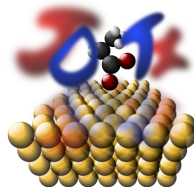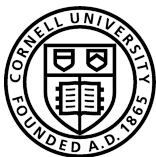# Nonlocal polarizable continuum models from joint density functional theory

Ravishankar Sundararaman   Kendra Letchworth-Weaver

Deniz Gunceler   Kathleen Schwarz   T.A. Arias

Department of Physics, Cornell University

June 14, 2013

Outline

- *Ab initio* studies of solvated systems
- Joint density functional theory (JDFT) overview
- Nonlocal polarizable continuum models from JDFT
- Demonstration: underpotential deposition of Cu on Pt(111)

Why study solvated systems?

- Technological applications
  - Electrochemical systems: fuel cell catalysts, battery materials (EMC^2, DOE)
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- Theory development
  - Constructing free energy functionals for liquids
  - Interactions between 'classical' liquids and quantum electrons
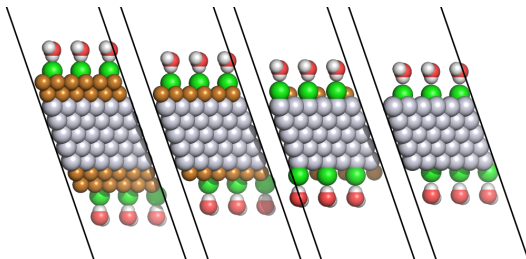
Solvent effects
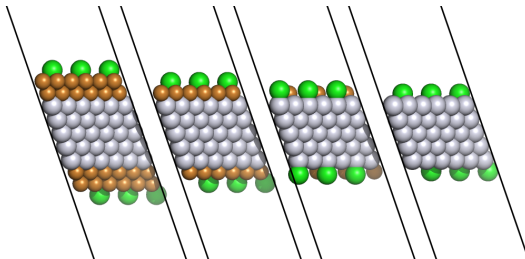
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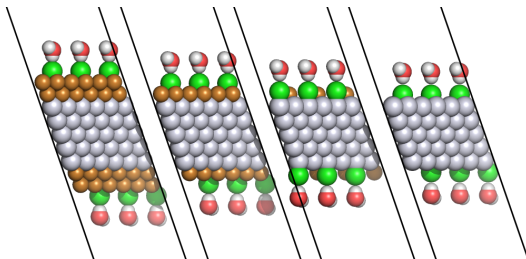
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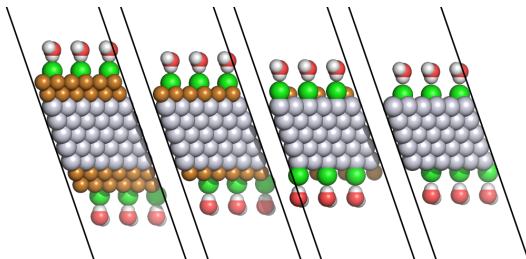
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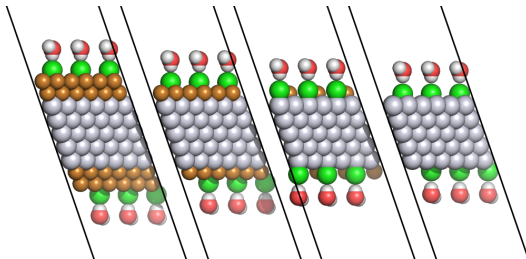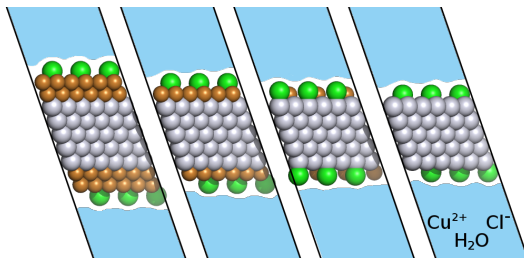
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Solvent effects

Cu²⁺ Cl⁻
H₂O

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- Single monolayer of water with hydrogen-bonded geometries chosen manually
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- Thermodynamic sampling with molecular dynamics significantly more expensive
- Additional complexity detracts from intuition towards the system of interest
- Capture and abstract away *equilibrium* effect of solvent

Joint density functional theory (JDFT)

- Exact variational principle after integrating out electrons of part of the system:

$$
\Phi = \min_{n, \{N_\alpha\}} \left[\Phi_{\text{JDFT}}[n, \{N_\alpha\}] + \int V \cdot n + \sum_\alpha \int V_\alpha \cdot N_\alpha \right]
$$

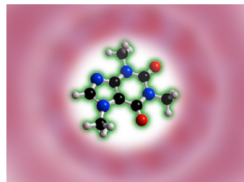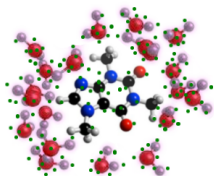S. A. Petrosyan et al, *Phys. Rev. B* **75**, 205105 (2007)

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- Decompose into physical pieces that can be approximated independently:

$$\Phi_{\text{JDFT}}[n, \{N_\alpha\}] = \underbrace{F_{\text{HKM}}[n]}_{\text{Electrons}} + \underbrace{\Phi_{\text{CDFT}}[\{N_\alpha\}]}_{\text{Liquid}} + \underbrace{\Delta\Phi[n, \{N_\alpha\}]}_{\text{Coupling}}$$

Approximation schemes

- Kohn-Sham electronic DFT with exact non-interacting energy

$$F_{HK}[n] \to F_{KS}[\{\phi_a\}] = \sum_a \int \frac{|\nabla \phi_a|^2}{2} + \int \frac{n(\vec{r})n(\vec{r}')}{2|\vec{r} - \vec{r}'|} + E_{XC}[n].$$

W. Kohn and L. Sham, *Phys. Rev.* **140**, A1133 (1965)

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Systematically improvable- can replace KS DFT with QMC:
K. Schwarz et al., *Phys. Rev. B* **85**, 201102(R) (2012)

