



# Role of Local Fields in Inter-ionic Interactions on Self-Diffusion of Liquid 3d Transition Metals: A Linear Trajectory Approach

Amitav Das, R. C. Ghosh

Department of Physics, University of Dhaka

National Conference on Physics - 2025, Organized by Bangladesh Physical Society



Scan for PDF

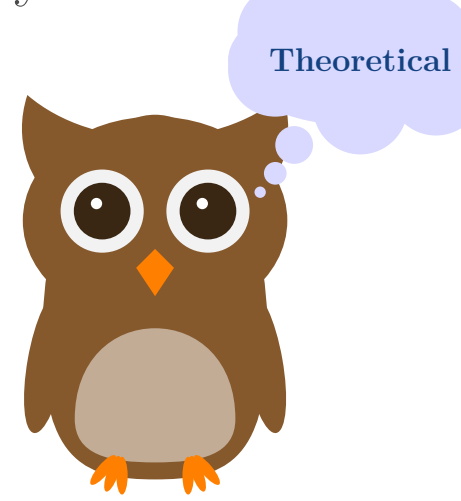
## Objectives

Diffusion is a measure of particle movement through a medium due to random thermal motion. The self diffusion has been studied in this work following linear trajectory approach.

- Investigate role of inter-ionic interaction on self-diffusion
- Compare existing *exchange and correlation* theories
- Identify constraints to accurate prediction of self-diffusion
- Calculate accurate diffusion coefficient
- Calculate accurate hard sphere diameter

## Introduction

- Motivation
  - Melting temperature → container's material + liquid metal → contaminated test sample
  - Such data can't describe self-diffusion accurately.
  - Simulation → computationally expensive.
  - Therefore, robust theoretical approach providing prompt accurate results is necessary.
- Practical Application
  - Heat transfer medium
  - Filament Material → 3D printing
  - Biocompatible material → Signal carrier
  - Smart material → Actuator → Mimic Human muscle
  - Liquid-mirror telescope → Astronomy
  - Atomic transport → metallurgy and material processing



## Liquid State Theory

### LWCA Theory

Equals  $g_{\sigma}(r)$  for  $r > \sigma$

$$B(r) = y_{\sigma}(r) \{ \exp[-\beta u(r)] - \exp[-\beta u_{\sigma}(r)] \}$$

Blip Function, large value when  $r \approx \sigma$

Cavity Function

$$\beta v(\sigma) = \ln \left( \frac{-2\beta\sigma v'(\sigma) + Y + 2}{-2\beta\sigma v'(\sigma) + Y + 2} \right) = \phi(\sigma)$$

### Linear Trajectory

Hard Core Repulsive Part

$$v(r) = v_H(r) + v_S(r)$$

Long Range Soft Part

$$v_H(r) = \infty \quad v_S(r) = 0, \quad r < \sigma$$
$$v_H(r) = 0 \quad v_S(r) = v(r), \quad r > \sigma$$

Accounts for both hard and soft part of the potential.

$$D_{LT} = \frac{k_B T}{\zeta}$$

Represents repulsive hard core interactions.

Net Friction Coefficient

$$\zeta_H = \frac{8}{3} n \sigma^2 (\pi M k_B T)^{\frac{1}{2}} g(\sigma)$$
$$\zeta = \zeta_H + \zeta_S + \zeta_{SH}$$

