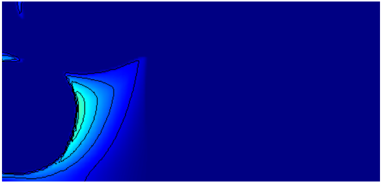
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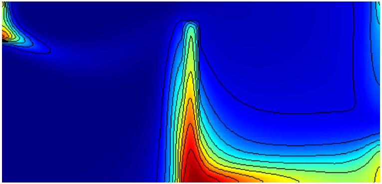
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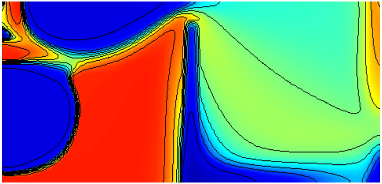
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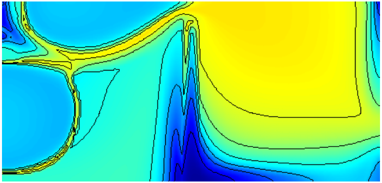
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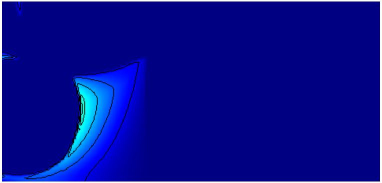
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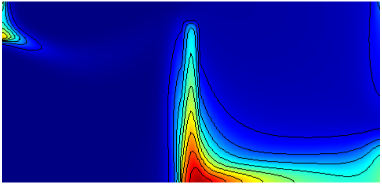

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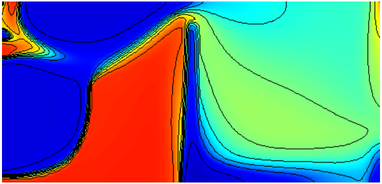

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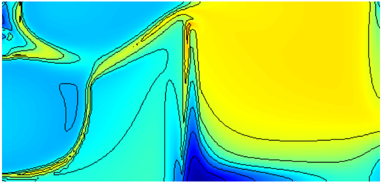

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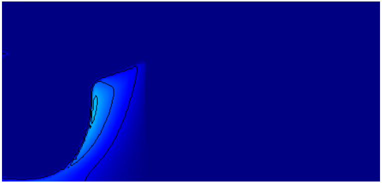

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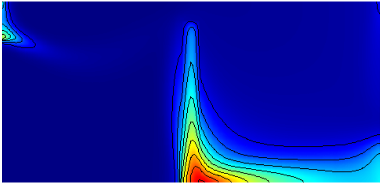

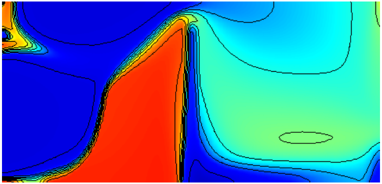

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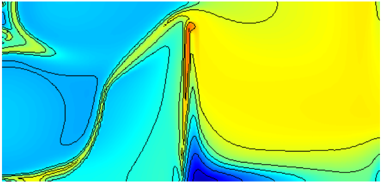

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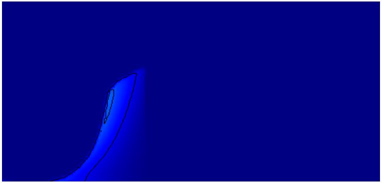

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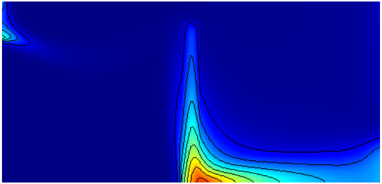

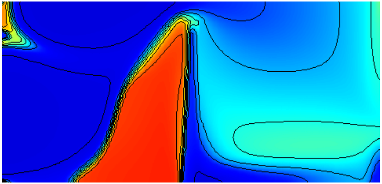

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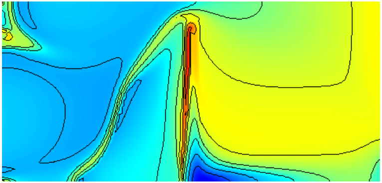

