Self-diffusion in single-component Yukawa fluids

Sergey Khrapak, Boris Klumov, and Lenaic Couedel

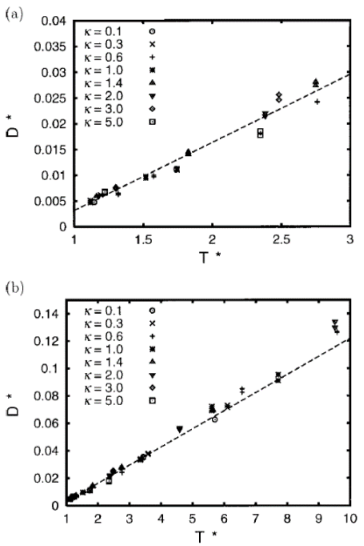
Institute for Materials Physics in Space, DLR, Oberpfaffenhofen, Germany;
Aix-Marseille-University, CNRS, Laboratoire PIIM, Marseille, France;
Joint Institute for High Temperatures, RAS, Moscow, Russia.

Content:

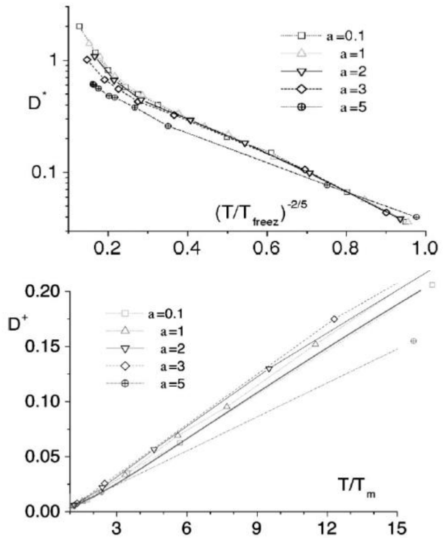
- Brief overview of previous studies
- De Gennes estimation of self-diffusion coefficient in liquids
- Motivation
- Results
    - Yukawa fluids
    - Yukawa melts
    - Universality of self-diffusion at freezing
- Conclusion

Some previous results (single component Yukawa systems in three dimensions)

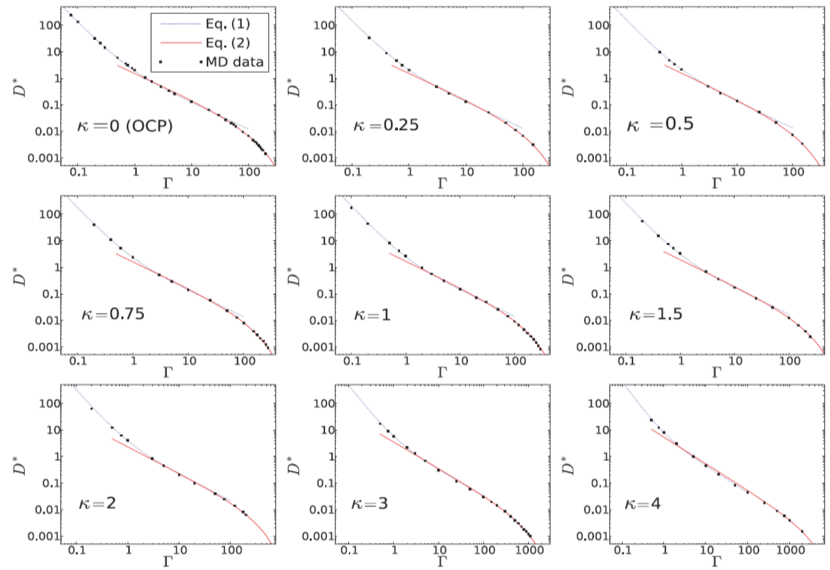
- Extensive MD simulation results tabulated by Ohta and Hamaguchi
- Rosenfeld: Excess entropy and freezing temperature scalings
- Daligault: MD simulations + fit



Ohta and Hamaguchi PoP (2000)



Rosenfeld PRE (2000)



