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

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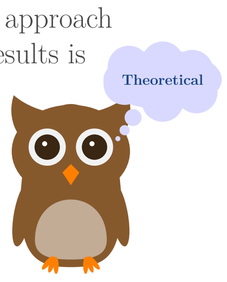
Objectives

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
  - At Melting temperature container's material reacts with liquid metal resulting in contaminated test sample. Data from such sample can't describe self-diffusion accurately.
  - Simulation on the other hand is computationally expensive. Therefore, robust theoretical approach providing prompt accurate results is necessary.



  - Mahir et al. successfully applied Linear Trajectory (LT) Theory to calculate diffusion coefficient of liquid less simple metals. [1] Here, we applied LT theory for 3d transition metals.
  - Gosh et al. applied BS pseudo-potential method to successfully calculate Hard Sphere Diameter, surface tension, viscosity coefficient.[2] Here we observe the effects of different Local Field Functions on BS pseudo-potential for 3d transition metals.
- 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 Perturbation Theory

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

$B(r)$: Blip Function, large value when $r \approx \sigma$; $y_\sigma(r)$: Equals $g_\sigma(r)$ for $r > \sigma$

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

Accounts for both hard and soft part of the potential.

Effective Potential

$$v(r) = v_H(r) + v_S(r); \qquad D_{LT} = \frac{k_B T}{\zeta}$$

Hard Core Repulsive Part

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

Long Range Soft Part

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

Net Friction Coefficient

$$\zeta = \zeta_H + \zeta_S + \zeta_{SH}$$

Represents repulsive hard core interactions.

$$\zeta_H = \tfrac{8}{3} n\sigma^2 (\pi M k_B T)^{\frac{1}{2}}\, g(\sigma)$$

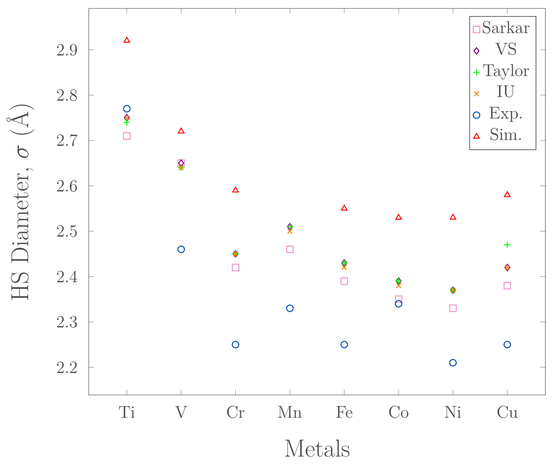
Accounts for attractive soft core interactions.

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

Cross effects between hard and soft forces.

$$\zeta_{SH} = -\tfrac{1}{3} n g(\sigma)\left(\tfrac{M}{\pi k_B T}\right)^{\frac{1}{2}} \int_0^\infty [q\cos(q\sigma) - \sin(q\sigma)] v_S(q)\, dq$$