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- Classical DFT with exact rigid-molecular ideal gas free energy

$$\Phi_{CDFT}[\{N_\alpha\}] \rightarrow \Phi_{CDFT}[\{p_\omega\}] = T \int p_\omega (\ln p_\omega - 1) + F_{ex}[\{N_\alpha\}]$$

in terms of orientation probability density $p_\omega(\vec{r})$

R. Sundararaman and T.A. Arias, *arXiv*:**1302.0026**

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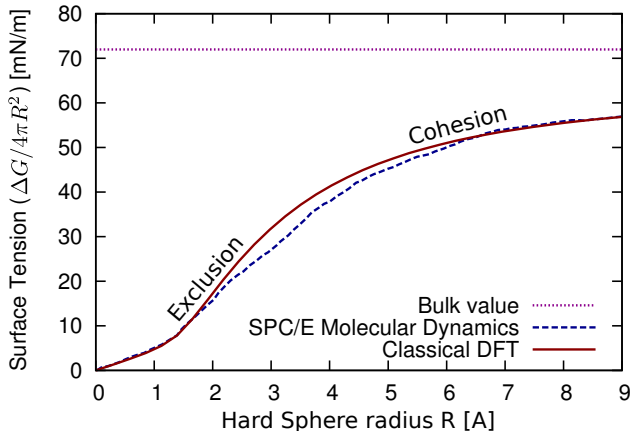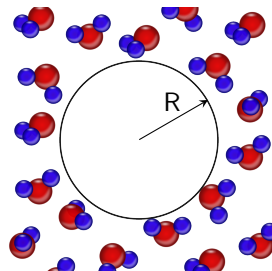
in terms of orientation probability density $p_\omega(\vec{r})$

- Density-only density functional approximation to fluid-electron interactions

$$\Delta\Phi[n, \{N_\alpha\}] \approx \underbrace{\int \frac{\rho_{el}\rho_{lq}}{|\vec{r} - \vec{r}'|}}_{\text{Coulomb}} + \underbrace{E_{TXC}[n + n_{lq}] - E_{TXC}[n] - E_{TXC}[n_{lq}]}_{\text{Kinetic−Exchange−Correlation}} - \underbrace{\int \frac{C_{6i\alpha}N_\alpha(\vec{r})}{f|\vec{R}_i - \vec{r}|^6}}_{\text{Dispersion}}$$
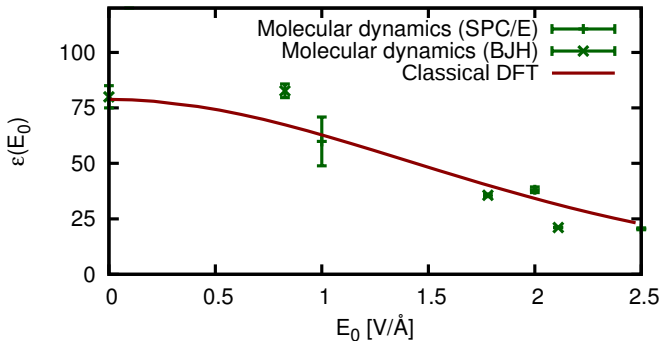
K. L.-Weaver, R. Sundararaman and T.A. Arias, (under preparation)
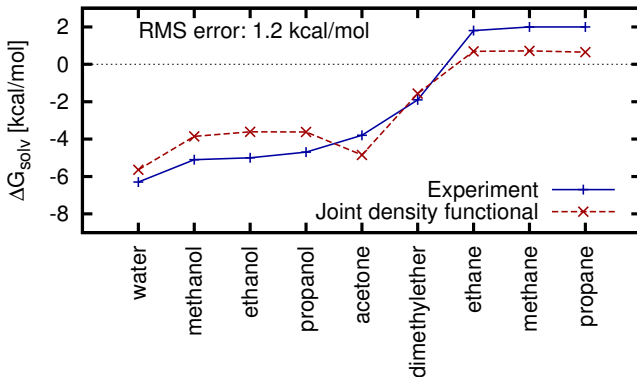
Hydration energy of microscopic cavities

SPC/E data: K. Ding et al *Phys Rev Lett* **59** 1698 (1987)
R. Sundararaman and T.A. Arias, *arXiv*:**1302.0026**

Nonlinear dielectric response

MD data: I.-C. Yeh and M. Berkowitz, *J. Chem. Phys.* **110**, 7935 (1999)

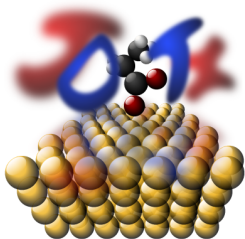R. Sundararaman and T.A. Arias, *arXiv*:**1302.0026**

Solvation energy of molecules

Single fit parameter: dispersion prefactor 's_6'

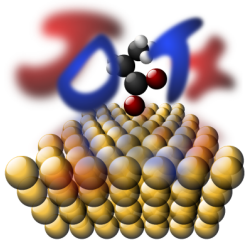K. L.-Weaver, R. Sundararaman and T.A. Arias, (under preparation)

Software for joint density functional theory

- Direct free energy minimization for stable convergence
- Plane-wave electronic DFT in:
  - Vacuum
  - Polarizable continua
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- DFT++ algebraic formulation: S. Ismail-Beigi and T.A. Arias, *Comp. Phys. Comm.* **128**, 1 (2000)
- Readable, efficient C++11 code
- Supports nVidia GPUs using CUDA^{TM}
- Intel MIC support under developement

