Role of angular orientation of dipoles on work function during Caesium deposition on a metal surface - a Phenomenological Model

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Outline

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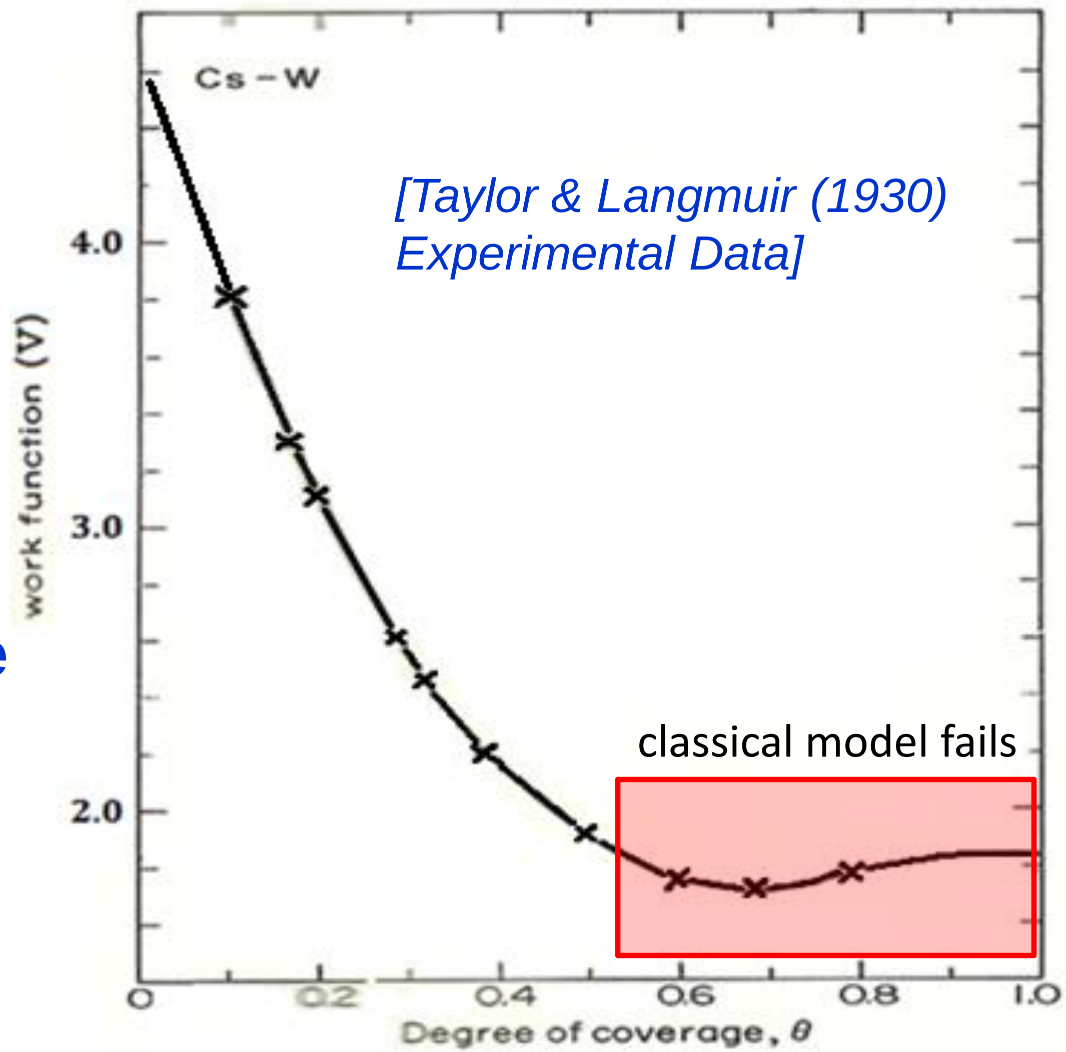
Motivation

