Screened cluster equation of state for hydrogen-helium mixtures

V. Ballenegger[✤], **D. Wendland** and **A. Alastuey**[★]

✤ ***Université de Bourgogne-Franche-Comté***, *Besançon, France*

★ ***Ecole Normale Supérieure de Lyon***, *Lyon, France*

Introduction

Goal: Very accurate equation of state (EOS) for H-He mixtures at low-densities

Physical picture:

H-He gas = quantum plasma of point particles interacting solely via the Coulomb potential $e_i e_j/|\boldsymbol{r}_i-\boldsymbol{r}_j|$.

⊖ **e**: electron

⊕ **p**: proton

⊕⊕ **α**: helium nucleus

Main idea: compute all terms, up to some order, in quantum low-fugacity expansions

→ **Screened cluster EOS** (based on analytical + numerical results)

The SC EOS accounts for

- **Formation/dissociation of atoms and molecules**, e.g. H, He, He^+, He^{2+}, H_2^+, H^-, …
- **Thermal excitations** and **effects of interactions**
- **Screening effects**:

  Deviations to the Debye potential $\phi(\vec{r}) = \dfrac{e^{-\kappa|\vec{r}|}}{|\vec{r}|}$ *due to quantum effects*

  → *modifications of atomic/molecular spectra at finite density*

Computation of the EOS

Grand-canonical ensemble:

independent variables: $V,\quad T,\quad \{\mu_\gamma\}$ or $\{z_\gamma = e^{\beta\mu_\gamma}\}$ (fugacities) γ = e, p, α

grand potential: $\Omega(V,T,\{\mu_\gamma\}) = U - TS - \sum_\gamma \mu_\gamma N_\gamma = -PV$

Compute Ω at low fugacities using **quantum Mayer diagrammatical expansions.**

Differentiate Ω All thermodynamical properties follow by differentiation.

$$P = -\frac{\partial}{\partial V}\Omega$$

$$S = -\frac{\partial}{\partial T}\Omega$$

$$\rho_\gamma = \frac{N_\gamma}{V} = -\frac{\partial}{\partial \mu_\gamma}\Omega/V = \rho_\gamma(T,\{z_\gamma\})$$

numerical inversion

$$z_\gamma(T,\{\rho_\gamma\})$$

Eliminate the fugacities

$$P(T,\{z_\gamma\}) \longrightarrow P(T,\{\rho_\gamma\})$$

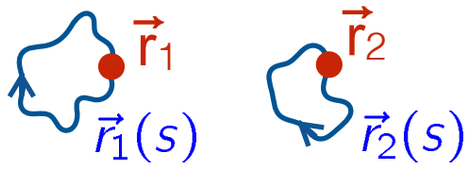
EOS for the pressure

Grand-potential: $\Omega(V, T, \{\mu_\gamma\}) = -k_B T \ln \Xi$ (Ξ = grand-canonical partition function)

Feynman-Kac **path integral**:

$$\langle \vec{r}_1, \vec{r}_2 | \, e^{-\beta H_N} \, | \vec{r}_1, \vec{r}_2 \rangle \quad = \quad \int \mathcal{D}[\vec{r}_1(\cdot)] \mathcal{D}[\vec{r}_2(\cdot)] \, e^{-\beta V(\mathcal{L}_1, \mathcal{L}_2)}$$

$\sum$ *over all closed paths (loops) in imaginary time s*

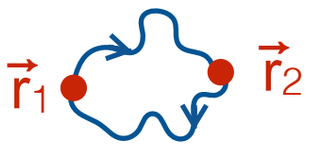


classical Boltzmann factor

$$V(\mathcal{L}_1, \mathcal{L}_2) = \int_0^1 \frac{e_{\gamma_1} e_{\gamma_2}}{|\vec{r}_1(s) - \vec{r}_2(s)|} \, ds$$

= Coulomb interaction *averaged along the paths*

$\langle \vec{r}_2, \vec{r}_1 | \, e^{-\beta H_N} \, | \vec{r}_1, \vec{r}_2 \rangle \longleftrightarrow$