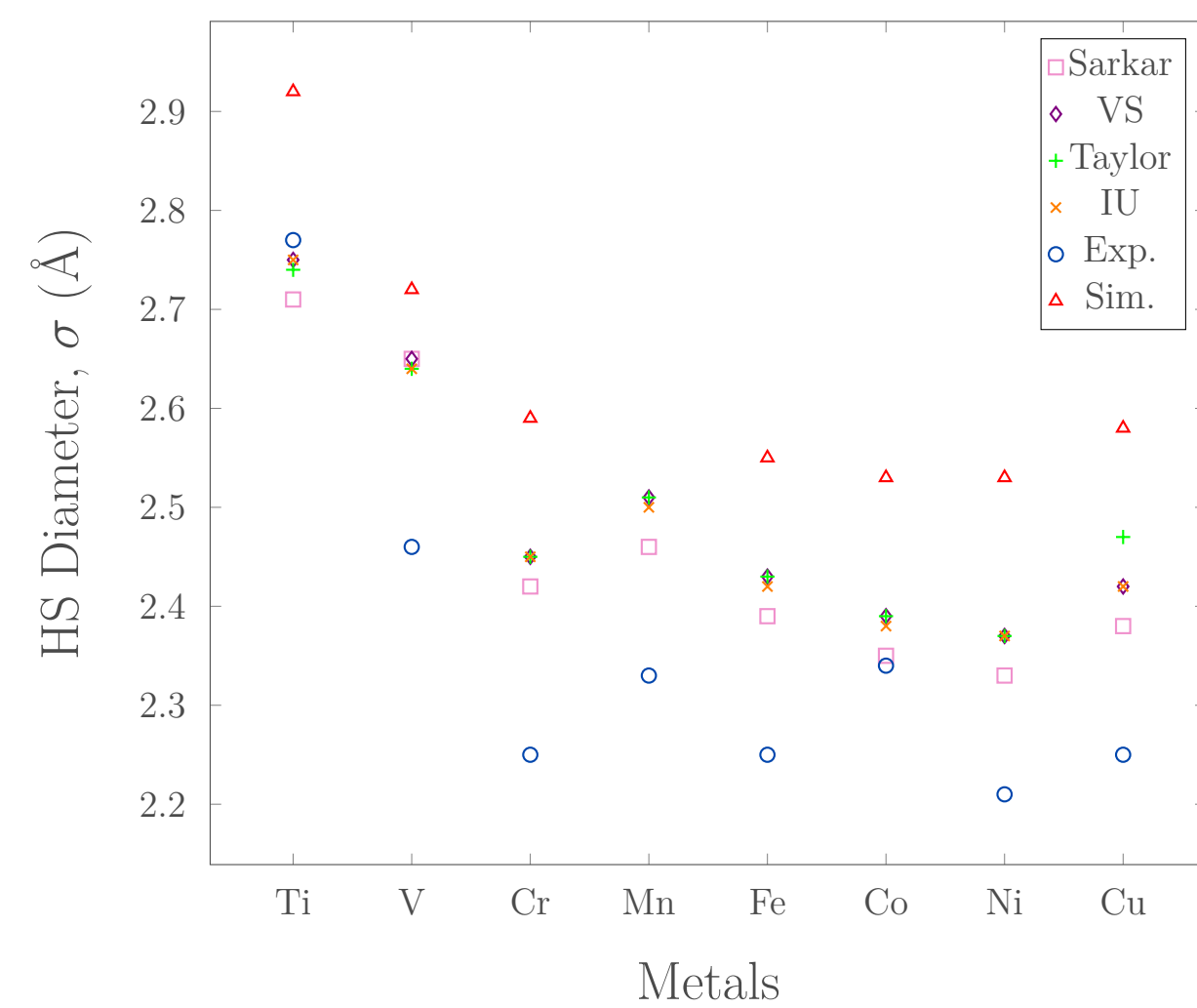
Accounts for attractive soft core interactions.

$$\zeta_S = -\frac{n}{12\pi^2} \left( \frac{\pi M}{k_B T} \right)^{\frac{1}{2}} \int_0^{\infty} q^3 v_S(q) h(q) dq$$

Cross effects between hard and soft forces.

$$\zeta_{SH} = -\frac{1}{2} n g(\sigma) \left( \frac{\pi M}{k_B T} \right)^{\frac{1}{2}} \int_0^{\infty} [g \cos(q\sigma) - \sin(q\sigma)] v_S(q) dq$$

## Hard Sphere Diameter



- Calculated Hard Sphere Diameter **conforms** to existing experimental and simulation data
- All LFF's are reasonably successful in predicting hard sphere diameter.

