Convex Solubility Parameters for Polymers

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Solubility Parameters

- Solubility parameters are three intermolecular forces that govern solubility in Hansen's model
- δ_d Dispersion forces: the attraction between all compounds based on instantanious changes in electron density
- δ_p Dipole-Dipole Forces: the attraction/repulsion based on permanent dipole
- δ_h Hydrogen Bonding: the attractive forces based on hydrogen bonding
- **Objective:** to gain a greater understanding of the solubility behavior of polymers, we want a more complete picture of the region in the parameter space that contains good solvents.
- **Method:** construct the convex hull representation of the four polymers found in [2] and compare to the existing approach (Hansen Solubility Parameters).

Introduction

- Solution: solute dissolved in solvent
- Based on the concept of "like dissolves like" - e.g., polar solvents dissolve polar solutes
- Additive combinations of good solvents should also be good solvents
- Hildebrand model: solubility is based on thermodynamics
- Hansen model: solubility is based on intermolecular forces

Hansen Solubility Parameters

- Difference between solubility parameters of solvent and solute give "solubility distance" R_a:

$$R_a^2 = 4(\delta_{d,1} - \delta_{d,2})^2 + (\delta_{p,1} - \delta_{p,2})^2 + (\delta_{h,1} - \delta_{h,2})^2$$

- HSP taken to be center of sphere
- Better solvents are closer to center
- **Issues:**
  - Spheres can be largely extrapolated - overestimates solubility region
  - Portions of sphere outside physical parameter range
  - Hydrogen Bonding is a sort of "catch all" for every force not listed above
  - Good solvents may lie outside sphere and poor solvents may be inside sphere

New Approach: Convex Solubility Parameters

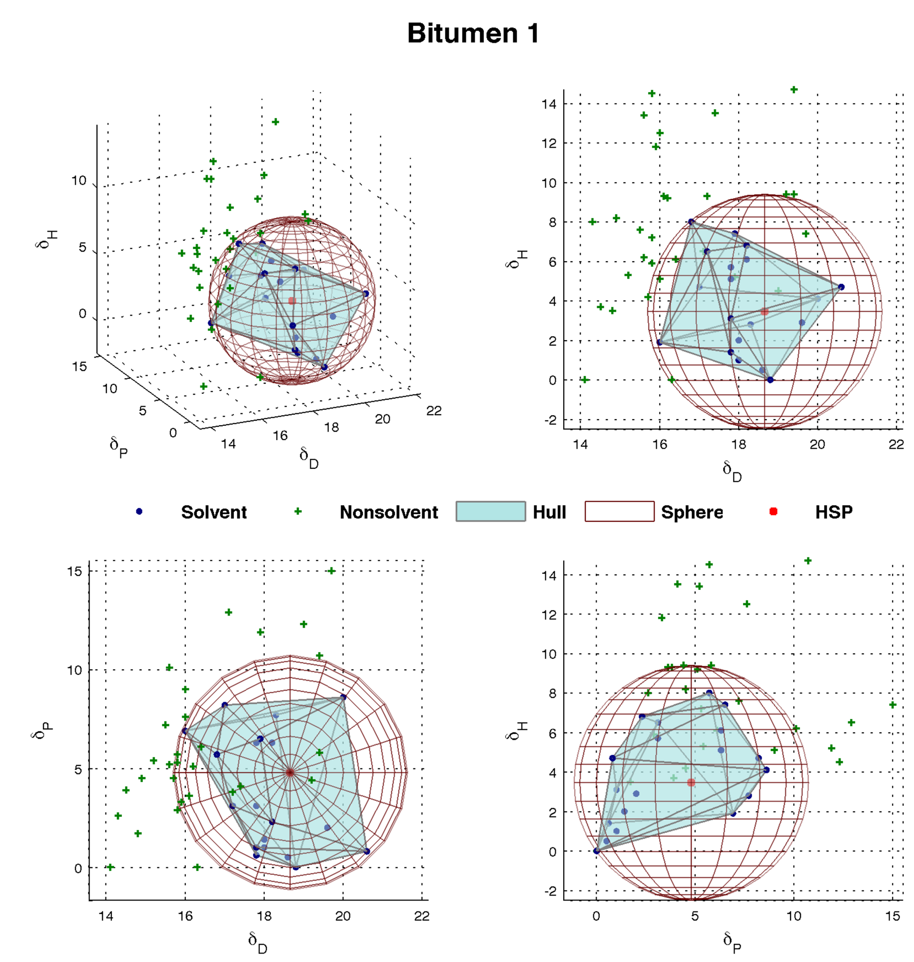
- Convex hull: smallest region in space that contains a given set of points and all line segments between those points
- Solubility region of polymer defined by the convex hull Q of all good solvents $x_1, \ldots, x_t$:

$$Q = \left\{ x \,\middle|\, x = \sum_{i=1}^{t} \lambda_i x_i,\ \sum_{i=1}^{t} \lambda_i = 1,\ \lambda_i \geq 0, i = 1, \ldots, t \right\}$$

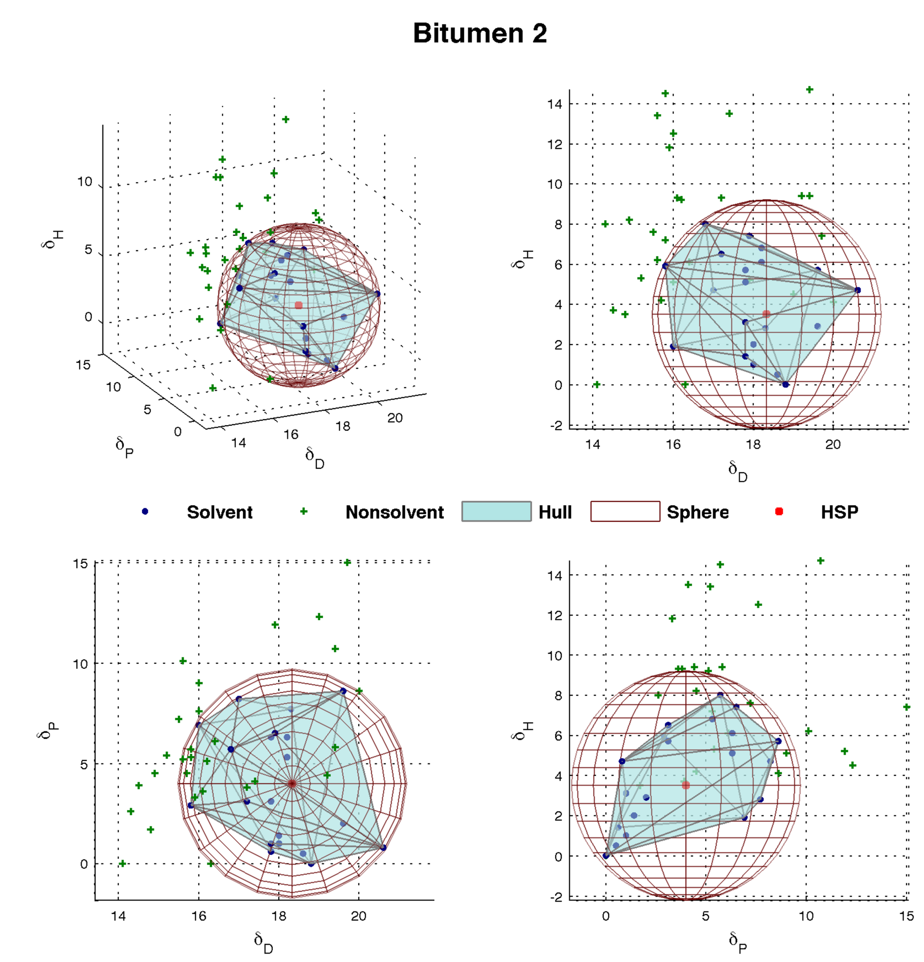
- Several candidate "centers" of the hull could serve as the Convex Solubility Parameter (CSP) of the polymer
- Determining if a solvent is inside the hull can be done by solving a linear feasibility problem:

$$\text{find } q$$
$$\text{such that } q = \sum_{i=1}^{t} \lambda_i x_i,\ \sum_{i=1}^{t} \lambda_i = 1,\ \lambda_i \geq 0,\ i = 1, \ldots, t$$