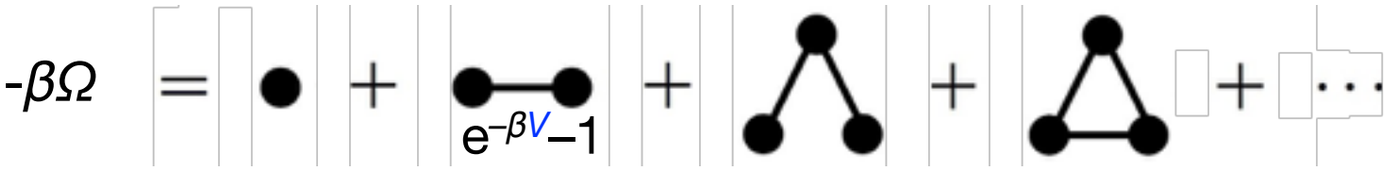
(quantum exchange)

Equivalence:

Quantum plasma $\longleftrightarrow$ **classical** plasma of **charged loops**

Screened cluster expansion

Fugacity expansion (Mayer diagrams):

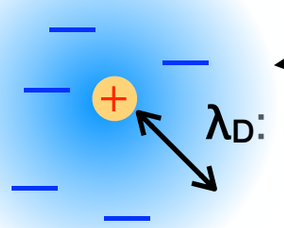


$$V(\ell_1,\ell_2) = \int_0^1 \frac{e_{\gamma_1} e_{\gamma_2}}{|\vec{r}_1(s) - \vec{r}_2(s)|}\, ds$$

Eliminate all Coulomb divergencies in the thermodynamic limit (Abe-Meeron resummations)

$$\lim_{\Lambda\to\infty} \frac{-\beta\Omega}{\Lambda} = \beta P =$$

Polarization cloud



λ_D: Debye screening length

(Quantum Mayer) screened cluster diagrams

$\phi(\ell_1,\ell_2)$: **screened Coulomb interaction**

≈ RPA interaction

Brydges & Martin (1999) (review)

A fugacity factor $z_\gamma = e^{\beta\mu_\gamma}$ is associated to every particle in every loop:

$$\beta P = \sum_\gamma C^{(1)}_\gamma(T,\kappa)\, z_\gamma + \sum_{\gamma_1,\gamma_2} C^{(2)}_{\gamma_1,\gamma_2}(T,\kappa)\, z_{\gamma 1} z_{\gamma 2} + \sum_{\gamma_1,\gamma_2,\gamma_3} C^{(3)}_{\gamma_1,\gamma_2,\gamma_3}(T,\kappa)\, z_{\gamma 1} z_{\gamma 2} z_{\gamma 3} + \ldots$$

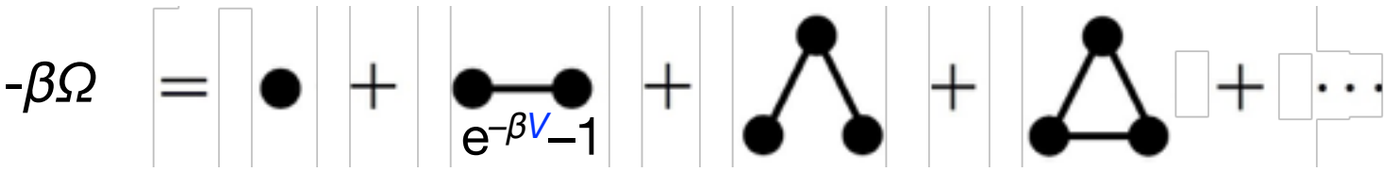
Screened cluster functions

Analogous to **virial functions**, but at *finite* density

Fugacity dependence via $\kappa = \sqrt{4\pi\beta \sum_\gamma e_\gamma^2 z_\gamma} = \lambda_D^{-1}$