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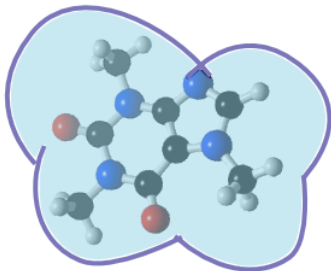- **Intuition:** A simpler model would, by construction, disentangle physical effects and provide insight into the results of the more complex model
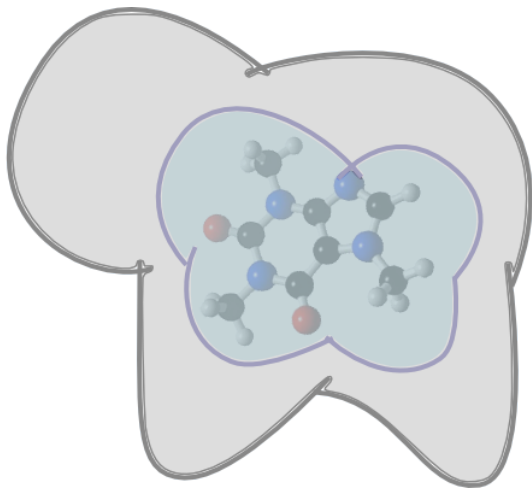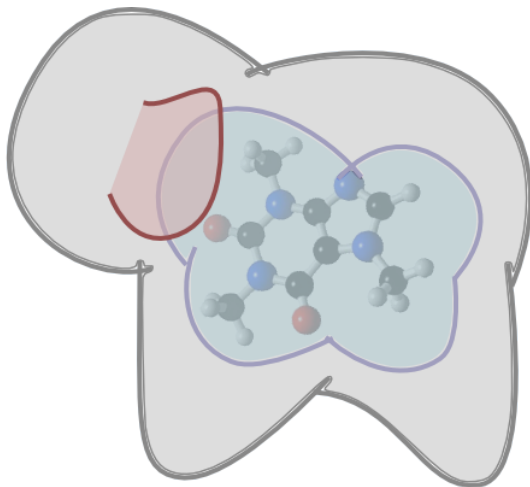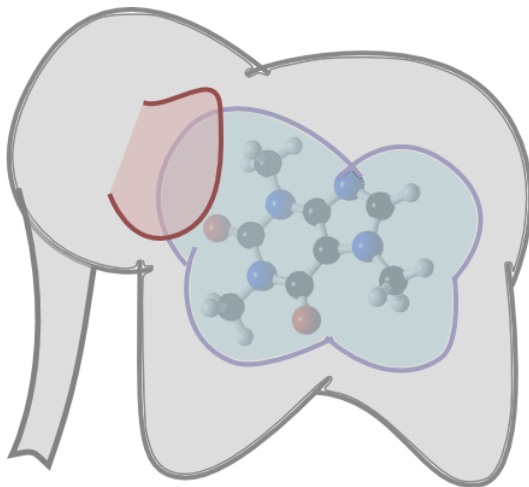
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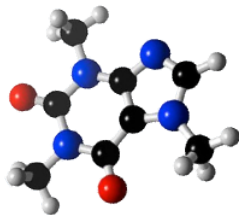
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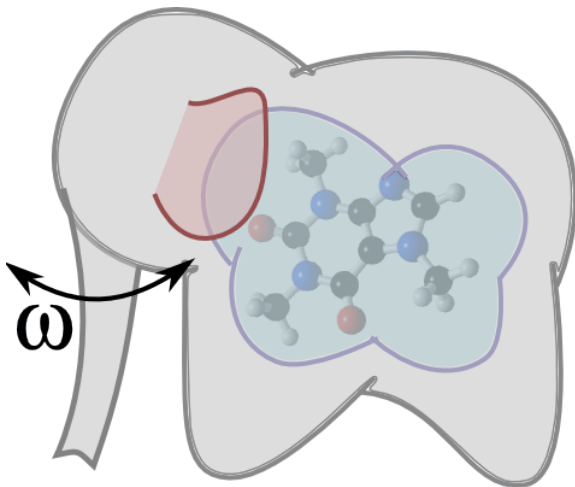
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- Uncontrolled extrapolation when applying to a solute drastically different from fit set

Spherically-averaged liquid susceptibility ansatz (SaLSA)

$$\Phi_{\mathsf{JDFT}}[n, \{N_\alpha\}] = \underbrace{F_{\mathsf{HKM}}[n]}_{\text{Electrons}} + \underbrace{\Phi_{\mathsf{CDFT}}[\{N_\alpha\}]}_{\text{Liquid}} + \underbrace{\Delta\Phi[n, \{N_\alpha\}]}_{\text{Coupling}}$$

Assumptions:

- Cavity density determined from overlap of solute and solvent electron densities
- Solvent molecules oriented randomly in the absence of electrostatics

Consequences:

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Consequences:

- **Repulsion** ← Kinetic-exchange-correlation terms in coupling
- **Dispersion** ← Pair potential vdW terms in coupling
- **Cavitation** ← Exclusion of classical density functional fluid
- **Electrostatics** ← Linear rotational and polarization response

R. Sundararaman, K. L.-Weaver, K. Schwarz and T.A. Arias, (under preparation)

Nonlocal electrostatic response

- Solvent molecule with charge density $\rho_{\mathsf{mol}}(\vec{r})$ and expand electronic and vibrational susceptibility in eigenbasis (obtain from DFT/DFPT)
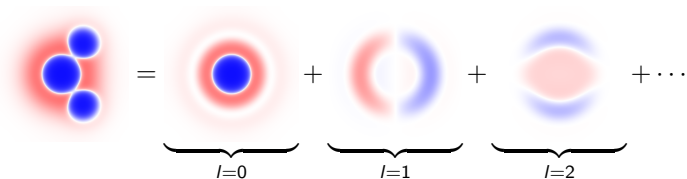
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- Decompose each ρ into angular momentum channels

$$\underbrace{}_{l=0} \qquad \underbrace{}_{l=1} \qquad \underbrace{}_{l=2}$$

Nonlocal electrostatic response

- Susceptibility of fluid of such molecules distributed as $N(\vec{r})$ is exactly

$$\chi(\vec{G}, \vec{G}') = -\tilde{N}(\vec{G} - \vec{G}') \sum_l \frac{P_l(\hat{G} \cdot \hat{G}')}{4\pi} \sum_m \left(\begin{array}{c} \frac{1}{T} \tilde{\rho}_{mol}^{lm}(G) \tilde{\rho}_{mol}^{lm*}(G') \\ + \sum_i X_i \tilde{\rho}_i^{lm}(G) \tilde{\rho}_i^{lm*}(G') \end{array} \right)$$

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- At $l = 1$ with rotations alone, computational costs of SaLSA and PCM are identical!