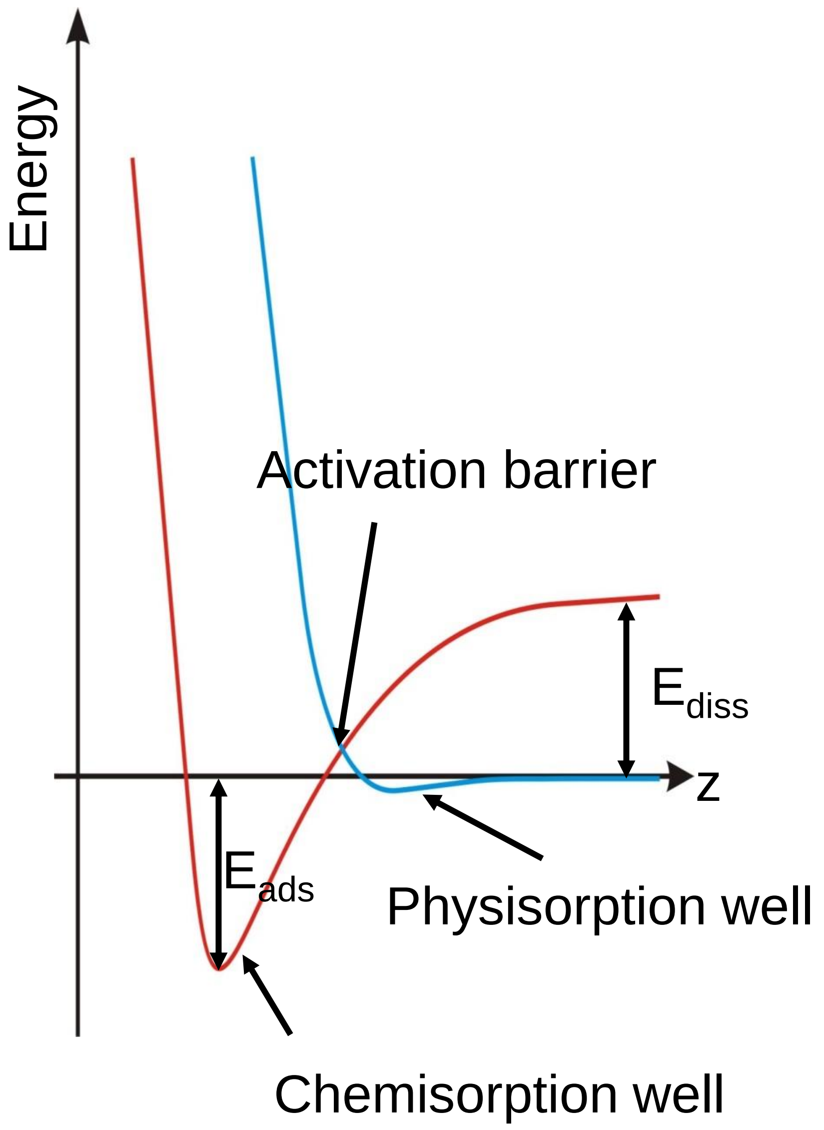
- **Simple classical model based on point dipole model** explains the experimental curve up to 0.5 coverage.
- QM Density Functional Theory able to explain complete experimental curve.
- **Can improved classical model explain the whole curve ?**
- *Angular rotation of point dipoles during higher coverage may have the answer.*



Adsorption

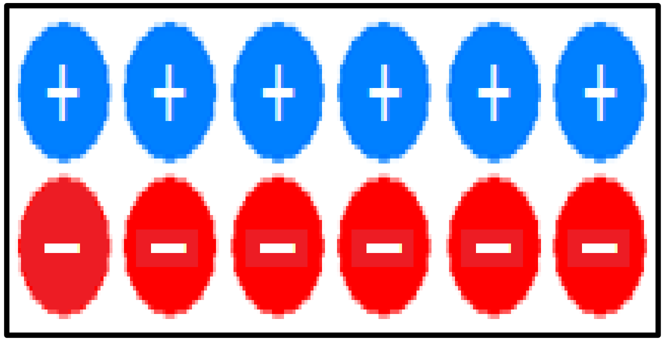
- **Physisorption:**
  - Heat of adsorption is low as weak Vander Wall's forces of attraction are involved.
  - **Multilayer adsorption.**
  - **Weakly bounded**

- **Chemisorption**:
  - High heat of adsorption as chemical bonds are formed.
  - **Monolayer adsorption**.
  - **Stronger bond**.