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

Accounts for d band when $n = 2$

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

Core Radius

softness parameter

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

Normalised energy-wavenumber characteristic

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

Effective Inter-ionic Pair Potential

Wave Number

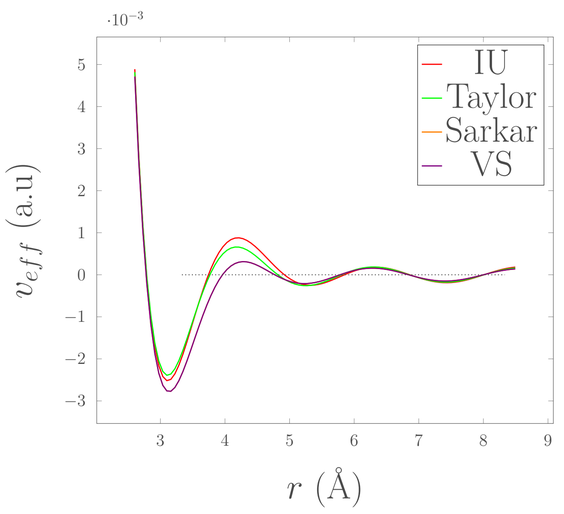
Local Field Function

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

Unscreened Form Factor

Dielectric Function

Effects on Inter-ionic 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

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

- Sarkar

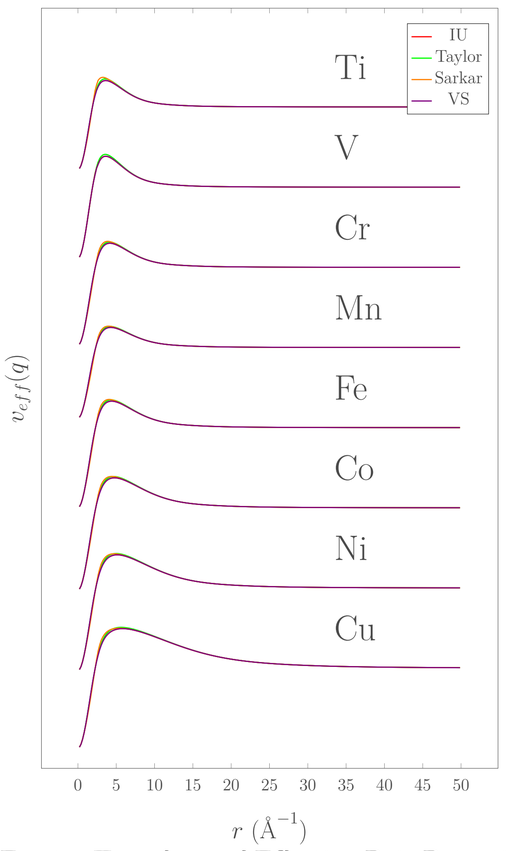
$$G(q) = A_S\left\{1 - \left[1 + B_S\left(\frac{q}{q_F}\right)^4\right]\exp\left[-C_S\left(\frac{q}{q_F}\right)^2\right]\right\}$$

- Vashishta–Singwi

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

- Ichimaru-Utsumi

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

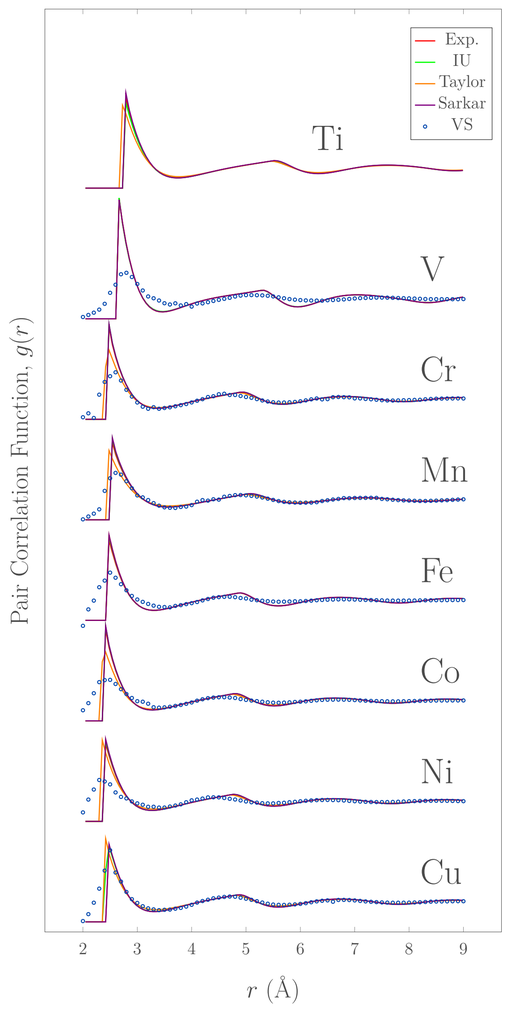


- Fourier Transform of Effective Pair Potentials for each metal for each LFF
- Curves of LFF's align.
- Peak at similar position suggests similar Fermi Wave vector.
- Some have slightly higher peak than others, suggesting stronger screening.

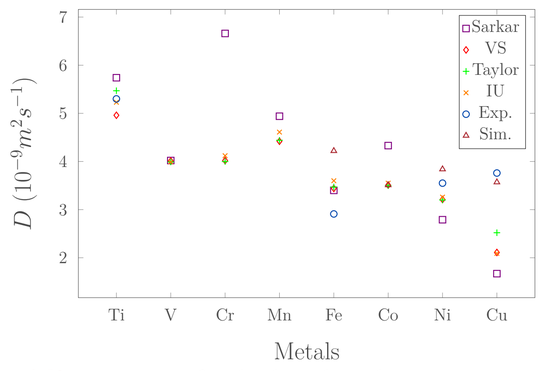
Can Linear Trajectory theory approximate self-diffusion?

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

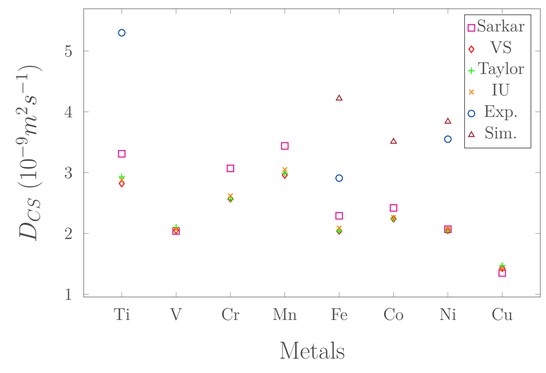
Agreement of Existing and Calculated Data



- **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, Vashishtat-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.

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

References

[1] Mahir Manna and R.C. Gosh. In: *Physica B: Condensed Matter* 649 (2023). ISSN: 0921-4526.

[2] R.C. Gosh, A. Pandit, and Shujal Sarkar. In: *Journal of Non-Crystalline Solids* 606 (2023). ISSN: 0022-3093.