Daligault PRE (2012)

de Gennes approach

- De Gennes (1959) related the self-diffusion coefficient in classical atomic liquids to the pairwise interaction potential $\phi(r)$ and liquid structure in terms of the radial distribution function (RDF) $g(r)$

$$D = \sqrt{\frac{\pi}{2}} \frac{v_{\mathrm{T}}^2}{\Omega_{\mathrm{E}}},$$

with the characteristic frequency (Einstein frequency)

$$\Omega_{\mathrm{E}}^2 = \frac{n}{3m} \int_0^{\infty} d\mathbf{r} g(r) \Delta\phi(r),$$

- Einstein frequency can thus be identified as a rough measure of momentum transfer (friction) rate in liquids

- The approach is not expected to be exact, buts suggests a useful normalization

$$D_E = D \left(\Omega_{\mathrm{E}} / v_{\mathrm{T}}^2 \right)$$

Motivation

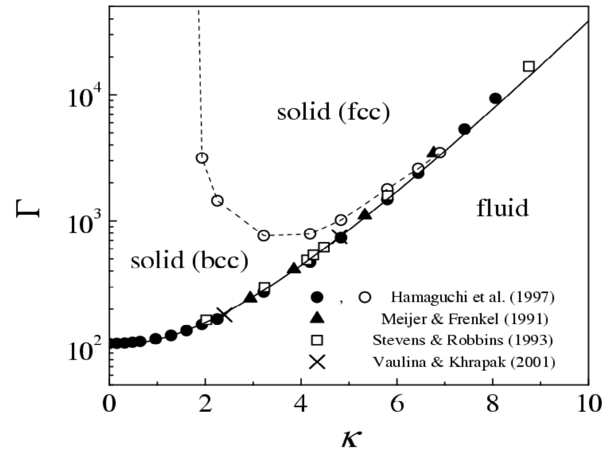
- Quantitative test of de Gennes prediction (using Yukawa systems)
- New data for self-diffusion of Yukawa melts
- Compare results for Yukawa melts with those for liquid metals and other related systems at the melting temperature
- Provide simple explanation of the observed quantitative similarity

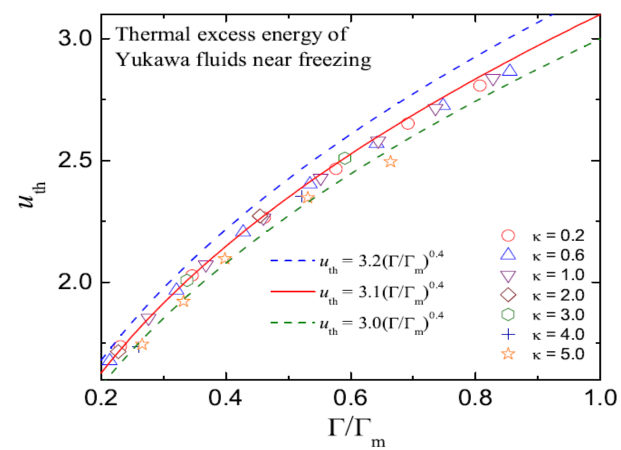
Physique des Interactions Ioniques et Moléculaires

Background information

- Yukawa potential $\phi(r) = (Q^2/r)\exp(-r/\lambda)$
- Phase state determined by the coupling $\Gamma = Q^2/aT$ and screening $\kappa = a/\lambda$ parameters
- Thermodynamics of Yukawa fluids and crystals is well understood
- Einstein frequency is trivially related to the excess internal energy

$$\Omega_{\rm E}^2 = \frac{2}{9}\frac{\kappa^2}{\Gamma}\omega_{\rm p}^2 u_{\rm ex} = \frac{2}{3}\frac{\kappa^2}{a^2}v_T^2 u_{\rm ex}$$





For thermodynamics see e.g. Khrapak et. al. PRE (2015), JCP (2015)