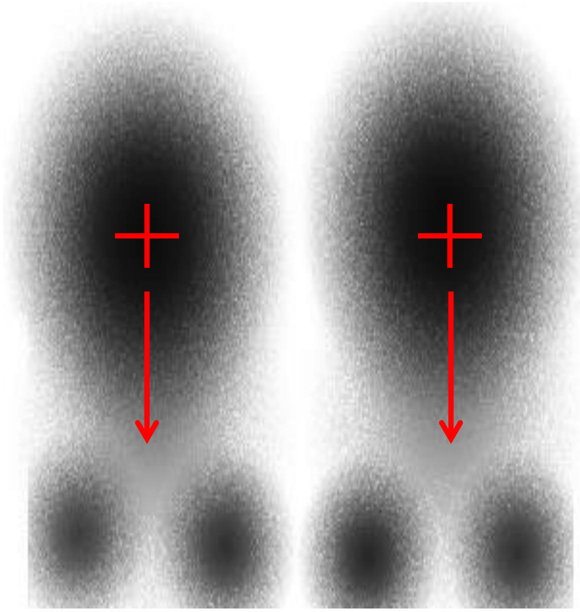
Work Function Change during Caseation

- Cs atom is approximately **twice as big as tungsten atom.**
- Cs deposition on tungsten is a **strong chemisorption process**.
- Cs adatoms forms an **electric double layer** (charge) with net positive charge outward.
- Cs adsorption on tungsten is an exothermic process.
- Cs adsorption **affects both work function** and **heat of adsorption** of bare substrate.



Surface dipoles (electric double layer) that lowers the work function

[Sharon Chou poster (2012)]



Possible distortion of electron cloud of Cs atom *[M. Prutton, Introduction to Surface physics.]*

Classical point dipole model

$$\boldsymbol{\Delta\phi = 4\pi e \sigma_1 \theta \frac{M_0}{[1+k]}}$$

Where,

- **$\Delta\phi$ is the change in substrate work function**
- σ_1 is the number of adatoms per unit area in one complete monolayer
- **Θ is the fractional monolayer coverage**
- M_0 is the initial dipole moment
- $k = \frac{9\alpha\theta}{a_1^3}$, α denotes the effective polarizability and a_1 is the distance between the dipoles at $\Theta = 1$

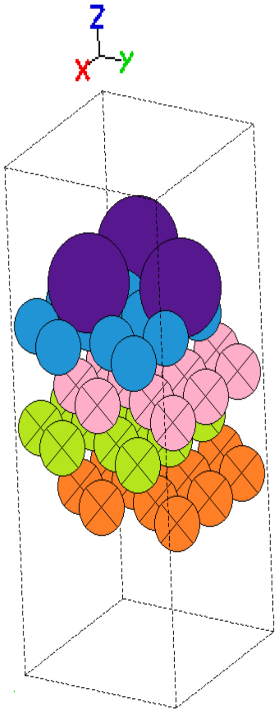
- The existing classical point dipole model is based on 2-D square lattice of parallel point dipoles with axis perpendicular to the line joining them. *[A. R. Miller, Proc. Cambridge philos. Soc. 42, 292 (1946)]*

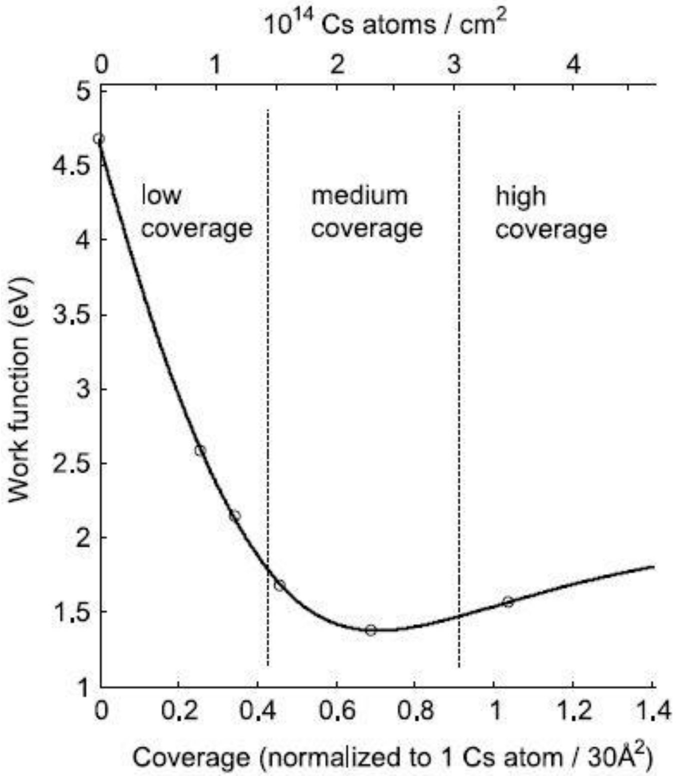
- The Classical point dipole model deviates at high coverage for Cs/W. Why?

