Ionic structure in Warm Dense Matter: ab initio Simulations versus HNC

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Structure for Multicomponent Systems

- **Pair distribution**

$$g_{ab}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{n_a n_b}\left\langle \sum_{\substack{i=1\\ i\neq j\ \forall\, a=b}}^{N_a}\sum_{j=1}^{N_b} \delta(\mathbf{r}_1-\mathbf{r}_i)\delta(\mathbf{r}_2-\mathbf{r}_j)\right\rangle$$

- **Static structure factor**

$$S_{ab}(\mathbf{k}) = \delta_{ab} + \sqrt{n_a n_b}\int d\mathbf{r}\,[g_{ab}(r)-1]\,\exp(i\mathbf{k}\cdot\mathbf{r})$$

- **Integral equation approach**

  Strong correlations in a classical system can be described by coupled integral equations with high accuracy

  – **Ornstein-Zernike relation**

$$h_{ab}(\mathbf{r}) = c_{ab}(\mathbf{r}) + \sum_c n_c \int d\bar{\mathbf{r}}\, c_{ac}(\bar{\mathbf{r}})\, h_{cb}(|\mathbf{r}-\bar{\mathbf{r}}|)\,.$$

  – **Closure relation**

$$g_{ab}(\mathbf{r}) = h_{ab}(\mathbf{r}) + 1 = \exp\{-\beta V_{ab}(\mathbf{r}) + h_{ab}(\mathbf{r}) - c_{ab}(r) + B_{ab}(\mathbf{r})\}$$

[1] J.P. Hansen and I.R. McDonald, *Theory of Simple Liquids*, (Academic Press, London, 1990).

[2] J.M.J. Van Leuwen, J. Groenveld, and J. DeBoer, Physica **25**, 792 (1959).

Hypernetted Chain Approach (HNC)

The neglect of the correlation covered by the bridge diagrams yields to the following **closure relation**

$$g_{ab}(r) = \exp\{-\beta V_{ab}(r) + h_{ab}(r) - c_{ab}(r)\}\,.$$

This approximation leads to good agreements with simulations up to moderate coupling strengths.

Models in the HNC approach

One component plasma (OCP): The electrons are considered as a uniform, structureless and neutralising background resulting in a Coulomb interaction between the ions.

Yukawa model (Y): The electrons are considered as a polarisable neutralising background resulting in the ion interaction being described by a statically screened Coulomb potential (Debye potential).

Yukawa model plus Lennard Jones repulsion (Y+LJ): Interaction of bound electrons cause an additional Lennard-Jones-type ($\sim 1/r^4$) repulsive potential for small distances.

Quantum pseudo-potentials: For the consideration of quantum effects in the classical approach, we apply quantum pseudo-potential that are designed to mimic the quantum nature of the electrons.

- Deutsch potential
- Kelbg potential
- Klimontiovich-Kreaft potential (KK)

[1] J.F. Springer, M. Pokrant, and F. Stevens, Jr., J. Chem. Phys. **58**, 4863 (1973).

[2] M. Baus and J. Hansen, Phys. Rep. **59**, 1 (1980).

[3] K. Wünsch, P. Hilse, M. Schlanges and D.O. Gericke, Phys. Rev. E **77**, 1 (2008).

[4] G. Kelbg, Ann. Phys. **12**, 219 (1964); Ann. Phys. **12**, 354 (1964).

[5] C. Deutsch, Phys. Lett. **60A**, 317 (1977).

[6] Y. Klimontovich and W.-D. Kraeft, High. Temp. Phys. (USSR) **12**, 212 (1974).

Mean Spherical Approximation (MSA)

The ions are considered as positively charged hard spheres (CHS) that interact in the uniform neutralising background of the electrons. The **closure relation** is given by

$$g(r) = 0 \;\text{ for } r < d \quad\text{and}\quad c(r) = -\beta v(r) \;\text{ for } r > d\,.$$

The model can be solved analytically for an OCP (MSA-OCP) in terms of the ion temperature and density.
Linear screening effects are taken into account by using an empty-core ionic pseudo-potential (MSA-Y).

[1] R.G. Palmer and J.D. Weeks, J. Chem. Phys. **58**, 4171 (1973).

[2] G. Gregori, A. Ravasio. A. Höll, S.H. Glenzer, and S.J. Rose, High Energy Density Phys. **3**, 99 (2003).

ab initio Simulation: DFT-MD

Born-Oppenheimer DFT-MD with VASP

We use first principle quantum simulations (density functional theory - DFT) for the electrons in combination with molecular dynamics (MD) for the classical ions via the Born-Oppenheimer approximation. This allows the proper treatment of strongly coupled ions as well as degenerate electrons.