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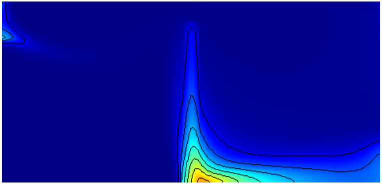

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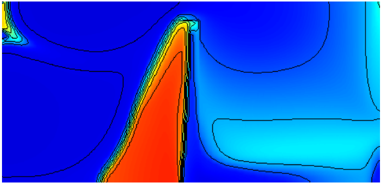

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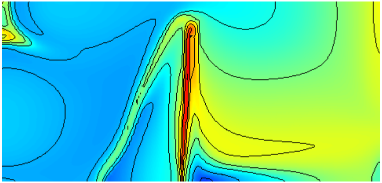

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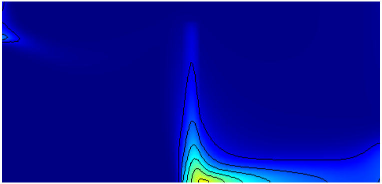

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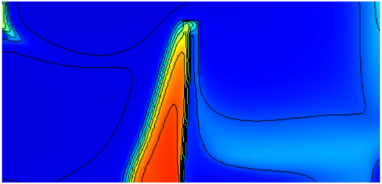

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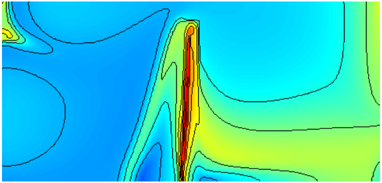

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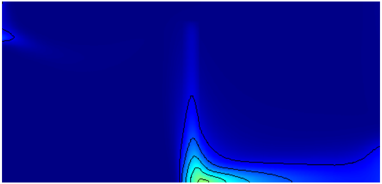

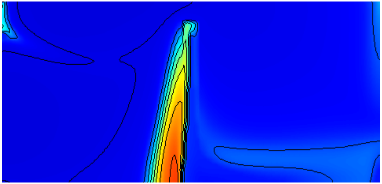

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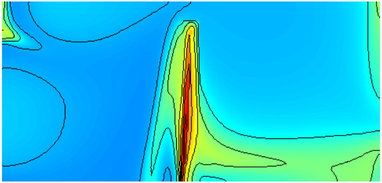

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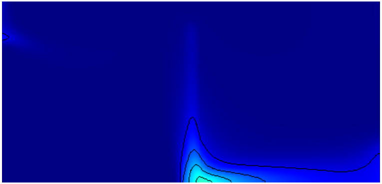

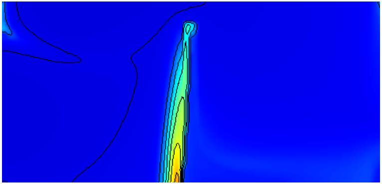

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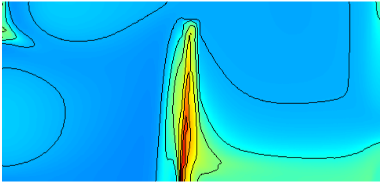

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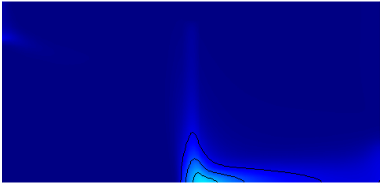
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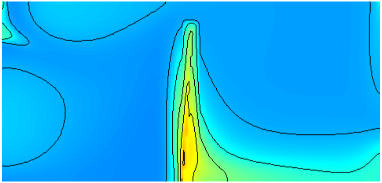
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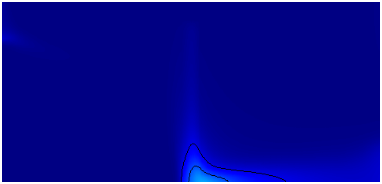