## Inter-Ionic Interaction

Bare Potential

$$v(r) = \begin{cases} \sum_{n=1}^2 B_n \exp\left(\frac{-r}{na}\right) & \text{for } r < R_c \\ -Z_s^2 \frac{e^2}{r} & \text{for } r > R_c \end{cases}$$

Accounts for  $d$  band when  $n = 2$

Core Radius

eff. no. of valance  $e^-$  per atom, Due to position uncertainty of  $s$   $e^-$

softness parameter

Normalised energy-wavenumber characteristic

$$v_{eff}(r) = \frac{Z_s^2 e^2}{r} \left( 1 - \frac{2}{\pi} \int_0^{\infty} F_N(q) \frac{\sin(qr)}{q} dq \right)$$

Effective Inter-ionic Pair Potential

Wave Number

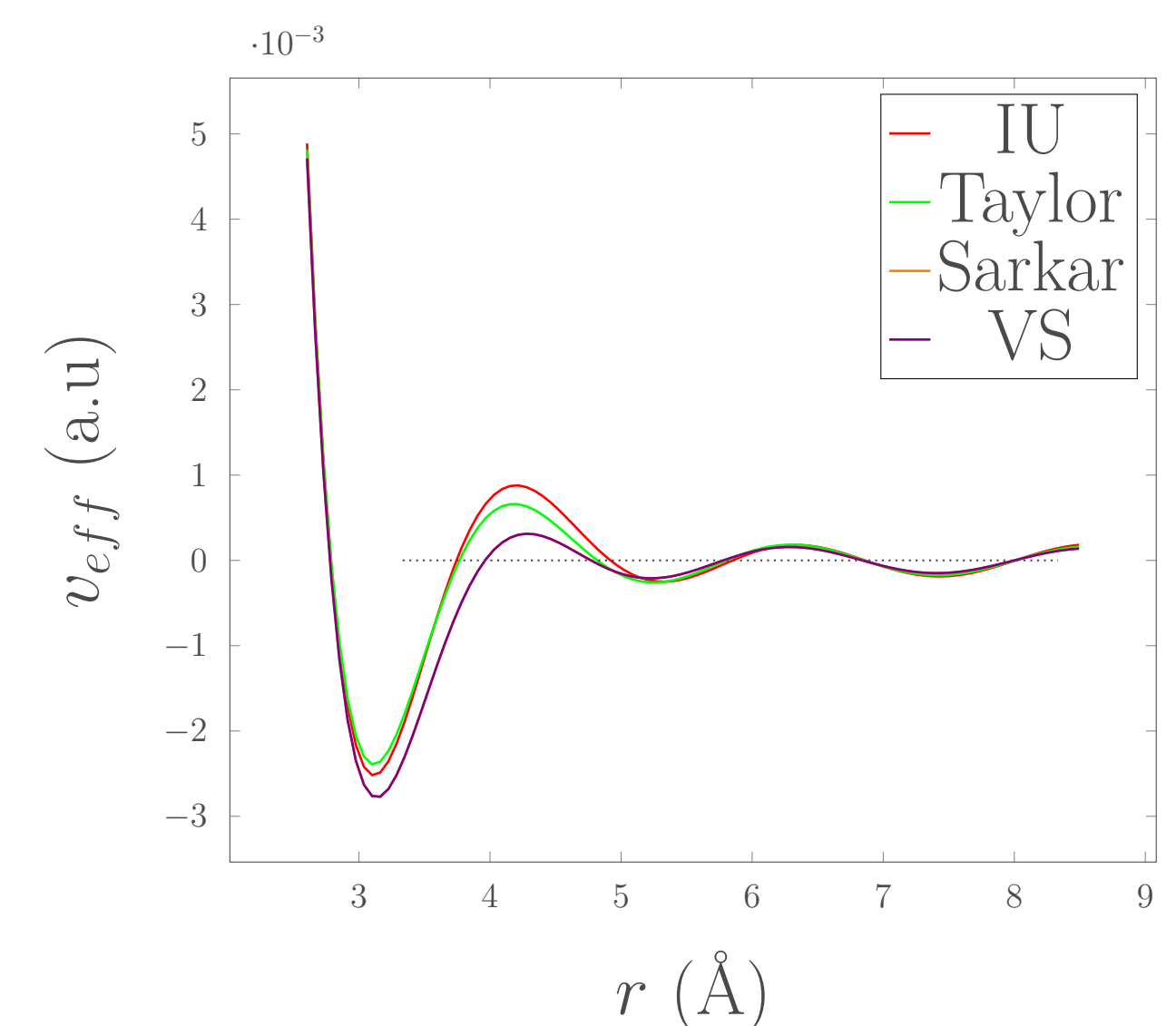
Local Field Function

$$F_N(q) = \left( \frac{q^2}{4\pi n Z_s e^2} \right)^2 (v(q))^2 \left[ 1 - \frac{1}{\epsilon(q)} \right] [1 - G(q)]^{-1}$$

Unscreened Form Factor

Dielectric Function

## Effects on Interionic Interaction



- Potential Profile of V for each LFF
- Vashishta-Singwi LFF gives deep potential suggesting low  $e^-$  screening
- Taylor LFF gives shallower potential suggesting high  $e^-$  screening

## Local Field Functions

Accounts for exchange and correlation effects of the liquid state.

