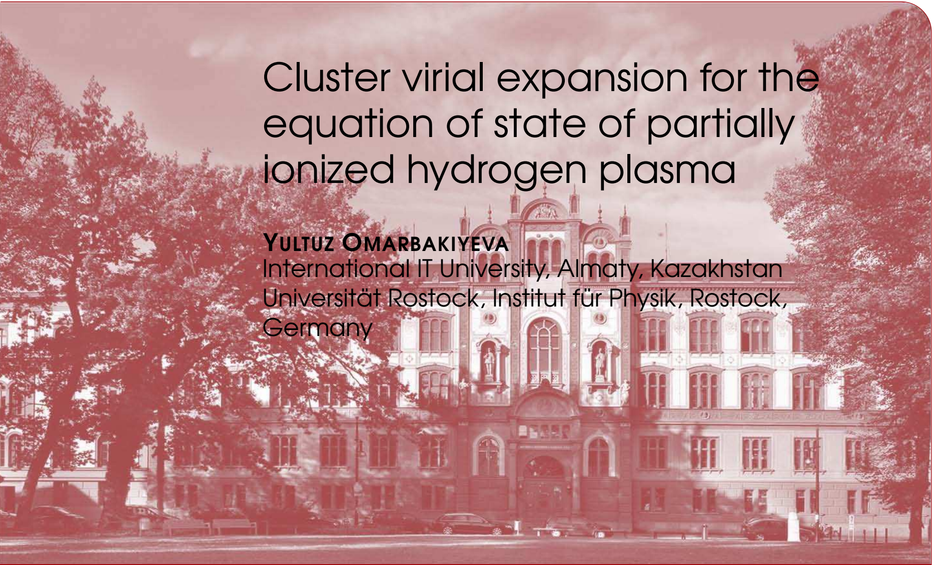

Cluster virial expansion for the equation of state of partially ionized hydrogen plasma

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Outline

- Thermodynamics of partially ionized plasma
- The Beth-Uhlenbeck formula
- Interaction of electrons with atoms
- Elastic scattering of electrons on hydrogen atoms
- Results for the second virial coefficient
- Comparison of the results with the excluded volume concept
- Generalized Beth-Uhlenbeck approach & Pauli blocking

Phase diagram of hydrogen

Temperature

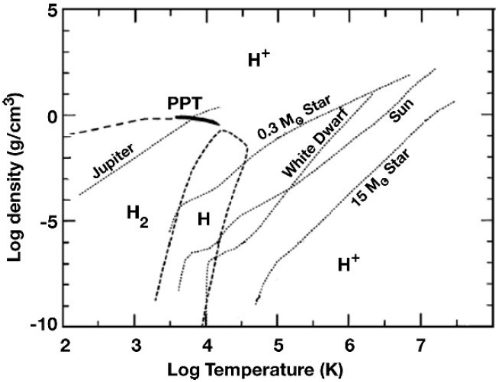
$$T = 5\times10^3 - 2\times10^4 K$$

Density

$$n_e^{\mathrm{total}} \leq 10^{22}\mathrm{cm}^{-3}$$

Parameters

$$\Gamma \leq 0.9 \quad \theta \geq 0.26$$



$$n_e^{\mathrm{total}} = n_e^{\mathrm{free}} + n_e^{\mathrm{bound}}$$

phase diagram was taken from D. Saumon, G. Chabrier and et al *High Pres. Res.* **16** 331 (2000)

Thermodynamics of partially ionized plasma

- bound states are important
- problem of $e - a$ interaction
- excluded volume concept

Physical picture

- treats the fundamental particles (electrons and protons)
- density virial expansion (contributions of interacting particles $e - e, e - i, e - a ...$)
- bound states appear in higher order virial coefficients
- Green function approach (expansion in e^2 for charged particles)[1]

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[1] W.D. Kraeft and et. al. *Quantum Statistics of Charged Particle Systems* 1986