Typical cavities and bound charge (in liquid water)
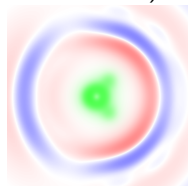
JDFT
(density
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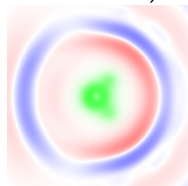
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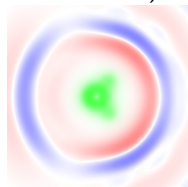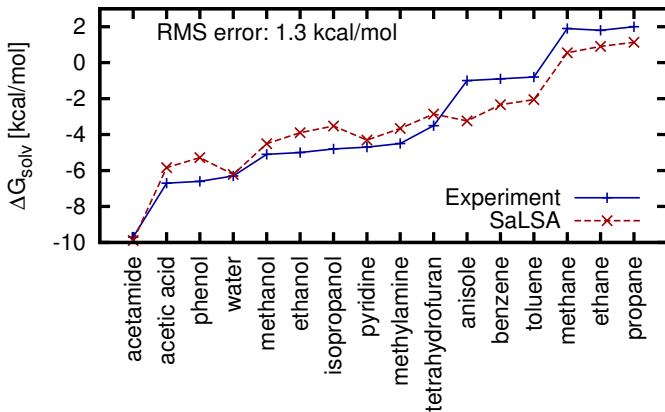# Typical cavities and bound charge (in liquid water)

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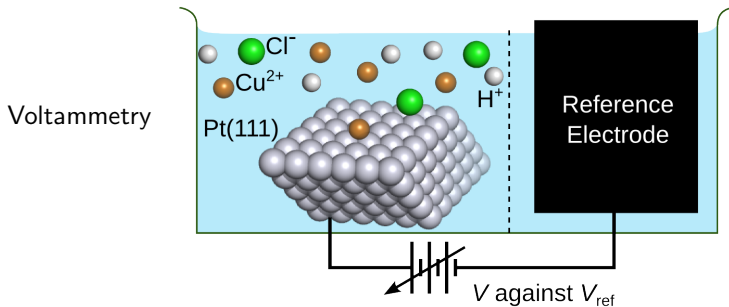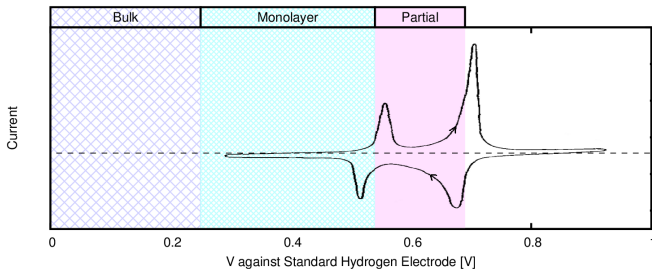SaLSA
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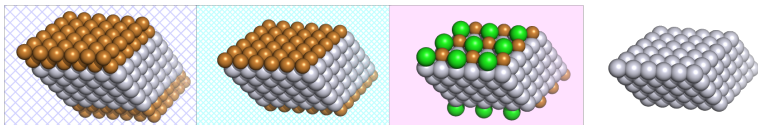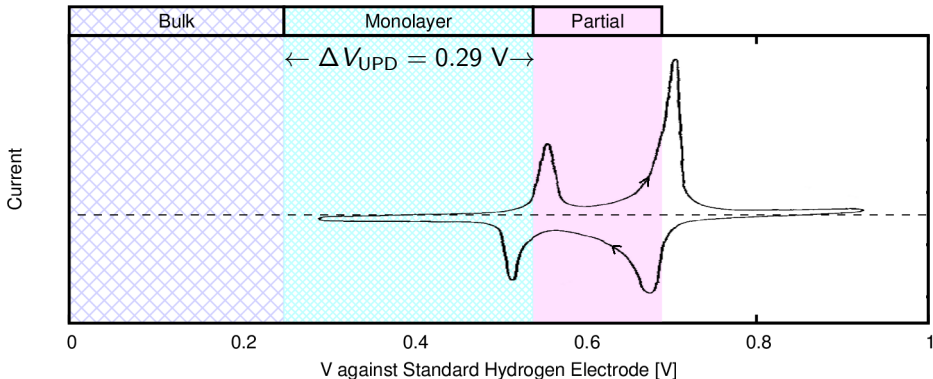
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Solvation energies

Single fit parameter: dispersion prefactor 's_6'

Under-potential deposition: Cu/Pt(111) [Cl$^-$]
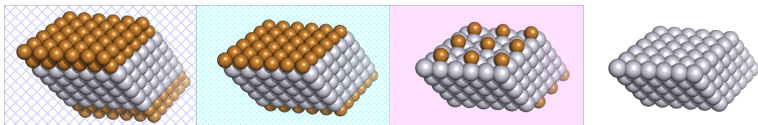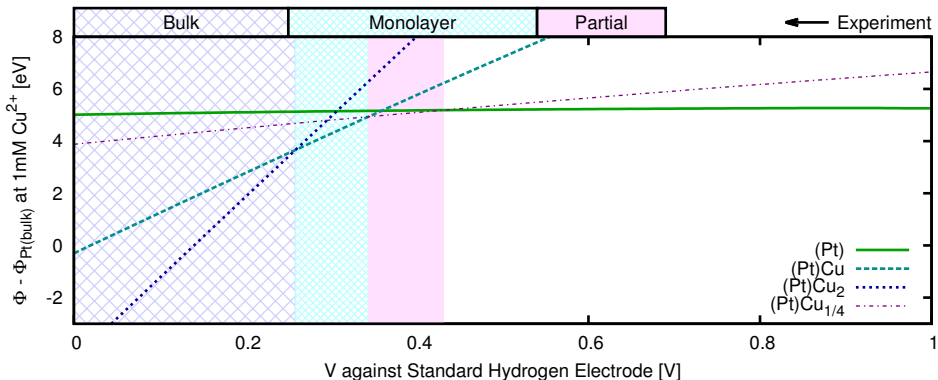