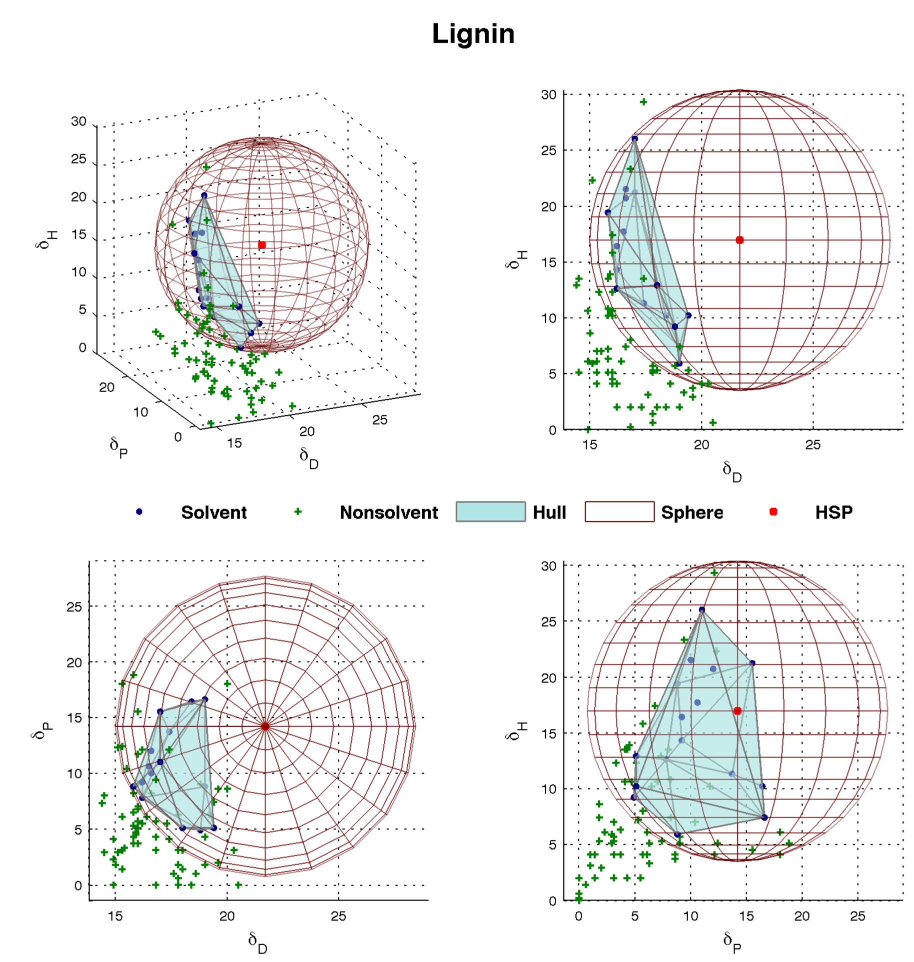
Bitumen 1



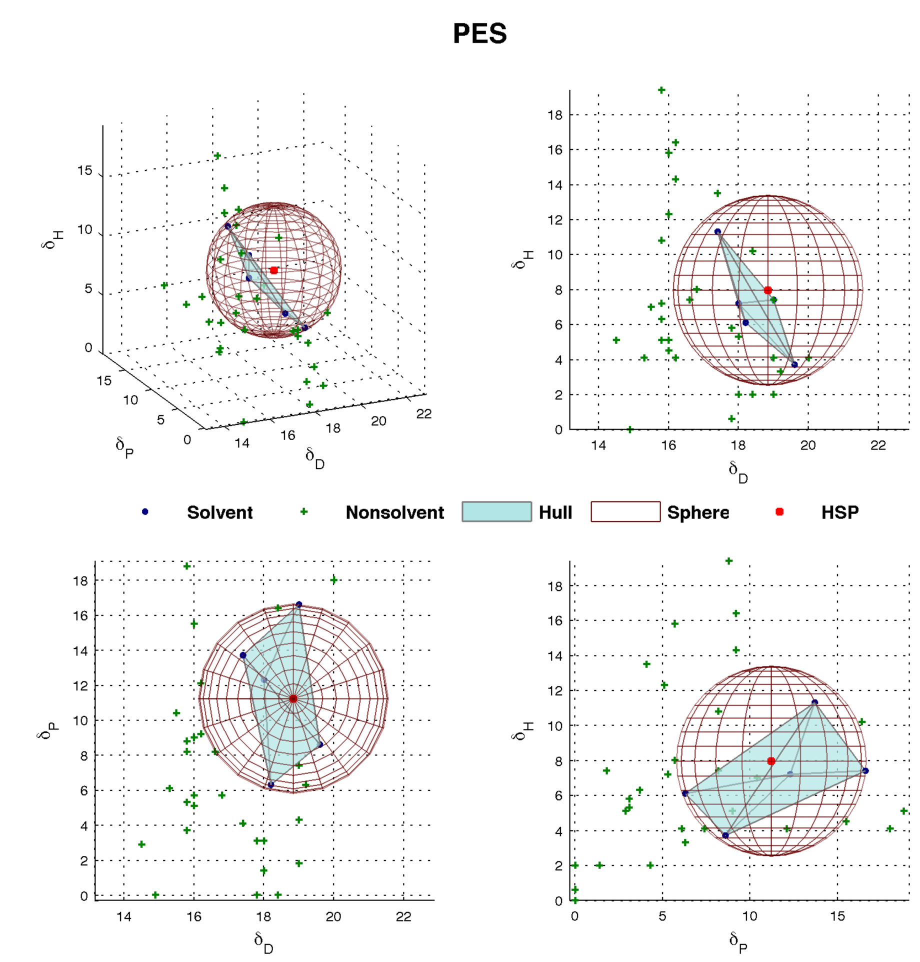
Bitumen 2



Lignin



Polyethersulfone



Methods for Computing the Convex Solubility Parameter

Method 1

Center of mass of the solubility region, treating the surface of the region with uniform density as an empty shell

Method 2

Center of mass of the solubility region, treating the region as a solid with uniform density

Method 3

Mean coordinates of all good solvents that lie on the boundary of the solubility region

Method 4

Mean coordinates of all good solvents on the boundary and within the solubility region

Method 5

Center of the largest sphere completely contained within the solubility region (known as the *Chebyshev center*)

Method 6