Thermodynamics of partially ionized plasma

Chemical picture

- treats all components of plasma as separate species
- Composition: electrons, ions, atoms (c)
- Mass Action Law n_c
  total electron & ion densities: $n_e^{tot} = n_e + n_H, n_i^{tot} = n_p + n_H$
- Ionization equilibrium $\mu_p + \mu_e = \mu_H$
- Ideal system, non-ideal (interacting) system
- excluded volume concept

Cluster-virial expansion for the equation of state[4] [5]

- from physical to chemical picture
- Bound states = New particles (atoms)
- expansion in density of clusters (atoms)
- bound states appear in lower order virial coefficients
- Beth-Uhlenbeck formula
- nuclear systems [2], electron-hole system[3]

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[2] G.Röpke, H.Schulz, L.Münchow *Nucl. Phys. A* **379** 536 (1982)
[3] W.D. Kraeft, K.Kilimann, D.Kremp *phys.stat.sol.(b)* **72** 461 (1975)
[4] C.J. Horowitz, A. Schwenk *Nuc. Phys. A* **776** 55 (2006)
[5] W.Ebeling, W.D. Kraeft, D.Kremp *Theory of bound states and ionization equilibrium in plasmas and solids* 1976

The second virial coefficient & the Beth-Uhlenbeck formula[6] [7]

$$b_{cd} = \frac{\Lambda_d^3}{g_d}\left[\delta_{cd}\tilde{b}_{cd}^{(0)} + \tilde{b}_{cd}^{\text{bound}} + \tilde{b}_{cd}^{\text{sc}}\right]$$

- $\tilde{b}_{cd}^{\text{bound}}$ is bound part of the second virial coefficient → binding energy
- $\tilde{b}_{cd}^{\text{sc}}$ is scattering part of the second virial coefficient → scattering phase shifts

The aim of the work

- partially ionized hydrogen plasma: electrons, protons and atoms (two-body cluster)
- focus on the electron-atom $(e-a)$ contribution → exact $b_{ea}(T)$
- interaction of electron with atom → scattering phase shifts
- dense medium → Pauli blocking → $b_{ea}(T, n_e)$

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[6] E. Beth, G.E. Uhlenbeck *Physica* **4** 915 (1937)

[7] Y. A. Omarbakiyeva, C. Fortmann, T. S. Ramazanov and G. Röpke *Phys.Rev.E* **82** 026407 (2010)

The Beth-Uhlenbeck formula for e-H interaction

Bound part

$$\tilde{b}_{ae}^{\text{bound},\ singlet} = \frac{1}{4}\sum_{\ell}(2\ell+1)\sum_{n}\mathrm{e}^{-\beta\, E_{n\ell}^{ae}}$$

- bound state exists only in singlet channel
- $E_{n\ell}^{ae}$ is binding energy for H^{-}
- $E_B^{eH} = -0.7542$ eV is taken from experiment [8]

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[8] K. E. McCulloh and J. A. Walker. *Chem. Phys. Lett.* **25** 439 (1974)

The Beth-Uhlenbeck formula for e-H interaction

Scattering part for singlet channel

$$\tilde{b}_{ae}^{\mathrm{sc,singlet}} = \frac{1}{4}\sum_{\ell=0}^{\infty}(2\ell+1)\left[\frac{1}{\pi}\int_0^{\infty} \mathrm{e}^{-\beta E}\,\frac{d}{dE}\,\eta_\ell^{ae,\mathrm{singlet}}(E)\;dE\right]$$

Scattering part for triplet channel

$$\tilde{b}_{ae}^{\mathrm{sc,triplet}} = \frac{3}{4}\sum_{\ell=0}^{\infty}(2\ell+1)\left[\frac{1}{\pi}\int_0^{\infty} \mathrm{e}^{-\beta E}\,\frac{d}{dE}\,\eta_\ell^{ae,\mathrm{triplet}}(E)\;dE\right]$$

- experimental data of the scattering phase shifts $\eta_\ell^{ae}(E)$ are taken from Williams [9]