- Taylor

$$G(q) = \frac{q^2}{4q_F^2} \left[ 1 + \frac{0.01534}{\pi q_F^2} \right]$$

- Ichimaru-Utsumi

$$G(Q) = A_{IU} Q^4 + B_{IU} Q^2 + C_{IU} + \left[ A_{IU} q^4 + \left( B_{IU} + \frac{8A_{IU}}{3} \right) Q^2 - C_{IU} \right] \left\{ \frac{4-Q^2}{4Q} \ln \left| \frac{2+Q}{2-Q} \right| \right\}$$

- Sarkar

$$G(q) = A_S \left\{ 1 - \left[ 1 + B_S \left( \frac{q}{q_F} \right)^4 \right] \exp \left[ -C_S \left( \frac{q}{q_F} \right)^2 \right] \right\}$$

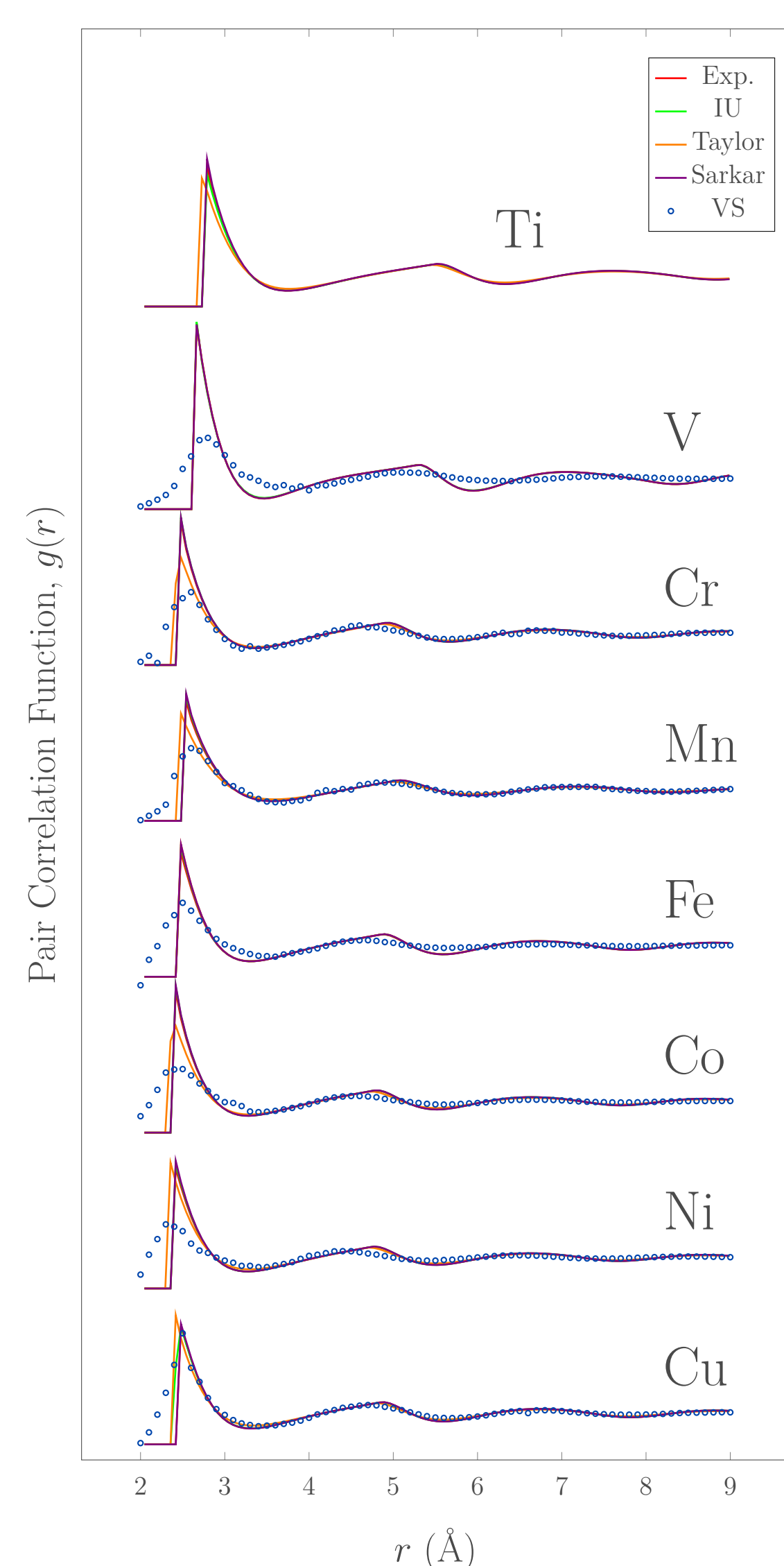
- Vashishta-Singwi

$$G(q) = A_{VS} (1 - e^{-B_{VS}(q/q_F)^2})$$

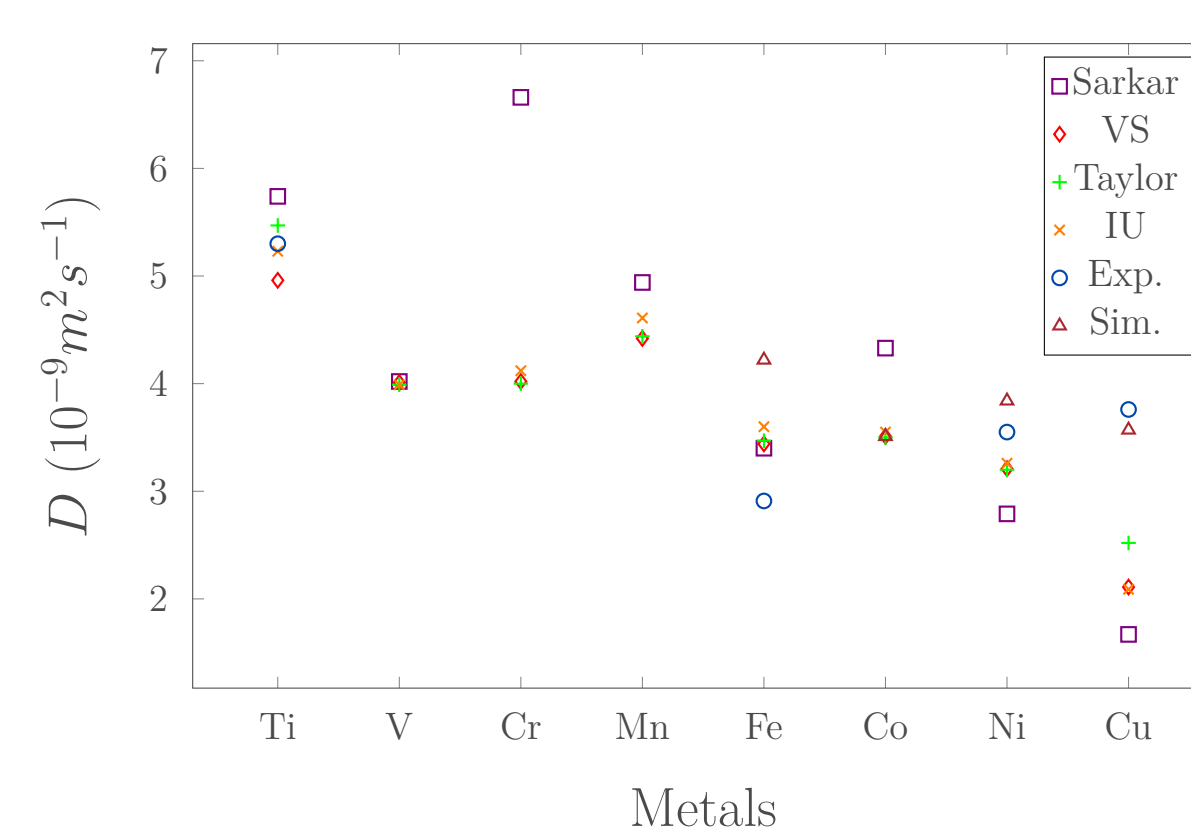
## Can Linear Trajectory theory approximate self-diffusion?