Screened cluster expansion

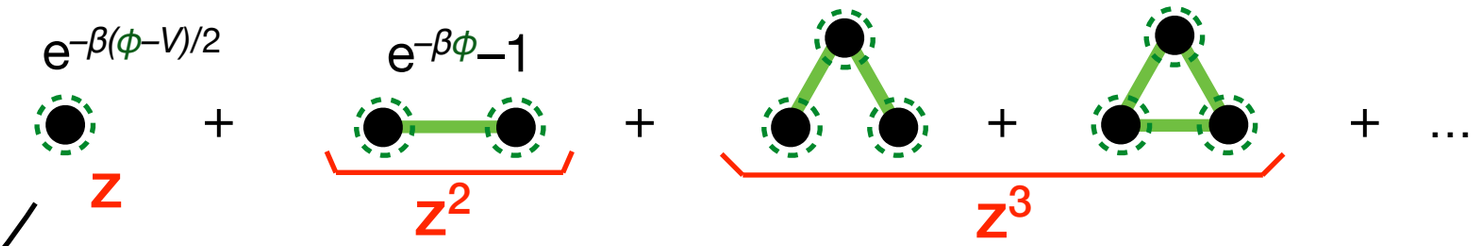
Fugacity expansion (Mayer diagrams):



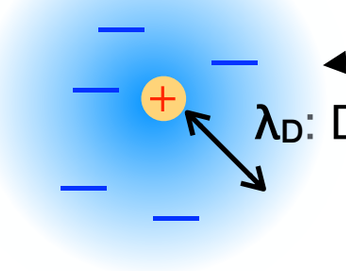
$$V(\mathcal{L}_1,\mathcal{L}_2) = \int_0^1 \frac{e_{\gamma_1} e_{\gamma_2}}{|\vec{r}_1(s) - \vec{r}_2(s)|}\, ds$$

Eliminate all Coulomb divergencies in the thermodynamic limit (Abe-Meeron resummations)

$$\lim_{\Lambda\to\infty} \frac{-\beta\Omega}{\Lambda} = \beta P =$$



Polarization cloud



λ_D: Debye screening length

(Quantum Mayer) **screened cluster diagrams**

$\phi(\mathcal{L}_1,\mathcal{L}_2)$: **screened Coulomb interaction**

≈ RPA interaction

Brydges & Martin (1999) (review)

A fugacity factor $z_\gamma = e^{\beta\mu_\gamma}$ is associated to every particle in every loop:

$$\beta P = \sum_\gamma C^{(1)}_\gamma(T,\kappa)\, z_\gamma + \sum_{\gamma_1,\gamma_2} C^{(2)}_{\gamma_1,\gamma_2}(T,\kappa)\, z_{\gamma 1} z_{\gamma 2} + \sum_{\gamma_1,\gamma_2,\gamma_3} C^{(3)}_{\gamma_1,\gamma_2,\gamma_3}(T,\kappa)\, z_{\gamma 1} z_{\gamma 2} z_{\gamma 3} + \ldots$$

Screened cluster functions

Analogous to **virial functions**, but at *finite* density

Fugacity dependence via $\kappa = \sqrt{4\pi\beta \sum_\gamma e_\gamma^2 z_\gamma} = \lambda_D^{-1}$

Screened cluster functions

$C_{\gamma}^{(1)}(T,\kappa)$: ideal term + plasma polarisation effect (at all orders in the charge e)

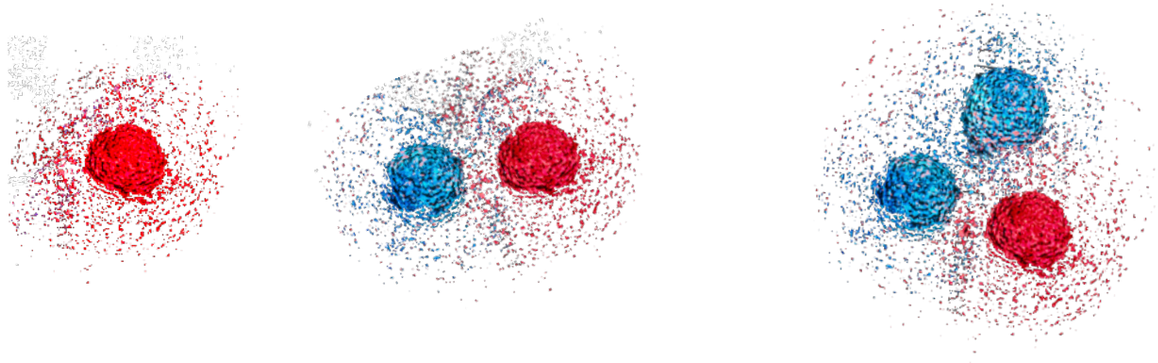
$C_{\gamma_1,\gamma_2}^{(2)}(T,\kappa)$: all 2-particle effects.
– interactions between 2 ionised charges
– atoms **H**, **He^+** (at finite density)