Voltammetry

Under-potential deposition: Cu/Pt(111) [Cl$^-$]

Based on ex-situ LEED from N.M. Markovik et al, *Surf. Sci.* **335**, 91 (1995)
and in-situ EXAFS from Y. Soldo et al, *Electrochimica Acta* **47**, 3081 (2002)
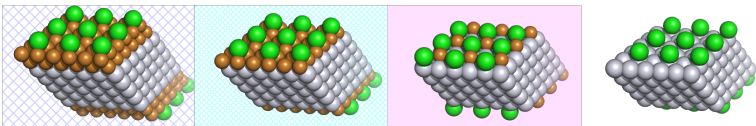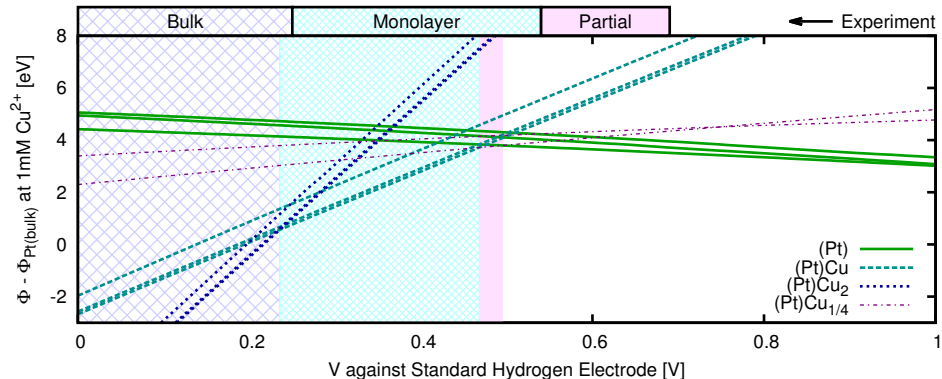
Explicit Pt and Cu, implicit solvent

Qualitative agreement, need explicit anions

Explicit Pt, Cu and Cl, implicit solvent

Partial monolayer susceptible to additional adsorbants (protons?)

Outlook

- JDFT: efficient description of electronic systems in liquids
- Scope to develop more accurate functionals for liquids and coupling
- Obtain efficient and minimally empirical contiuum models as limit of JDFT
- Explore complex electrochemical systems by specifying atomic positions only of relevant subsystems

Thank you for your attention!

Acknowledgements:
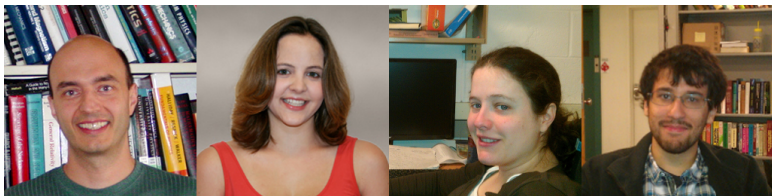
Tomas Arias   Kendra L.-Weaver   Katie Schwarz   Deniz Gunceler

Iso-density-product cavity determination

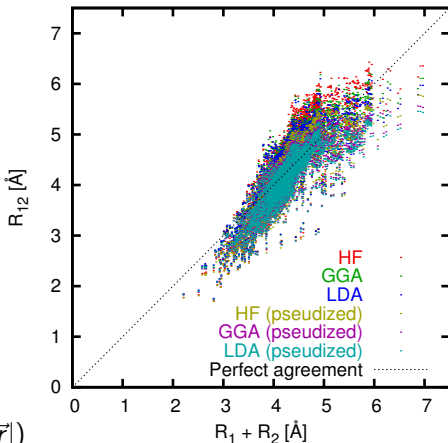- Correlate overlap of atom electron densities with vdW radii

- Fit n_c to minimize discrepancy between $R_1 + R_2$ and R_{12} defined by

$$\int d\vec{r}\, n_1(\vec{r}) n_2(\vec{r} + R_{12}\hat{e}_z) = n_c$$

- Best fit $n_c = 1.2 \times 10^{-3}$ insensitive to electronic structure method.

- Analogously determine cavity from solute *and* spherically-averaged solvent molecule electron denisties:

$$s(\vec{r}) = \frac{1}{2}\,\text{erfc}\,\log\frac{\int d\vec{r}'\, n(\vec{r}') n_{\text{mol}}(|\vec{r}' - \vec{r}|)}{n_c}$$

Scatter plot with axes $R_1 + R_2$ [Å] (horizontal, 0 to 7) and R_{12} [Å] (vertical, 0 to 7). Legend: HF, GGA, LDA, HF (pseudized), GGA (pseudized), LDA (pseudized), Perfect agreement.