Midpoint of the parameter range of each of the good solvents

Method	Polyethersulfone	Bitumen 1	Bitumen 2	Lignin
Hansen	(18.84, 11.22, 7.95)	(18.66, 4.79, 3.45)	(18.33, 3.99, 3.49)	(21.71, 14.18, 16.93)
Method 1	(18.44, 11.53, 7.24)	(18.28, 4.29, 3.93)	(18.04, 4.26, 4.03)	(17.77, 11.00, 14.42)
Method 2	(18.41, 11.63, 7.25)	(18.27, 4.42, 4.00)	(17.98, 4.38, 4.15)	(17.70, 10.35, 14.32)
Method 3	(18.44, 11.50, 7.14)	(18.03, 4.28, 4.28)	(17.80, 4.33, 4.34)	(17.68, 10.24, 13.38)
Method 4	(18.44, 11.50, 7.14)	(18.13, 3.79, 3.93)	(17.99, 3.90, 4.11)	(17.38, 10.29, 14.81)
Method 5	(18.32, 12.16, 7.28)	(18.25, 5.65, 4.07)	(17.88, 4.24, 4.71)	(17.56, 8.11, 12.77)
Method 6	(18.50, 11.45, 7.50)	(18.30, 4.30, 4.00)	(18.20, 4.30, 4.00)	(17.60, 10.75, 15.95)