$C_{\gamma_1,\gamma_2,\gamma_3}^{(3)}(T,\kappa)$: all 3-particle effects.
– atoms/mols: **He**, **H_2^+**, **H^-**
– **atom**-charge interactions, etc.

Cluster functions given by **formally simple path integral formulae.**

Path integral approach	Mayer diagrams	Direct space: ***r***, *s*	**all orders** in the charge e
Thermo. Green fct. approach	Feynman diagrams	Fourier space: ***k***, ω	**perturbative** wrt charge e

Computation of all diagrams ≤ 3 particles :



➜ Tabulation of the 21 cluster fcts

➜ **SC EOS** at 3rd order for **H-He mixtures**

Screened cluster functions

$C_{\gamma}^{(1)}(T,\kappa)$: ideal term + plasma polarisation effect (at all orders in the charge e)

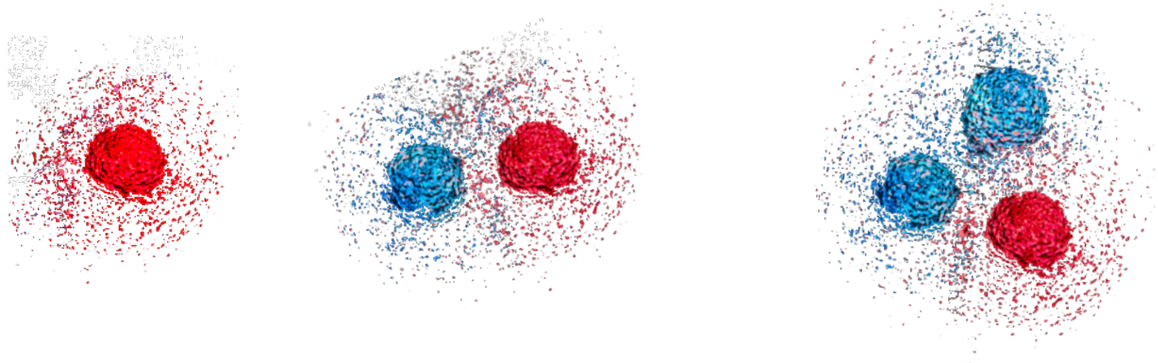
$C_{\gamma_1,\gamma_2}^{(2)}(T,\kappa)$: all 2-particle effects.
– interactions between 2 ionised charges
– atoms **H**, **He^+** (at finite density)

$C_{\gamma_1,\gamma_2,\gamma_3}^{(3)}(T,\kappa)$: all 3-particle effects.
– atoms/mols: **He**, **H_2^+**, **H^-**
– **atom**-charge interactions, etc.

Cluster functions given by **formally simple path integral formulae.**

Path integral approach	Mayer diagrams	Direct space: ***r***, *s*	**all orders** in the charge e
Thermo. Green fct. approach	Feynman diagrams	Fourier space: ***k***, ω	**perturbative** wrt charge e

Computation of all diagrams ≤ 3 particles :