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[9] J.F. Williams *J. Phys. B,* **8** 1683 (1975)

Scattering theory

Methods:

- Variational method [10]- Experimental proved data
- Close-coupling approximation [11]
- Semiclassical method (WKB-approximation) [12]
- Wave expansion method (Calogero equation) [13]

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[10] C. Schwartz *Phys.Rev.* **124** 1468 (1961)

[11] P.G. Burke, M.J. Seaton *Meth. Comput. Phys.* **10** 1 (1971)

[12] L.D. Landau, E.M. Lifschitz, Quantum mechanics III, 1989

[13] V.V. Babikov, The Method of Phase Functions in Quantum Mechanics, 1988

Theoretical phase shifts for e-H scattering

Calogero equation[14]

$$\frac{d}{dr}\eta_\ell^{cd}(k,r) = -\frac{1}{k}\,U_{cd}(r)\left[\cos\eta_\ell^{cd}(k,r)\,j_\ell(kr) - \sin\eta_\ell^{cd}(k,r)\,n_\ell(kr)\right]^2$$

- $U_{cd}(r) = \frac{2\mu_{cd}}{\hbar^2}V_{cd}(r)$, $V_{cd}(r)$ is the interaction potential.
- $j_\ell(kr)$ and $n_\ell(kr)$ are the Ricatti-Bessel functions
- Initial condition $\eta_\ell^{cd}(k,0) = 0$
- The phase shifts are defined $\eta_\ell^{cd}(k) = \lim_{r\to\infty}\eta_\ell^{cd}(k,r)$

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[14] V.V. Babikov, The Method of Phase Functions in Quantum Mechanics, 1988

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[14] V.V. Babikov, The Method of Phase Functions in Quantum Mechanics, 1988

Phase shifts for e-H scattering

Levinson theorem $\eta(0) = n\pi$

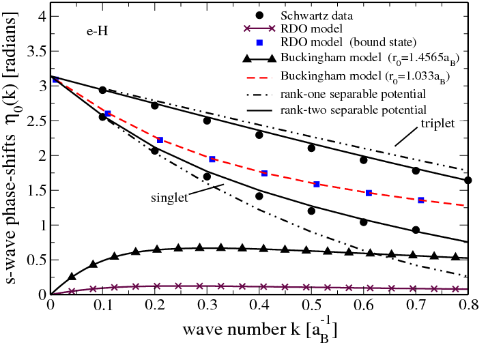
bound state: singlet channel

interaction models:

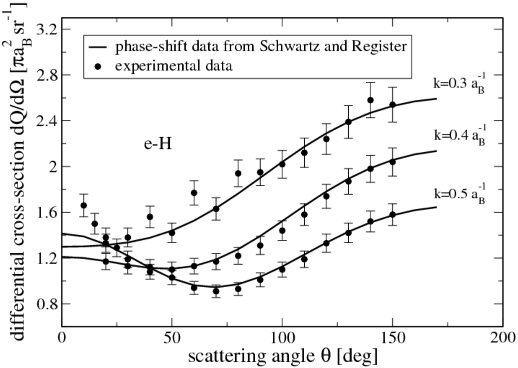
- no bound states
  with ordinary parameters

separable potential:

- good agreement with
  "experimantal proved" data



Experimental phase shifts for e-H scattering[15]



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[15] J.F. Williams *J. Phys. B*, **8** 1683 (1975)