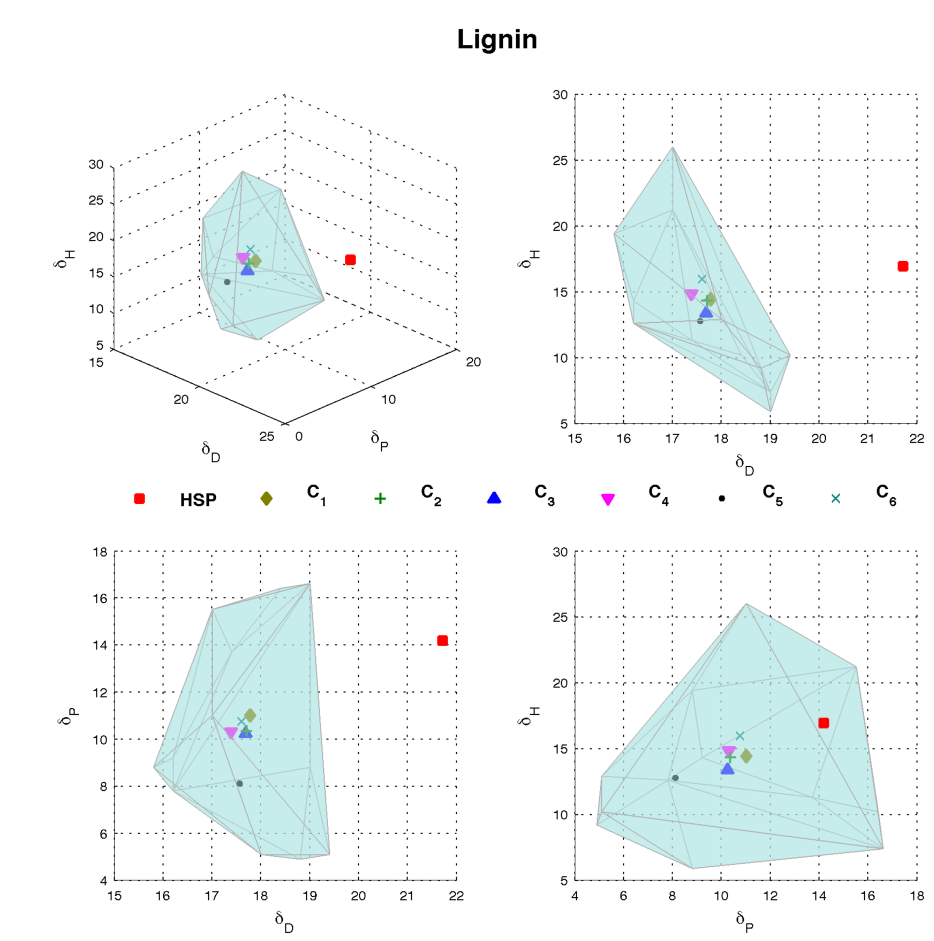
Advantages of the Convex Hull Approach

- All good solvents and additive combinations contained in solubility region
- No assumption of isotropy
- Always unique and reproducible
- Always physically reasonable
- Easily generalized to include more parameters
- Much smaller solubility region

Comparison of Solubility Region Volumes

Polymer	Hansen Sphere Volume	Solubility Region Volume	Hull/Sphere Volume Ratio
PES	333.47	9.02	0.027
Bitumen 1	438.95	94.85	0.216
Bitumen 2	389.91	98.75	0.253
Lignin	5095.95	191.04	0.037

Lignin CSP



Conclusion

Solubility region generated using convex hull of coordinates of good solvents in parameter space. A reasonable choice for Convex Solubility Parameter is the center of mass of the hull when treated as a solid of uniform density. These results are the product of an independent study course in Spring 2015 and have been submitted to the *Journal of Polymer Science Part B: Polymer Physics*.

References

[1] Hansen, C.M. Hansen Solubility Parameters: A User's Handbook, Second Edition, CRC Press, 2007.
[2] Vebber, G. C., Pranke, P., and Pereira, C. N. Calculating Hansen solubility parameters of polymers with genetic algorithms, Journal of Applied Polymer Science 131 (2014), 1097-4628.

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