Weighted density cavitation energy

- Measure neighbour occupancy with $\bar{s} = \frac{\delta(r - R_{\text{vdw}})}{4\pi R_{\text{vdw}}^2} * s(\vec{r})$
- Constrain weighted density approximation to limits:

$$\Phi_{\text{cav}}[s] = N_{\text{bulk}} T \int \bar{s}(1 - \bar{s})\left(\bar{s} + \gamma(1 - \bar{s}) + C\bar{s}(1 - \bar{s})\right)$$

where $\gamma \equiv \ln \dfrac{p_{\text{vap}}}{N_{\text{bulk}} T} - 1$

$$C \equiv \frac{\sigma_{\text{bulk}}}{R_{\text{vdw}} N_{\text{bulk}} T} + \frac{1 + \gamma}{6}$$

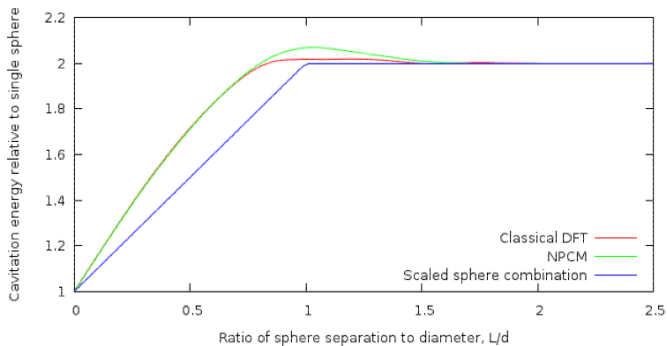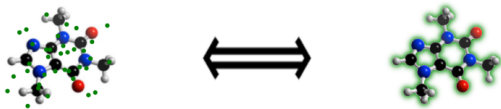# Cavity model vs classical DFT
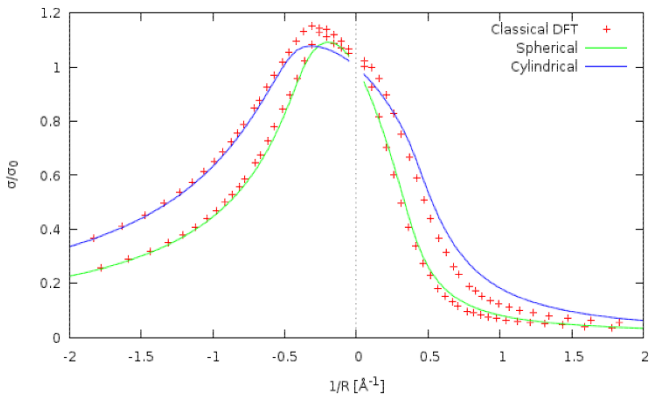
Size consistency

Density functional theory

- Ground state energy of many-electron system from ground state density $n(\vec{r})$ alone

$$E = \min_{\psi}\langle\psi|(\hat{H} + V)|\psi\rangle = \min_{n}\left[F_{\text{HK}}[n] + \int V \cdot n\right]$$

P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964)

Density functional theory

- Helmholtz free energy of many-electron system from equilibrium density $n(\vec{r})$ alone

$$A = \min_{\hat{\rho}} \mathrm{Tr}(\hat{H} + V)\hat{\rho} = \min_{n} \left[F_{\mathsf{HKM}}[n] + \int V \cdot n \right]$$

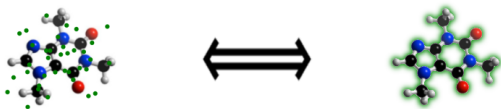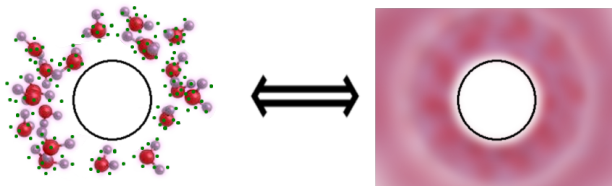N.D. Mermin, *Phys. Rev.* **137**, A1441 (1965)

Density functional theory

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$$A = \min_{\hat{\rho}} \text{Tr}(\hat{H} + V)\hat{\rho} = \min_n \left[F_{\text{HKM}}[n] + \int V \cdot n \right]$$

- Grand free energy of many-body nuclear system from equilibrium densities $\{N_\alpha(\vec{r})\}$ alone

$$\Phi = \min_{\hat{P}} \text{Tr}(\hat{H} + \vec{V})\hat{P} = \min_{\{N_\alpha\}} \left[\Phi_{\text{CDFT}}[\{N_\alpha\}] + \sum_\alpha \int V_\alpha \cdot N_\alpha \right]$$

'Classical' DFT is fully quantum, not even Born-Oppenheimer approximation!

Free energy functionals for real liquids

- Employ exact free energy of non-interacting classical fluid (analogous to Kohn-Sham) in terms of orientation probability density p_ω

$$\Phi_{\text{CDFT}}[\{N_\alpha\}] \rightarrow T \int p_\omega(\ln p_\omega - 1) \qquad \text{Non-interacting free energy}$$
$$+$$

R. Sundararaman and T.A. Arias, arXiv:**1302.0026**

R. Sundararaman, K. L.-Weaver and T.A. Arias, J. Chem. Phys **137**, 044107 (2012)

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Fundamental measure theory: Y. Rosenfeld, *Phys. Rev. Lett.* **63**, 980 (1989)

Free energy functionals for real liquids

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$$
\begin{aligned}
\Phi_{\text{CDFT}}[\{N_\alpha\}] \to \; & T \int p_\omega (\ln p_\omega - 1) && \text{Non-interacting free energy} \\
& + \Phi_{\text{HS}}[N] && \text{Hard-sphere entropy corrections} \\
& + \int N_\alpha Z_\alpha \cdot \frac{1}{2|\vec{r} - \vec{r}'|} \cdot N_\beta Z_\beta && \text{Mean-field Coulomb interactions} \\
& +
\end{aligned}
$$

R. Sundararaman and T.A. Arias, *arXiv*:**1302.0026**

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$$+ \int N A_{\text{ex}}(w * N) \qquad \text{Weighted density excess functional}$$

$$+$$

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& + \int N A_{\text{ex}}(w * N) && \text{Weighted density excess functional} \\
& + \alpha \int P^2 && \text{Local polarization correlations}
\end{aligned}
$$