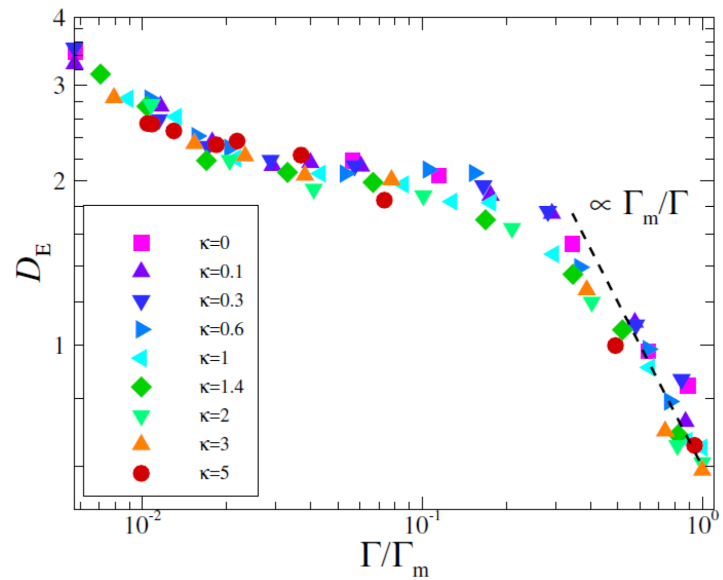
DLR

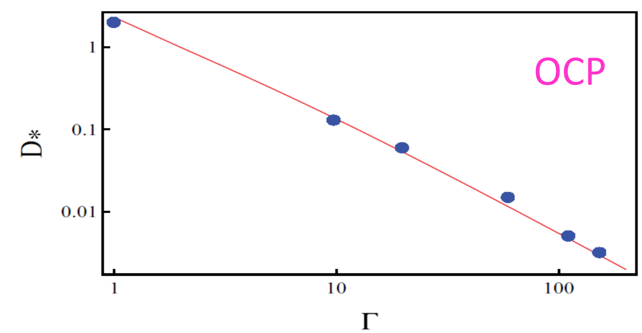
Self diffusion coefficient of Yukawa fluids

- When plotted vs $\Gamma/\Gamma_{\mathrm{m}}$ self-diffusion shows no systematic dependence on κ
- Weak dependence of self-diffusion on coupling – success of de Genes approach
- A simple estimate is accurate to within a factor of two in the fluid regime

$$D \simeq v_T^2/\Omega_{\mathrm{E}}$$

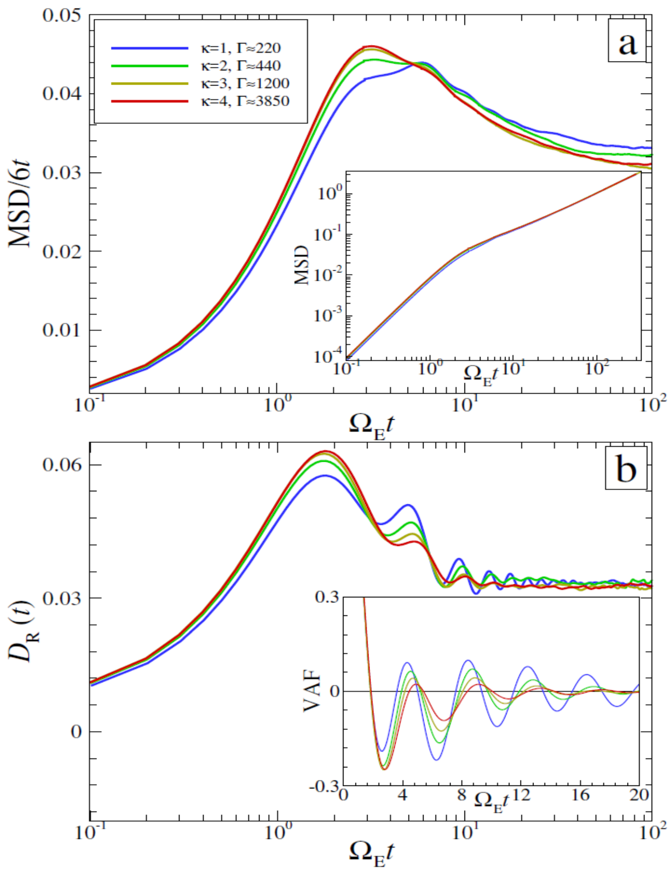
- Three regimes of self-diffusion can be identified (weak coupling regime, plateau-like behavior, approach to freezing)