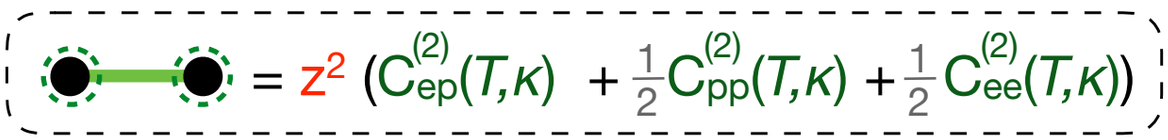


➜ Tabulation of the 21 cluster fcts

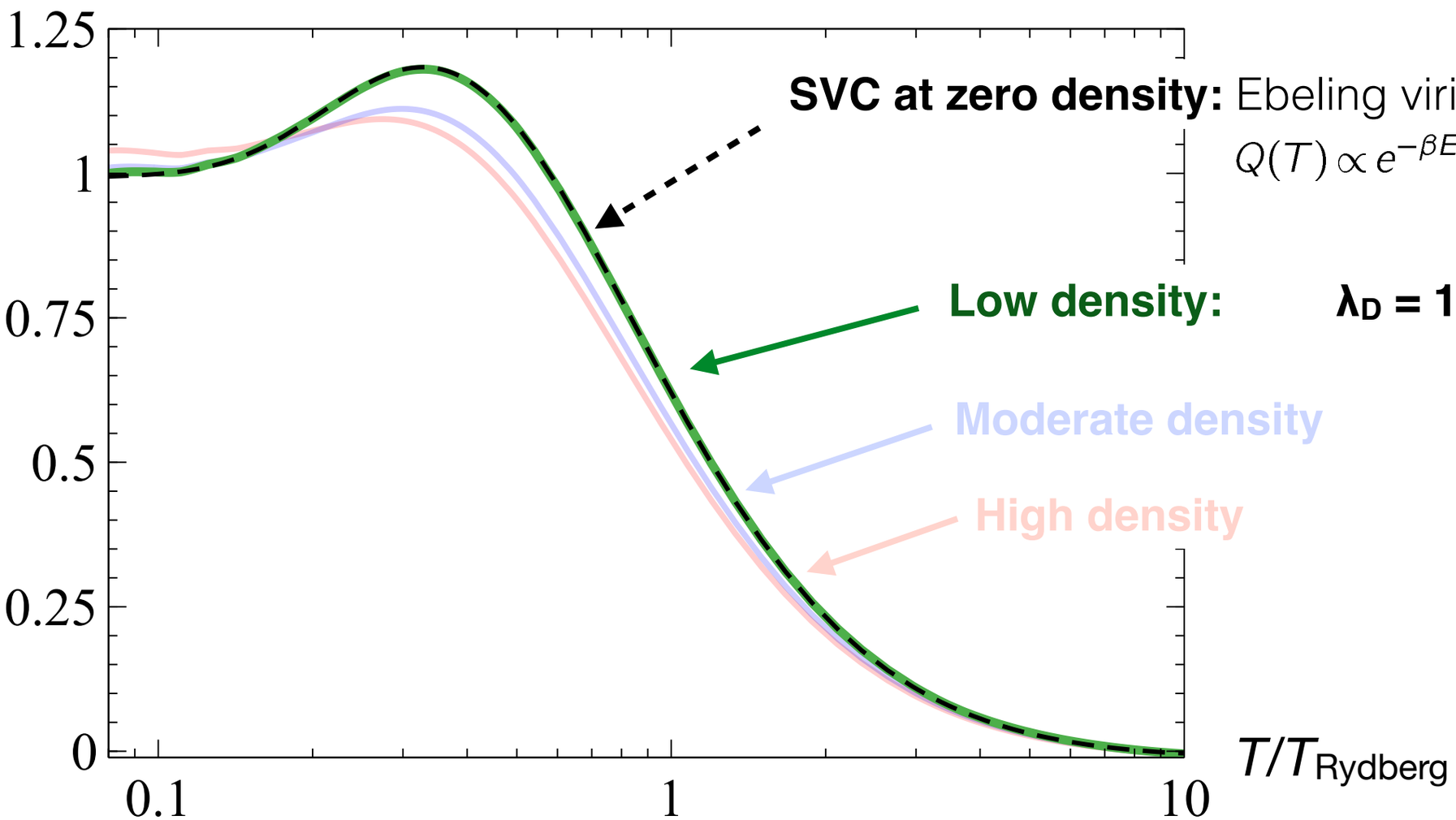
➜ **SC EOS** at 3rd order for **H-He mixtures**