Density Functional Theory Approach

$$\phi = \phi_{Vacuum} - E_{Fermi}$$

- DFT solves the Kohn-Sham approximation of TISE.
- DFT works in terms of electron density $n(r)$.
- Ground state energy $E\big(n(r)\big)$ is a functional of electron density.
- Can calculate work function from $\mathrm{n}(r)$ and matches experimental curve.





[Sharon Chou et. al., J. Phys.: Condense. Matter 24 (2012) 445007]

Model for Cs over layer on W[110]

- Wood's notation:

Low coverage

$\theta = 0.25$

$p(2 \times 2)$

Medium coverage

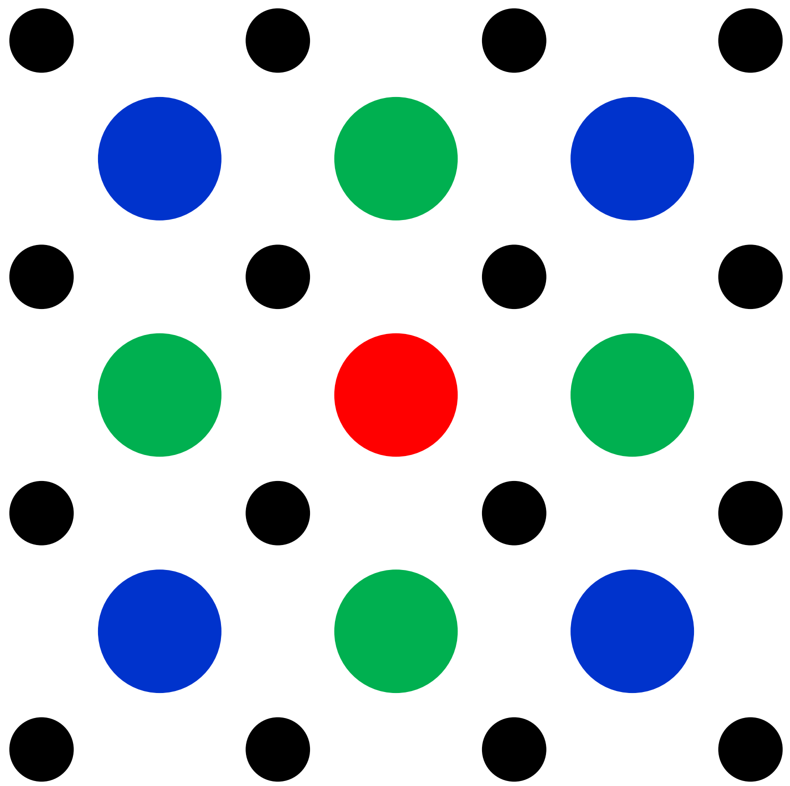
$\theta = 0.5$

$c(2 \times 2)$

High coverage

$\theta = 1$

2-D square array



Cs over layer on W [110]

Role of angular orientation of dipoles: a phenomenological model

$$\Delta\phi = 4\pi e\sigma_1\theta\frac{M_0}{[1+k]}\cos(\beta)$$

- Where, $cos(\beta)$ is the effective Angular Orientation Factor (AOF).