R. Sundararaman and T.A. Arias, *arXiv*:**1302.0026**

R. Sundararaman, K. L.-Weaver and T.A. Arias, *J. Chem. Phys* **137**, 044107 (2012)
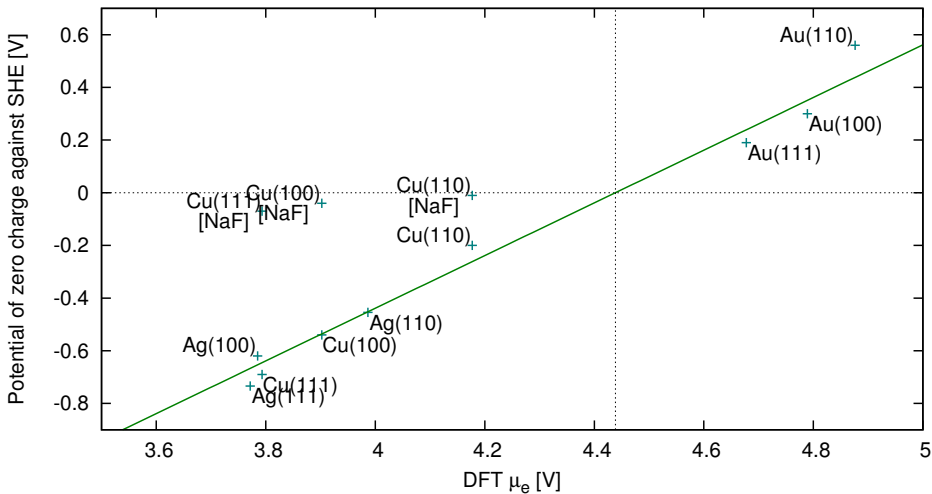
Radial distribution around hard spheres
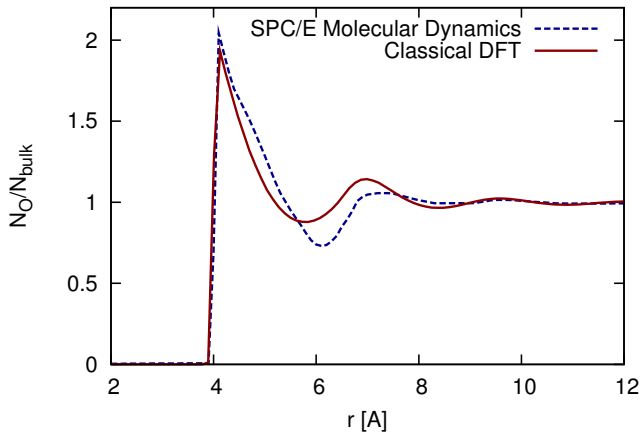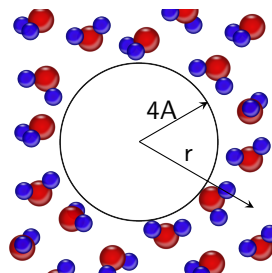
SPC/E data: K. Ding et al *Phys Rev Lett* **59** 1698 (1987)
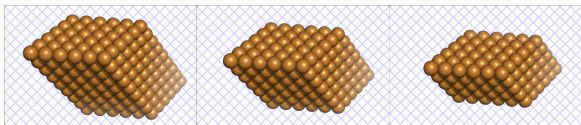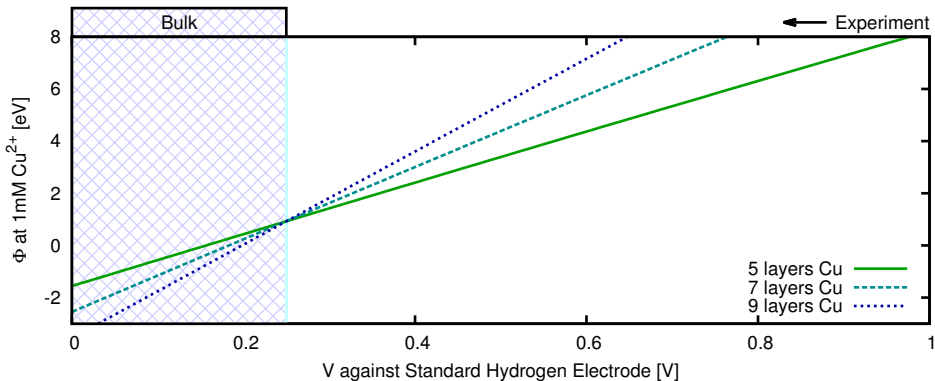R. Sundararaman and T.A. Arias, *arXiv*:**1302.0026**
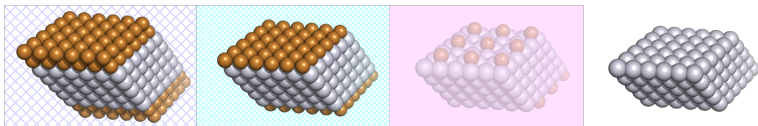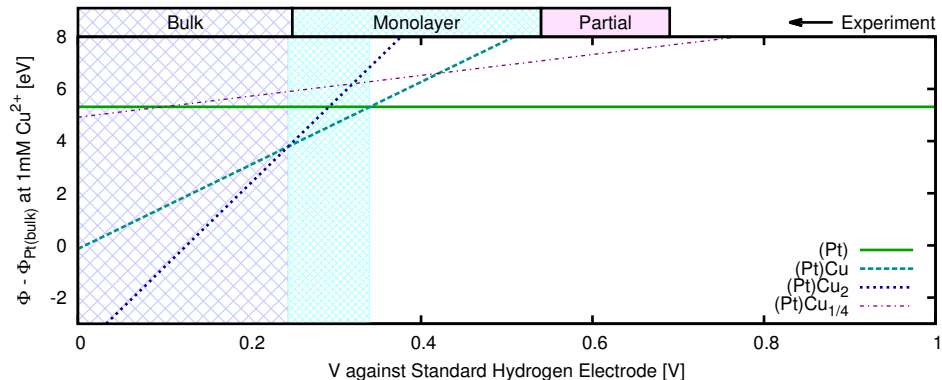
Voltage reference calibration