We compare the hard sphere diameter, pair correlation function and diffusion coefficient with existing simulation and experimental data.

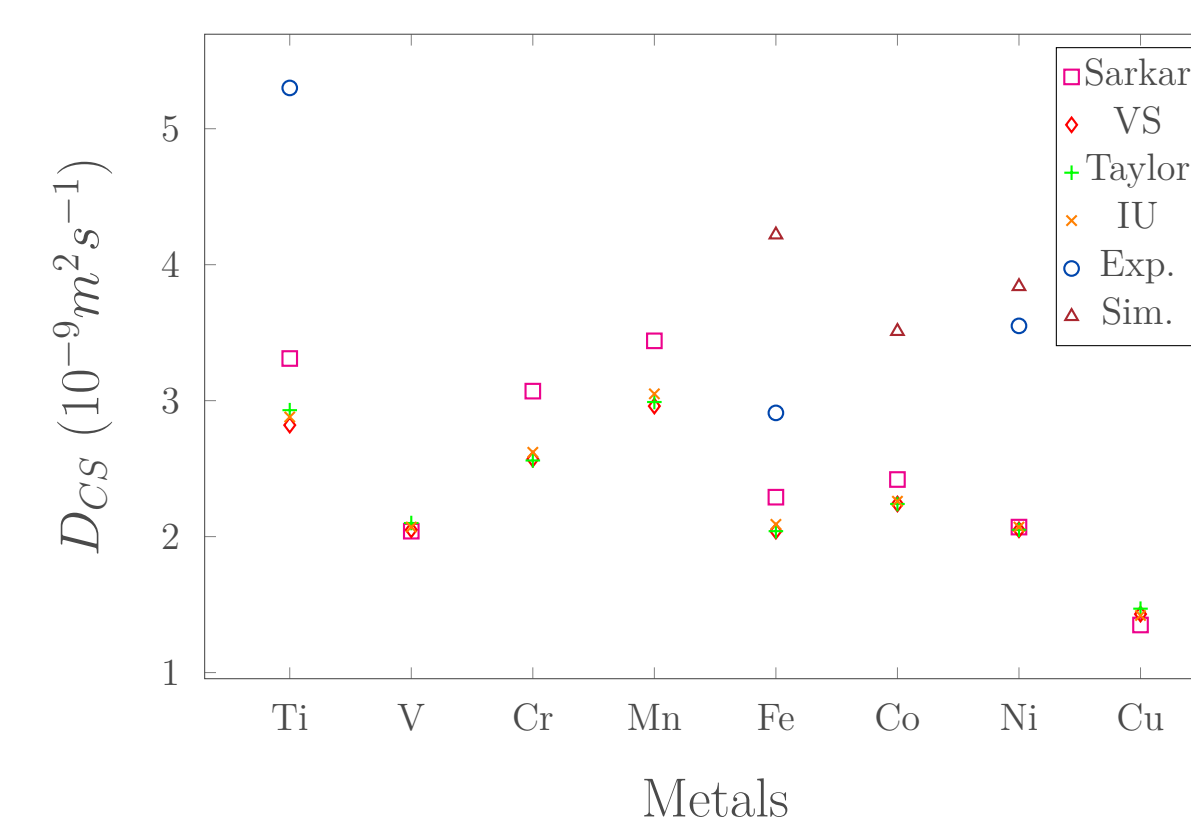
## Agreement of Existing and Calculated Data