RESULTS for the second virial coefficient for the singlet channel

T, K	$\tilde{b}_{ae}^{\mathrm{sc,sing}}$, s	$\tilde{b}_{ae}^{\mathrm{sc,sing}}$, p	$\tilde{b}_{ae}^{\mathrm{sc,sing}}$, d	$\tilde{b}_{ae}^{\mathrm{b,sing}}$	$\tilde{b}_{ae}^{\mathrm{sing}}$ full
5000	-0.0499	0.0012	0.0007	1.4401	1.3922
10000	-0.0670	0.0021	0.0015	0.6000	0.5366
20000	-0.0873	0.0024	0.0029	0.3873	0.3054
30000	-0.1004	0.0022	0.0043	0.3347	0.2409
40000	-0.1099	0.0019	0.0057	0.3111	0.2089
50000	-0.1172	0.0016	0.0072	0.2978	0.1894
60000	-0.1230	0.0015	0.0088	0.2892	0.1765
70000	-0.1276	0.0015	0.0105	0.2833	0.1678
80000	-0.1312	0.0017	0.0125	0.2789	0.1620
90000	-0.1340	0.0022	0.0148	0.2755	0.1584
100000	-0.1361	0.0028	0.0172	0.2728	0.1568

Thermodynamical properties

using the second virial coefficient

- Free energy
- Pressure
- Chemical potential
- Internal energy

The excluded volume concept [17]

- hard-sphere model
- effective volume, occupied by atoms $V^* = V(1-\eta)$
- filling parameter $\eta = V^{HS}/V = \frac{4}{3}\pi r_a^3 n_a$
- r_a is empirical parameter
- free energy $F = F^{id}(T, V^*, N_c)$ [16]
- second virial coefficient $b_{ea}^{ex} = -\frac{2}{3}\pi r_a^3$
- comparison with the triplet part of the second virial coefficient

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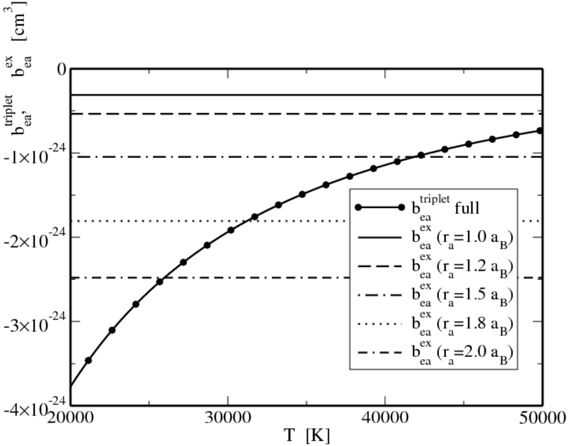
[16] R. Redmer, B. Holst, H.Juranek, N. Nettelmann, V.Schwarz *J.Phys.A* **39** 4479 (2006)

[17] W.Ebeling, A. Förster, V.E. Fortov and et al *Thermophysical properties of hot dense plasmas* 1991

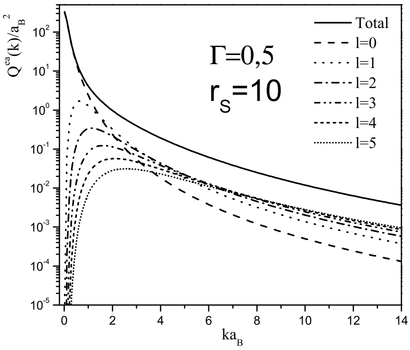
Triplet second virial coefficient & the excluded volume concept



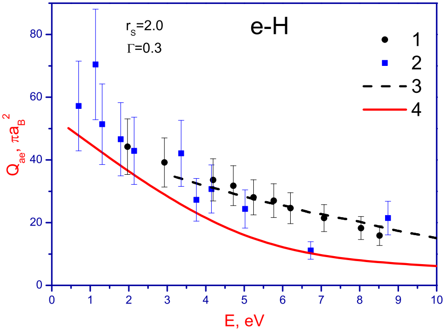
Conclusions

- First principle results for $e-a$ contribution for the equation of state (data tables) are presented
- The second virial coefficient for $H-H$ and $e-H$ pairs is considered by the Beth-Uhlenbeck formula
- The different type of interaction potential models are used and compared with empirical data
- The accurate calculation of the free energy excess due to electron-atom interaction is compared with excluded volume results
- Influence of the Pauli blocking on the thermodynamic properties of partially-ionized dense hydrogen is studied