[1] Kresse *et al.*, Phys. Rev. B **47**, RC558 (1993).

[2] Kresse *et al.*, Phys. Rev. B **59**, 1758 (1993).

Motivation

Structural information for warm dense matter (WDM) are of interest for the understanding of astrophysical plasmas as in giant gas planets and for inertial confinement fusion where it occurs as a transient state. In particular, the well-pronounced ionic structure strongly influences the equation of state as well as transport coefficients. As WDM is characterised by near solid densities and temperatures around a few electronvolts, the ions are strongly coupled and the electrons are partially degenerate. The combination of both makes usual expansion techniques as well as many other standard procedures inapplicable.
Two applications for the structural information in a plasma are:

Thermodynamics

- mean potential energy

$$\langle E_{pot}\rangle = 2\pi V \sum_{ab} n_a n_b \int \mathrm{d}\mathbf{r}\; r^2\, V_{ab}(\mathbf{r})\, g_{ab}(\mathbf{r})$$

- Equation of State

$$p = p_0 + \frac{2\pi\beta n_a n_b}{3}\int \mathrm{d}\mathbf{r}\;\mathbf{r}^3 \frac{\partial V_{ab}(\mathbf{r})}{\partial r} g_{ab}(\mathbf{r})$$

X-ray Scattering

Power spectrum of the scattered radiation (light elements)

$$\frac{\mathrm{d}^2P(\mathbf{k},\omega)}{\mathrm{d}\Omega\,\mathrm{d}\omega} \propto S_{ee}^{tot}(\mathbf{k},\omega) = \underbrace{Z_f S_{ee}^0(\mathbf{k},\omega)}_{\text{electron feature}} + \underbrace{|f_i(k)+q(k)|^2\, S_{ii}(\mathbf{k},\omega)}_{\text{Ion feature}}$$

– **Electron feature:** scattering contribution of the free electron

– **Ion feature:** describes electrons co-moving with the ions:
$f_i(k)$ - atomic form factor $\quad q(k)$ - screening cloud

⇒ Structural properties are required for both applications
⇒ Ion structure more pronounced due to stronger coupling

[1] D. Kremp, M. Schlanges, and W.-D. Kraeft, *Quantum Statistics of Nonideal Plasmas*, (Springer, Berlin, 2005).

[2] J. D. Lindl, *Inertial Confinement Fusion*, (Springer-Verlag, New York, 1998).

[3] A. Grinenko, D.O. Gericke, S. Glenzer, J. Vorberger, submitted to Phys. Rev. Lett.

[4] W.-D. Kraeft *et al.*, Contrib. Plasma Phys. **47**, 253 (2007).

[5] B. Militzer, W.-B. Hubbard, J. Vorberger, I. Tamblyn, S.A. Bonev, submitted to ApJL.

[6] S.H. Glenzer *et al.*, Phys. Rev. Lett. **90**, 175002 (2003).

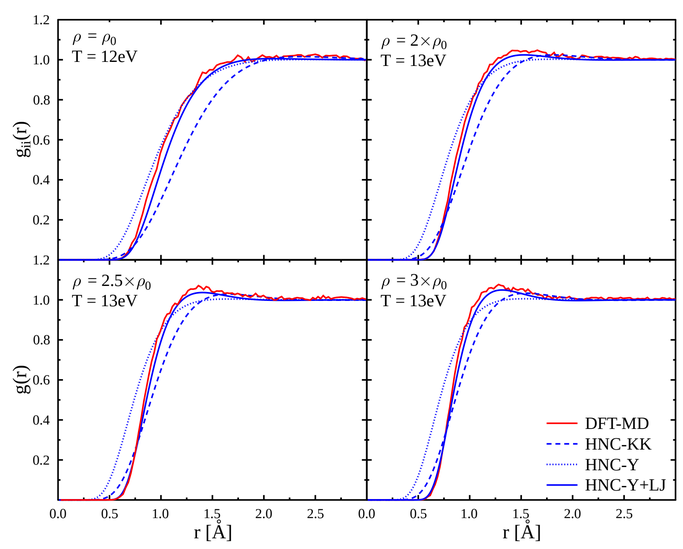
[7] G. Gregori, *et al.*, Phys. Rev. E **67**, 026412 (2003).