I. Second Virial Coefficient: density dependence (pure H gas)

As $z \to 0$, the coefficient of z^2 is determined by:



PIMC code to calculate $\int d\vec{r}_1 \int \mathcal{D}[\vec{r}_1(\cdot)]\mathcal{D}[\vec{r}_2(\cdot)]\,(e^{-\beta\phi(\mathcal{L}_1,\mathcal{L}_2)}-1+\beta\phi-\frac{(\beta\phi)^2}{2})e^{-\frac{1}{2}\beta[\phi_{ph}(\mathcal{L}_1)+\phi_{ph}(\mathcal{L}_2)]}$

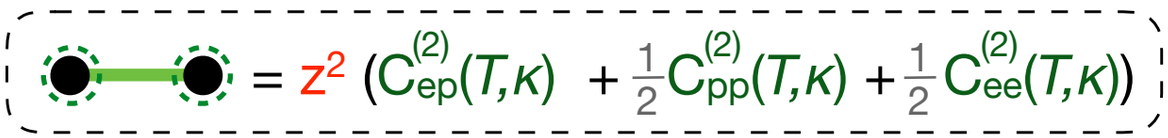


Deviations at finite density due to **broadening** and **shifts** in the atomic spectrum.

[Ballenegger et al., 2017]

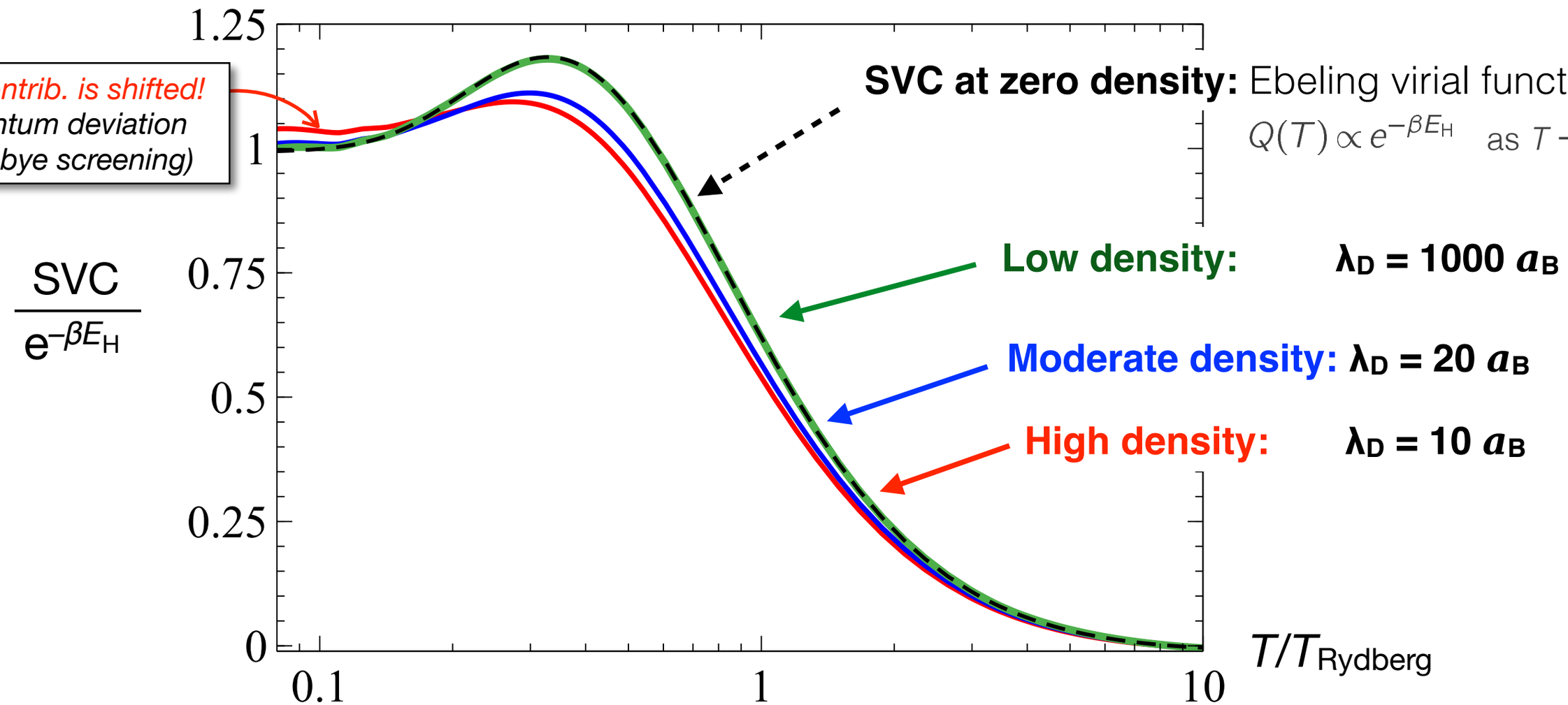
I. Second Virial Coefficient: density dependence (pure H gas)