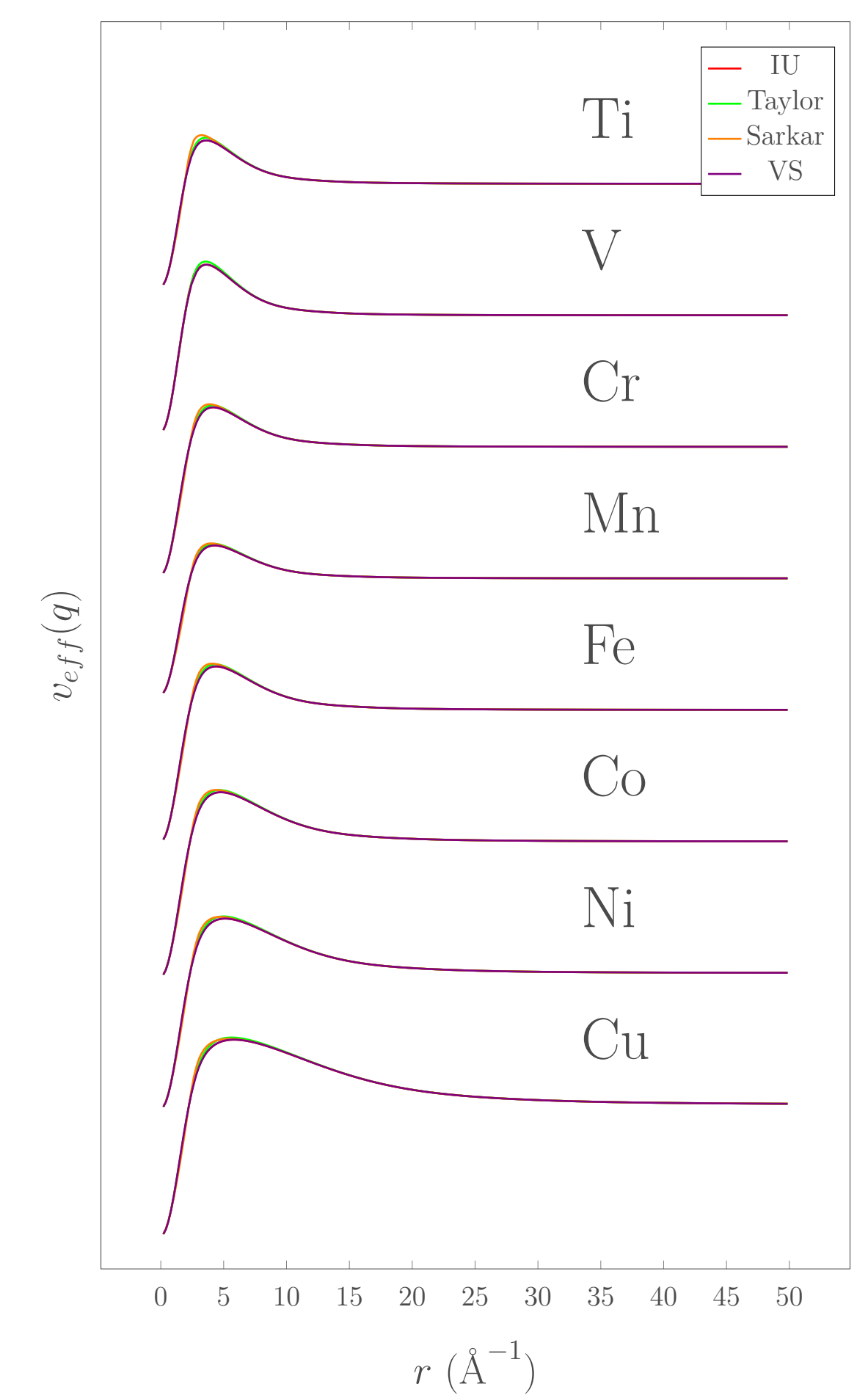
- Agreement** between calculated and existing data of pair correlation function.
- Abrupt peak due to the **Hard Sphere** assumption of LWCA **Perturbation** theory which predicts zero interaction before hard sphere diameter



- Alignment** of calculated and existing Diffusion Coefficient data.
- For Ti, Cr, and Ni Ichimaru-Utsumi and for Fe, Sarkar LFF align with experimental data.
- For Co, Sarkar LFF agrees well with existing simulation data.
- For Mn, Vashishta-Singwi LFF works best with respect to existing theoretical studies.
- Taylor LFF follows Cu's self-diffusion trend better than others. However, numerical precision remains poor.



- Deviation** of Diffusion Coefficient calculated using CS approximation from existing data.



- Fourier Transform of Effective Pair Potentials for each metal for each LFF
- Curves of LFF's align.
- Peak at similar position suggests similar Fermi Wave vector.
- Some have slightly higher peak than others, suggesting stronger screening.

## Conclusion

- LWCA theory using BS pseudo-potential and Linear Trajectory Theory describes Liquid state of most 3d transition metals well.
- Cu's  $e^-$  configuration may be reason for deviation observed.

## Prospective Research

- Scaling Law can be explored for better outcome for Cu.
- Simulation may be explored as a reference for metals that do not have available experimental data.