Best fit $\Rightarrow \mu_{SHE} = (-4.44 \pm 0.02)$ V

Cu^{2+} chemical potential calibration
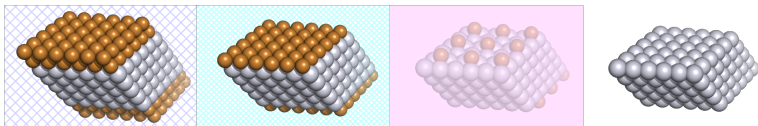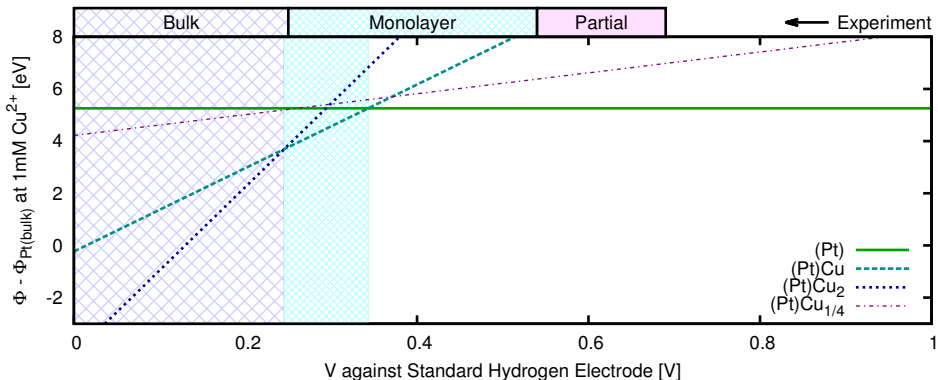

Relevant free energy: $\Phi(\mu_e) = A(N_e) - \mu_e N_e - \mu_{Cu^{2+}} N_{Cu} - \mu_{Cl^-} N_{Cl_-}$

Vacuum DFT predictions

Linearized $\Phi(\mu_e) = A(N_e^0) - \mu_e N_e^0$ assumes fixed N_e

Neutral PCM predictions

Linearized $\Phi(\mu_e) = A(N_e^0) - \mu_e N_e^0$ assumes fixed N_e

Polarizable continuum models

- Threshold electron density at n_c to define a cavity in the fluid (described by shape function $s(\vec{r}) = 0$ in the cavity and 1 in the fluid)

A. Andreussi, I. Dabo and N. Marzari, *J. Chem. Phys.* **136**, 064102 (2012)

Polarizable continuum models

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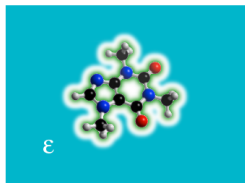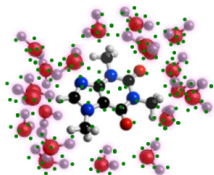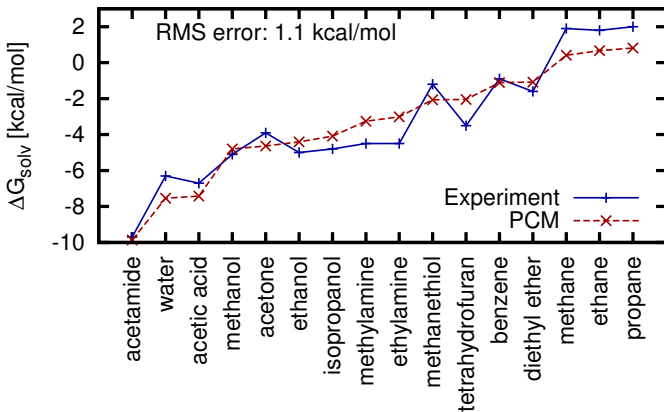
Polarizable continuum models

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- Approximate effect of fluid by electrostatic response of nonuniform dielectric with $\epsilon(\vec{r}) = 1 + (\epsilon_b - 1)s(\vec{r})$
- Add empirical corrections for subdominant contributions (dispersion, cavity formation etc.)

$$\Phi_{\text{PCM}}[n] = \underbrace{F_{\text{HKM}}[n]}_{\text{Electrons}} + \underbrace{\frac{1}{2} \int \rho_{\text{el}} \left(\left(\hat{K}^{-1} - \hat{\chi} \right)^{-1} - \hat{K} \right) \rho_{\text{el}}}_{\text{Dielectric response}} + \underbrace{\sigma_{\text{eff}} \int \nabla s}_{\text{Cavity tension}}$$

A. Andreussi, I. Dabo and N. Marzari, *J. Chem. Phys.* **136**, 064102 (2012)

Parameter fit: n_c and σ_{eff} to solvation energies

Nonlinear PCM free energy functional

- Electrostatic contribution to the free energy is

$$\Phi_\epsilon = \int T N_{\mathsf{mol}} s(\vec{r}) \left[\varepsilon^2 \left(f(\varepsilon) - \frac{\alpha}{2} f^2(\varepsilon) + \frac{X}{2}(1 - \alpha f(\varepsilon))^2 \right) - \log \frac{\sinh\varepsilon}{\varepsilon} \right]$$
$$+ \int \frac{\rho_{\mathsf{lq}}(\rho_{\mathsf{el}} + \rho_{\mathsf{lq}}/2)}{|\vec{r} - \vec{r}'|}$$

where

$$\rho_\epsilon(\vec{r}) \equiv -\vec{\nabla} \cdot [p_{\mathsf{mol}} N_{\mathsf{mol}} s(\vec{r}) \vec{\varepsilon}(f(\varepsilon) + X(1 - \alpha f(\varepsilon)))]$$

$$f(\varepsilon) \equiv (\varepsilon \coth \varepsilon - 1)/\varepsilon^2$$

$$X = \frac{T(\epsilon_\infty - 1)}{4\pi N_{\mathsf{mol}} p_{\mathsf{mol}}^2}$$

$$\alpha = 3 - \frac{4\pi N_{\mathsf{mol}} p_{\mathsf{mol}}^2}{T(\epsilon_b - \epsilon_\infty)}$$

D. Gunceler, K. L.-Weaver, R. Sundararaman et al., *arXiv*:**1306.1889**