As $z \to 0$, the coefficient of z^2 is determined by:



PIMC code to calculate $\int d\vec{r}_1 \int \mathcal{D}[\vec{r}_1(\cdot)]\mathcal{D}[\vec{r}_2(\cdot)]\,(e^{-\beta\phi(\mathcal{L}_1,\mathcal{L}_2)}-1+\beta\phi-\frac{(\beta\phi)^2}{2})e^{-\frac{1}{2}\beta[\phi_{ph}(\mathcal{L}_1)+\phi_{ph}(\mathcal{L}_2)]}$

GS contrib. is shifted! (quantum deviation to Debye screening)



SVC at zero density: Ebeling virial function

$Q(T) \propto e^{-\beta E_H}$ as $T \to 0$

Low density: $\lambda_D = 1000\ a_B$

Moderate density: $\lambda_D = 20\ a_B$

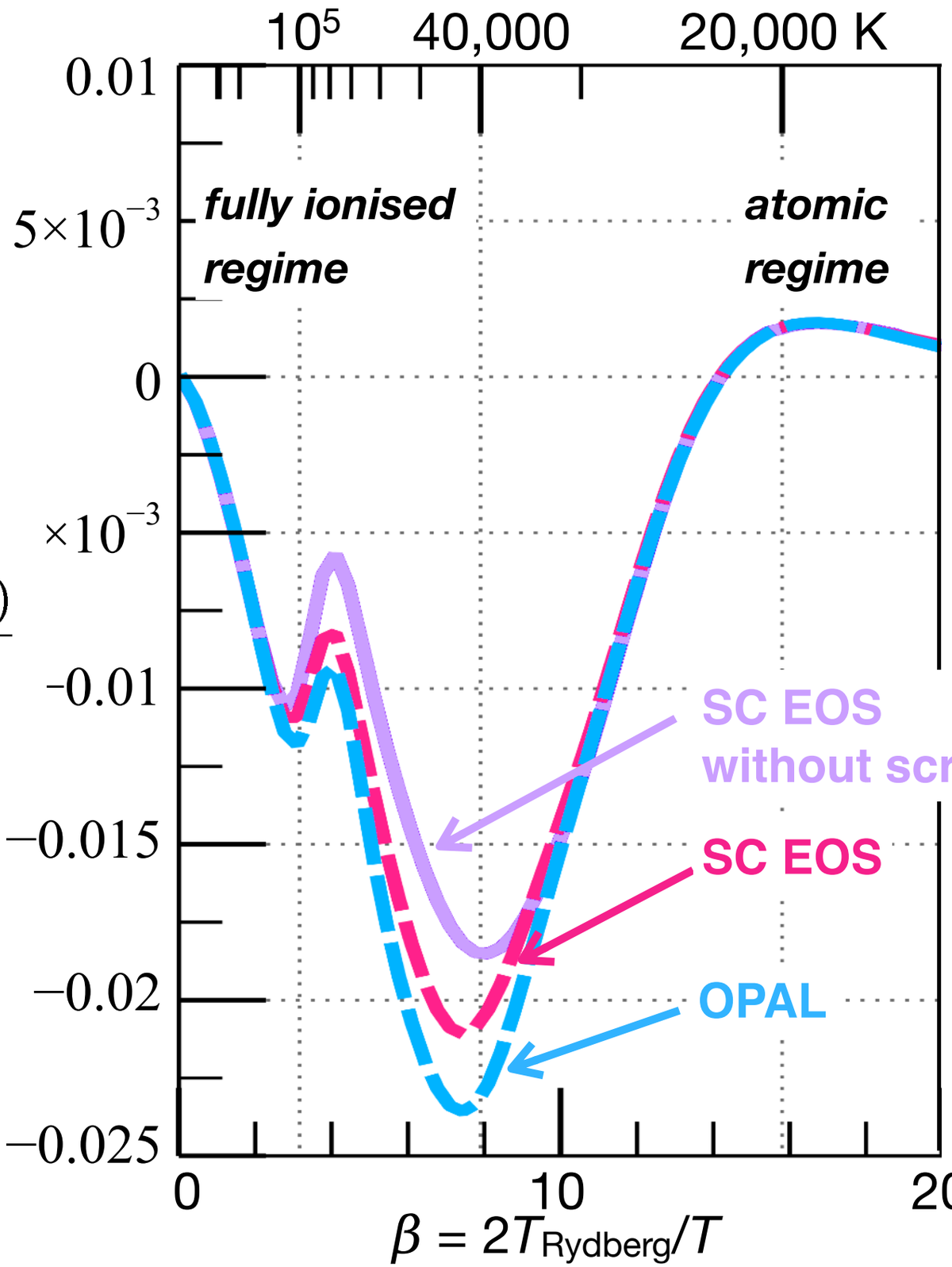
High density: $\lambda_D = 10\ a_B$

Deviations at finite density due to **broadening** and **shifts** in the atomic spectrum.

[Ballenegger et al., 2017]

II. **Pressure isochore** in a **H-He mixture**

75% H
25% He



$\rho = 10^{-5}\, a_B^{-3}$

Transition region:
small differences SC / OPAL

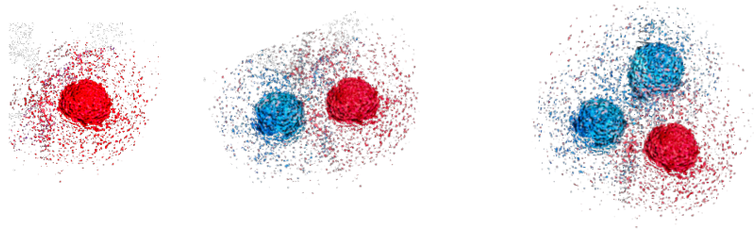
λ_D modified by He^+ ions.

Bound states
H, He, He^+, H_2^+, H^-
+ atom-charge interactions
treated without approximation

Wendland, PhD thesis (2015)

Conclusions

Screened cluster EOS at 3rd order



It accounts for **all 1, 2 and 3-particle effects** in a quantum plasma.

✔ **Few-particle cluster functions** calculated with a PIMC code.

→ *ρ-dependence of virial coeffs*

→ *2-particle* (**H, He^+**) *and 3-particle* (**He, H_2^+, H^-**) *cluster functions*

Effective interaction φ (≈ RPA potential) which includes quantum corrections to Debye screening.

✔ No **double-counting of bound/scatt. states** contributions to thermodynamics

- **no arbitrary regularisation** for internal partition fcts
- **no modelization** for atom-charge interactions

✔ **Modular**: easy to add/remove effects in Ω.

Validity conditions

- not too strong coupling and degeneracy
- non relativistic

~ OK for solar conditions

Perspectives

- Guide to more phenomenological theories at higher density
- 4-particle cluster fct: exact H-H interactions
  exact partition function for H_2 molecule