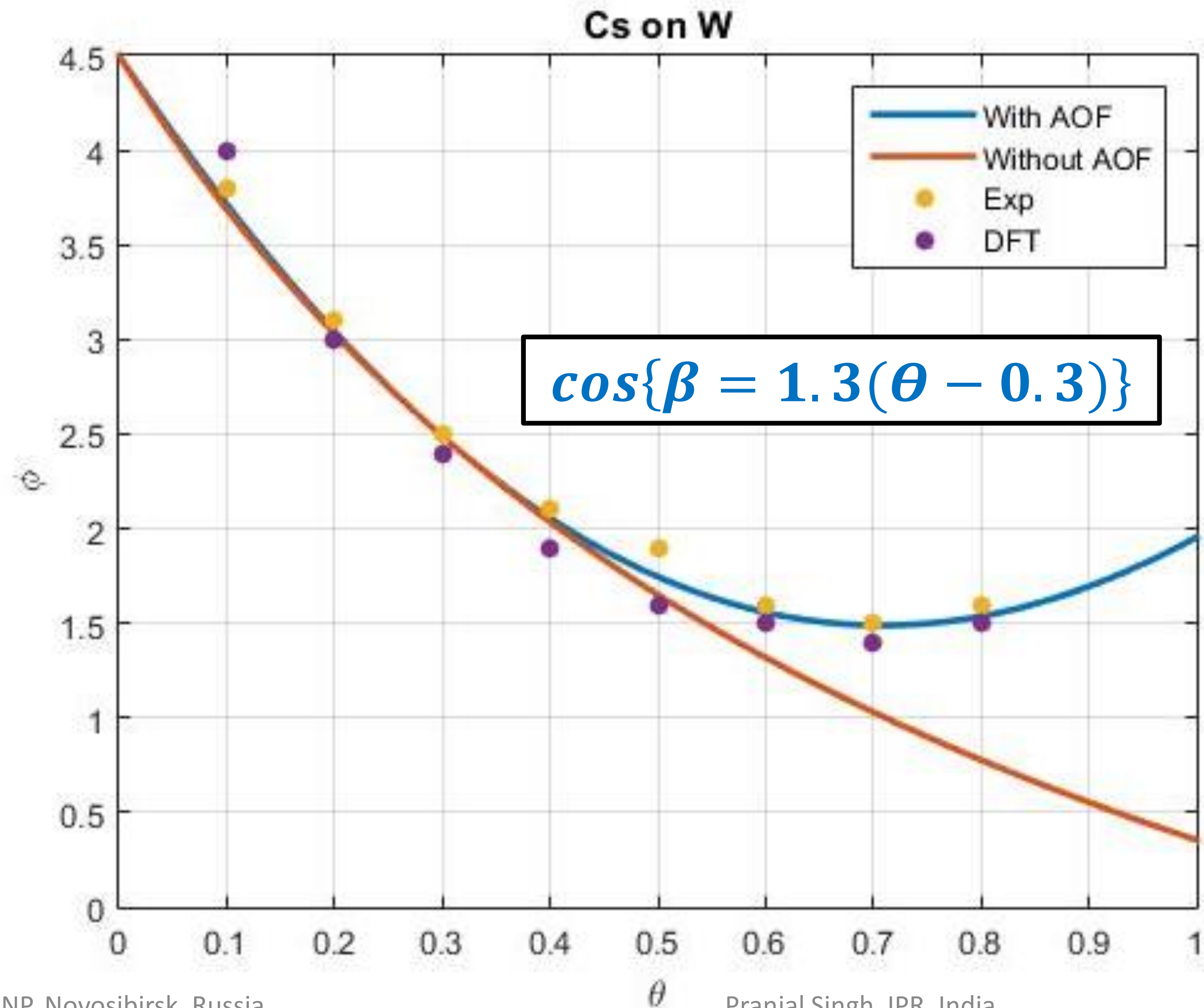
$$\beta = c(\theta-\theta_0);\quad 0\le\theta\le 1$$

- **At low coverage of adatoms, surface dipoles are non-interacting** owing to which they tend to form **an array of mutually parallel dipoles and perpendicular to the line joining them**.

- However, **at high coverage in addition to the point depolarization we propose that the self-interaction of dipoles may lead to change in the orientation** of the dipoles with respect to surface normal.

- The **nature of orientation follows a fitting equation which is function of coverage fraction** θ and **needs deeper investigation to understand the relationship.**

Dependence of work function on dipole orientation



$$cos\{\beta = 1.3(\theta - 0.3)\}$$

Summary

- **Phenomenological model** is an extension of existing electric dipole based classical model, which able to explain full work function variation experimental curve as a function of Cs monolayer coverage.
- With increasing monolayer fraction coverage, **repulsive interaction between dipoles increases, which lead to the orientation factor in the Phenomenological model** .
- A fitting equation as a function of Cs monolayer coverage is identified.
- **Further investigation is needed to verify our conjecture and to connect with the physical picture of electronic structures of Cs and W within the electric dipole layer between interacting dipoles.**

Thank You!