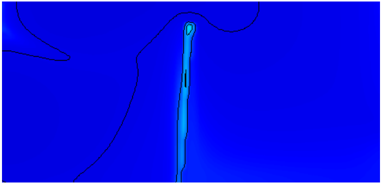

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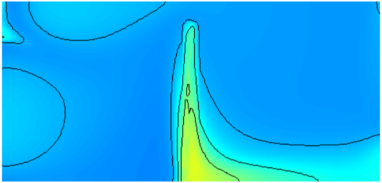

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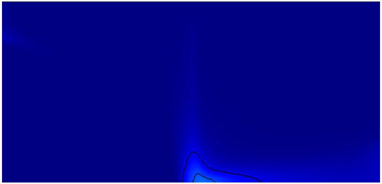

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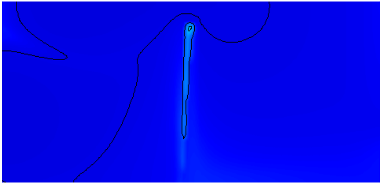

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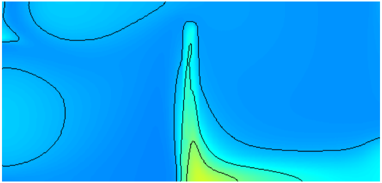

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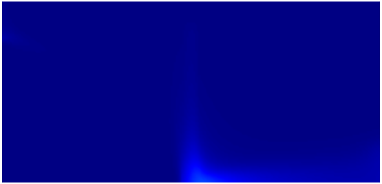

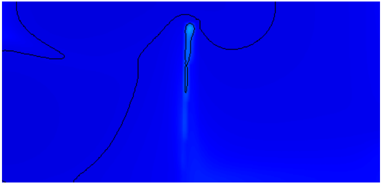

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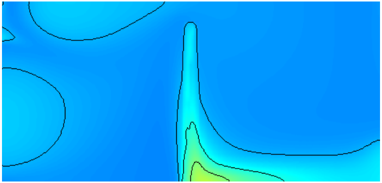

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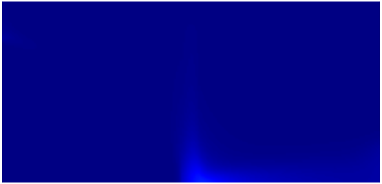

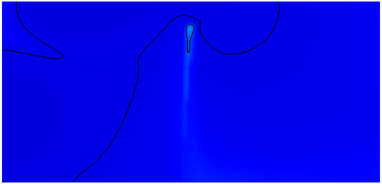

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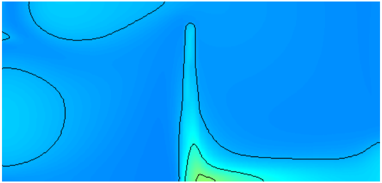

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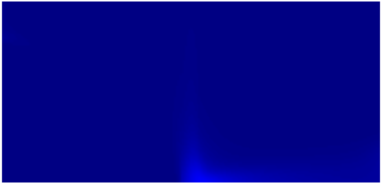

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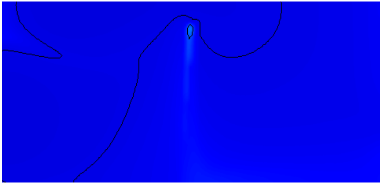

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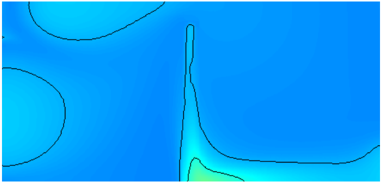