Total and partial cross sections for e-H scattering for the RDO-model



Total cross section for e-H scattering for the RDO-model



1- R.T. Brackmann and W.L.Fite *Phys.Rev.* **112** 1157 (1958)
2- P.N.Eisner PhD thesis, New York, 1969
3- R.Neynaber, L.L. Marino, et al *Phys.Rev.* **124** 135 (1961)

4- data of present work

Density virial expansion

Start with the canonical partition function of an interacting many-particle system

$$Z^{\mathrm{can}}(T,V,N_c) = \mathrm{Tr}\left\{\exp(-\beta H)\right\} ,$$

The Hamiltonian

$$\begin{aligned} H = {} & \sum_{j=1}^{N_e} \frac{p_j^2}{2m_e} + \sum_{k=1}^{N_i} \frac{p_k^2}{2m_i} + \sum_{l=1}^{N_a} \frac{p_l^2}{2m_a} + \sum_{j=1}^{N_e}\sum_{k=1}^{N_i} V_{ei}(\vec{r_j} - \vec{r_k}) \\ & + \sum_{j=1}^{N_e}\sum_{l=1}^{N_a} V_{ea}(\vec{r_j} - \vec{r_l}) + \sum_{k=1}^{N_i}\sum_{l=1}^{N_a} V_{ia}(\vec{r_k} - \vec{r_l}) \\ & + \frac{1}{2}\sum_{j<j'}^{N_e} V_{ee}(\vec{r_j} - \vec{r_{j'}}) + \frac{1}{2}\sum_{k<k'}^{N_i} V_{ii}(\vec{r_k} - \vec{r_{k'}}) + \frac{1}{2}\sum_{l<l'}^{N_a} V_{aa}(\vec{r_l} - \vec{r_{l'}}) \end{aligned}$$

Density virial expansion

Free energy

$$F(T,V,N_c) = F_{\rm id}(T,V,N_c) - k_{\rm B}TV\left\{\sum_{cd} n_c n_d b_{cd} + \sum_{cde} n_c n_d n_e b_{cde} + ...\right\}$$

Pressure

$$p(T,V,N_c) = p_{\rm id}(T,V,N_c) - k_{\rm B}T\left\{\sum_{cd} n_c n_d b_{cd} + 2\sum_{cde} n_c n_d n_e b_{cde} + ...\right\}$$

Chemical potential

$$\mu_c(T,V,N_c) = \mu_{c,\rm id}(T,V,N_c) - k_{\rm B}T\left\{2\sum_{d} n_d b_{cd} + 3\sum_{de} n_d n_e b_{cde} + ...\right\}$$

b_{cd} and b_{cde} are the second and third virial coefficients

Fugacity virial expansion

Start with the grand canonical partition function including fugacities

$$\Omega(z_c, T, V) = 1 + \sum_{c=e,i,a} z_c \Omega_c(T, V) + \sum_{c,d} z_c z_d \Omega_{cd}(T, V) + \mathcal{O}({z_c}^3)\,.$$

- Function of fugacity

$$\boxed{z_c = e^{\beta(\mu_c - E_c^{(0)})}}$$

- $E_c(0)$ is binding energy
- Pressure

$$P(z_c, T, V) = \frac{k_\mathrm{B} T}{V} \ln \Omega(z_c, T, V)$$

Cluster virial expansion

Pressure

$$\frac{P(z_c, T, V)}{k_\mathrm{B} T} = \sum_c \frac{g_c}{\Lambda_c^3} \left(z_c + \sum_d z_c z_d \tilde{b}_{cd} \right)$$

- $g_c = 2s_c + 1$ is the spin degeneracy factor
- $\Lambda_c = \left(2\pi\hbar^2 / m_c k_\mathrm{B} T\right)^{1/2}$ is the thermal wavelength
- second virial coefficient $\tilde{b}_{cd} = \frac{g_d}{\Lambda_d^3} b_{cd}$
- free energy, chemical potential, entropy, internal energy, number densities (mass action law)