[8] S.H. Glenzer *et al.*, Phys. Rev. Lett. **98**, 065002 (2007).

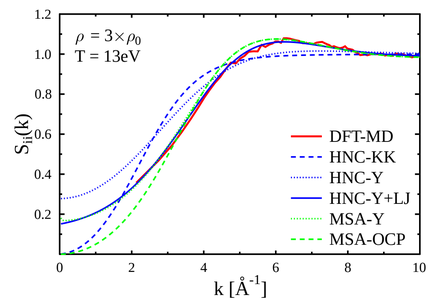
Results & Comparison of the Models

We present HNC-results, MSA and DFT-MD simulations for several plasmas used in current scattering experiments.

Beryllium



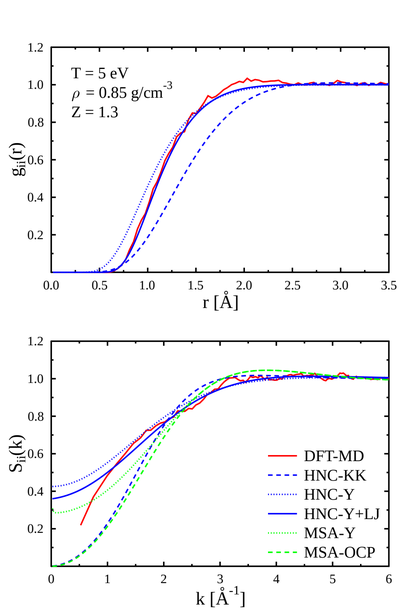
Ion-ion pair distribution function for beryllium at different compression levels ($\rho_0 = 1.848 g/cm^3$ is the solid density) comparing HNC calculation in several models with quantum DFT-MD simulations.



Ion-ion structure factor for beryllium with threefold solid density, $T = 13eV$ and charge $Z = 2$. Different theories are compared.

- multicomponent HNC with effective quantum pseudo-potentials cannot describe correlations correctly
  ⇒ limit of applicability of quantum potentials is exceeded
- one component model using linear screening with degenerate electrons yields good agreements with DFT-MD results
- improvement by Lennard-Jones-type repulsive potential insight gained: inner 1s shell is still intact
- screened MSA calculation yields a good agreement

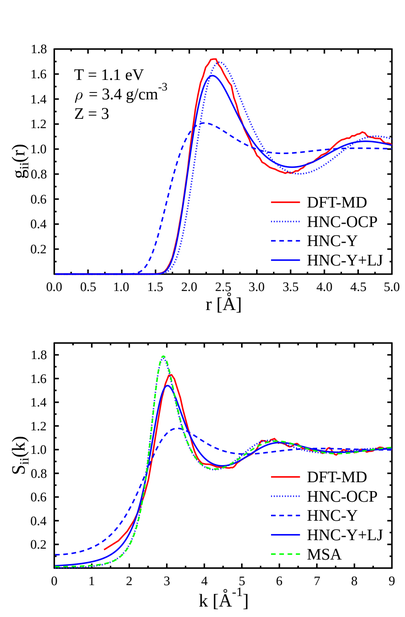
Lithium



Ion-ion pair distribution function and structure factor for lithium.

- comparison shows that method of quantum pseudo-potentials is overstressed
- agreement with Yukawa+LJ model suggests the existence of a full inner (1s) shell
- MSA model displays significant differences at small k-values

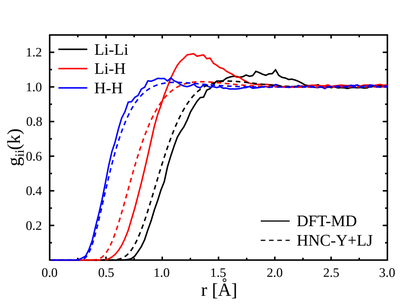
Aluminium



Ion-ion pair distribution function and structure factor for aluminium.

- simple Yukawa model underestimates the correlations in the system
- tightly bound inner electrons yield a strong repulsion between the ions, described by a Leannard-Jones-type potential
- MSA approach overestimates structure

Lithium-Hydride



Partial ion-ion pair distribution functions for LiH with the plasma parameters $n_i = 0.78 g/cm^{-3}$ and $T = 2.2eV$.

- multi-ion HNC approach cannot describe the structure correctly
- due to the ionisation state of the plasma, the neutral ions require separate treatment

Further work:

- developing interacting potentials based on the DFT-MD simulations
- more investigations on partially ionised multicomponent systems
- applying the structural information to thermodynamics and x-ray scattering