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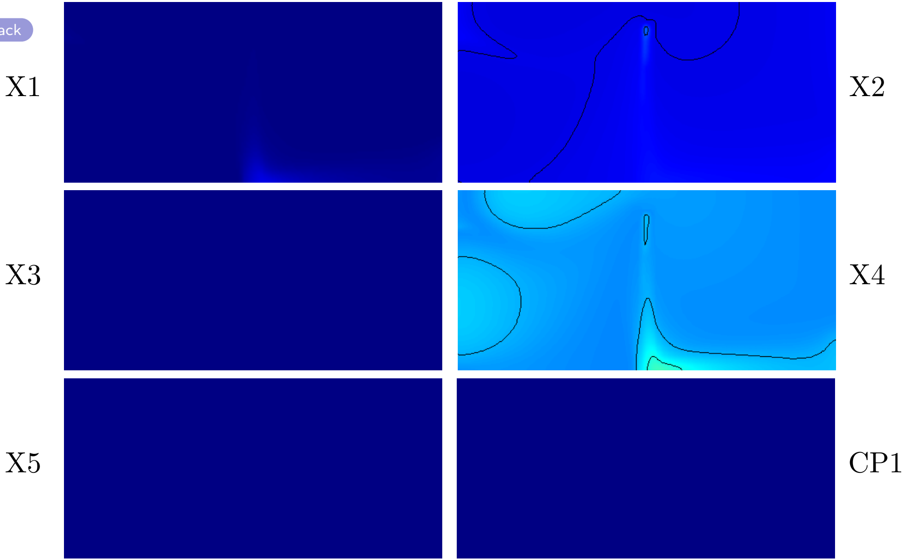

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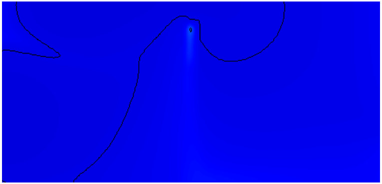

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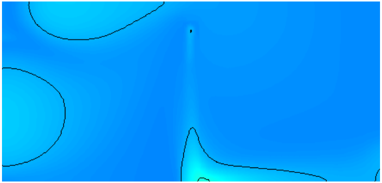

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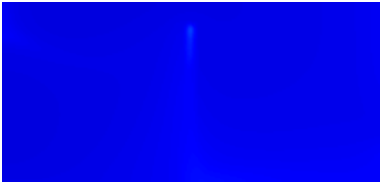

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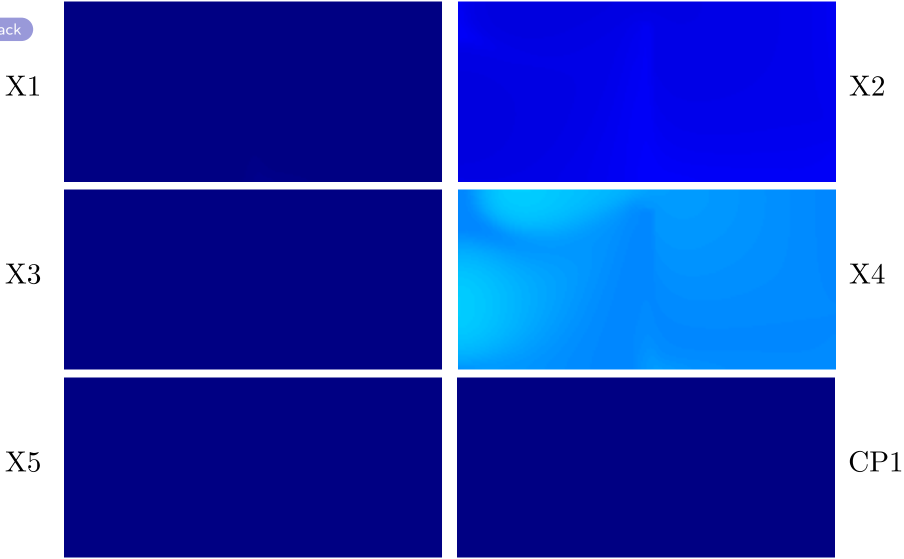

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