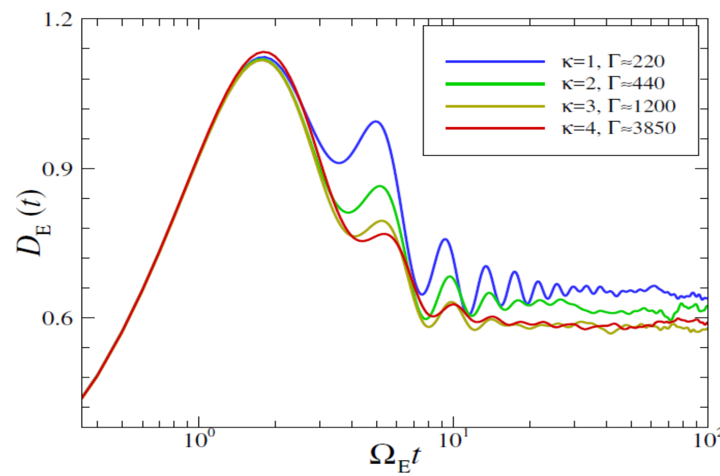


MD data for fluids by Ohta and Hamaguchi (2000); melts – present work

Self-diffusion in Yukawa melts



- Two possibilities to determine SD coefficient
  - MSD
  - Green-Kubo relation
- Two normalizations: $D_{\rm R} = Dn^{1/3}/v_T$ and $D_{\rm E}$
- At freezing $D_{\rm R} \simeq 0.03$ and $D_{\rm E} \simeq 0.6$



Simulations by Klumov&Couedel

Understanding the value of the self-diffusion coefficient at freezing

- Near the melting point

$$\frac{1}{2}m\Omega_{\rm E}^2\langle\delta r^2\rangle \sim \frac{3}{2}T.$$

- According to the Lindemann melting rule $\langle\delta r^2\rangle \sim L^2\Delta^2$, where $L \sim 0.1$

- From this the following relation between different normalizations emerges

$$D \simeq 0.6\frac{v_T^2}{\Omega_{\rm E}} \simeq \frac{0.6L}{\sqrt{3}}v_T\Delta \simeq 0.03 v_T n^{-1/3}$$

- Coincides with what we have documented for Yukawa melts

How universal is self-diffusion at freezing?

- Similar values $D_R \simeq 0.03$ observed for several other simple fluids (Hertz, GCM, IPL)
- Liquid metals demonstrate the same magnitude (see Table)
- In the OCP limit $D_R \simeq 0.031$
- In the HS limit $D_R \simeq 0.02$
- Universality for soft enough interactions?

Pond et al. Soft Matter (2011)

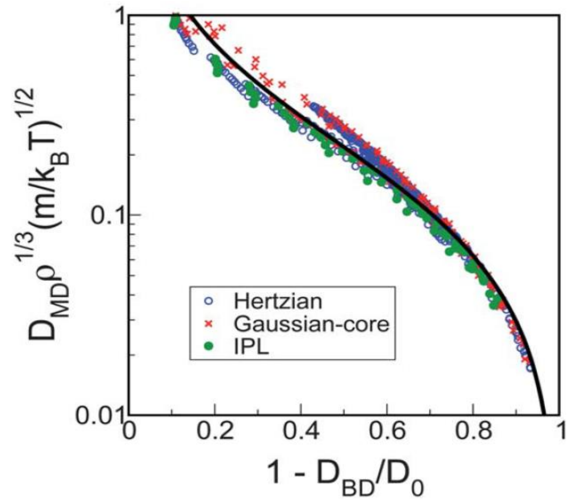


TABLE I. Reduced diffusion constants D_R of ten liquid metals at the corresponding melting points as calculated from the data summarized in Ref. 45.

Li	Na	K	Rb	Cu	Ag	Pb	Zn	In	Hg
0.029	0.033	0.032	0.034	0.040	0.031	0.035	0.027	0.032	0.034

Recalculated from the data summarized in March and Tosi book

Conclusion

- De Gennes prediction is inexact, but useful
- Constancy of self-diffusion at freezing -> Dynamic freezing criterion for simple soft atomistic systems?
- Application: Momentum transfer in strongly coupled plasmas (complex plasmas)
- Other transport properties (e.g. viscosity)

Thank you for your attention!

Acknowledgments

- Studies at Aix-Marseille-University have been supported by the A*MIDEX grant (Nr. ANR-11-IDEX-0001-02) funded by the French Government "Investissements d'Avenir" program

- Structure and dynamical data analysis supported by RSF 14-50-00124