Ion-correlative model of dense plasmas:

structural and thermodynamical properties of warm dense matter

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РФЯЦ–ВНИИТФ
Предприятие госкорпорации «Росатом»

Contents

RDFs — Radial Distribution Functions

Plasmas with correlated non-ideal ions

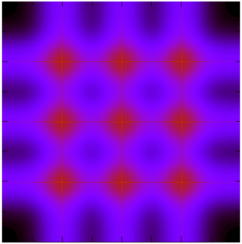
Ion-Ion Coulomb parameter (for simple elements)

$$\Gamma \sim \frac{E_{\text{Coul.}}}{E_{\text{kin.}}}, \qquad \Gamma \equiv \frac{\overline{Z}^2 e^2}{r_0 T}, \qquad r_0 = \left(\frac{3}{4\pi n_I^0}\right)^{1/3}, \; k_B = 1$$

$\overline{Z}$ — mean ion charge, $n_I^0 = N_A \rho / A$ — ionic density

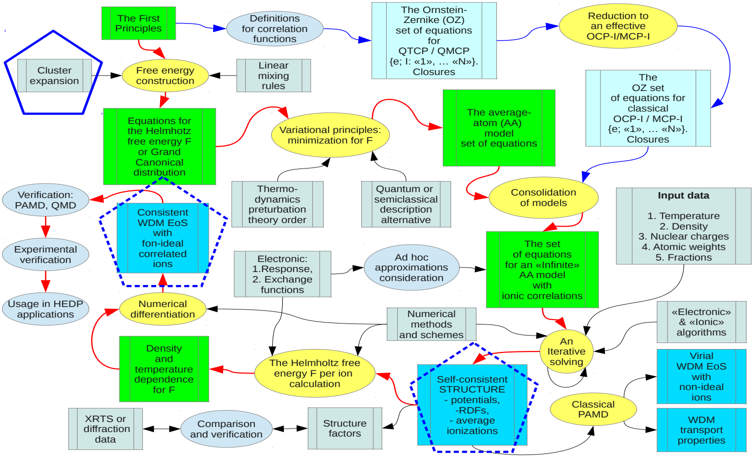
- $\Gamma \ll 1$ — ideal ion gas (Debye);
- $1 \leqslant \Gamma \leqslant 150$ — **WDM** regime with strong ionic correlations;
- $\Gamma \geqslant 150 \div 220$ — phase transition («?») into the plasmas Coulomb crystal (Wigner)

Example:



2D dynamic plasmas phase plate for CO_2 laser, 400 ps after illumination, carbon microfilaments at $T_e = T_i \sim 0.1$ keV

Generating EOS data
by using AA models with ion correlations



⊡ — **statements and results,** ◯ — **actions and transformations,**

$$dF = -SdT - pdV \;\Rightarrow\; p = -\left(\frac{\partial F}{\partial V}\right)_{|T}, \;\; E = F + TS - \widetilde{E_0} = F - T\left(\frac{\partial F}{\partial T}\right)_{|V} - \widetilde{E_0}$$

Helmholtz free energy

Treatment of ion correlations in various plasma models

- Thomas-Fermi-Dirac, INFERNO, VAAQP, ... $\Leftarrow$
  $\Leftarrow\ g_{II}(r) = \Theta\,(r - r_0)$
- THERMOS, RESEOS $\Leftarrow$ Phenomenology —
  charged hard spheres: excluded volume +
  + OCP of interacting ions (crude correction to pressure)
- Chemical-picture models $\Leftarrow$ Phenomenology —
  hard spheres (excluded volume) +
  + OCP of interacting ions (consistent treatment via F)
- Perrot, Rosenfeld $\Leftarrow$ TF $+ V_{II}^{eff}\,[r, g_{II}, V_{tot}\,[g_{II}]] +$
  + Ornstein & Zernike (OZ) equations (1914) for $g_{II}(r)$

$$\boxed{\Downarrow\ V_{el}\,[g_{II}]\ \Rightarrow\ n_e\,[V_{el}]\ \Rightarrow\ V_{II}\,[n_e, c_{Ie}, c_{ee}, ...]\ \Rightarrow\ g_{II}(r)\ \circlearrowleft}$$

- QHNC $\Leftrightarrow$ Average atom $\bigcup$ TCP (e-I) model $\bigcup$ «jellium»
- Rozsnyai $\Leftarrow$ $c_{Ie},\ c_{II}$ — «pure» Coulomb without LFC +
  + g_{II} — from OZ set of equations
- TFSC, QMSC (Starrett & Saumon) $\Leftarrow$ $c_{Ie},\ c_{II}$ —
  with LFC + g_{II} — from OZ set of equations with hypernetted chain (HNC) closure ...

OZ set of equations — J.-P. Hansen, I. R. McDonald. Theory of Simple Liquids. — N.-Y., «Acad. Press» (2006).
HNC closure — J. M. J. van Leeuwen, J. Groeneveld, J. de Boer. Physica 25, 792 (1959).

The model of C. E. Starrett & D. Saumon: generalization for plasmas of dense mixtures

$(\beta_e = \beta_i = \beta = 1/T;\quad i = \overline{1, N},\quad N$— **the number of ion species**$)$

$$\left\{\begin{array}{l}\boxed{\mathrm{A}^{(1)}_{\varkappa_1}\mathrm{A}^{(2)}_{\varkappa_2}\ldots\mathrm{A}^{(N)}_{\varkappa_N}}\\ \mathrm{Cu_{38.1}Zn_{4.12}Al}\end{array}\right. \Rightarrow \omega_i = \frac{\varkappa_i \mathrm{A}^{(i)}}{\sum\limits_{j=1}^{N}\varkappa_j \mathrm{A}^{(j)}},\; x_i = \frac{\varkappa_i}{\sum\limits_{j=1}^{N}\varkappa_j},\; \left\{\begin{array}{l}\sum\limits_{i=1}^{N}\omega_i = 1,\\ \sum\limits_{i=1}^{N}x_i = 1.\end{array}\right.$$

$$\boxed{F_{tot} = \sum_{i=1}^{N}\omega_i F_i = \sum_{i=1}^{N}\omega_i\left(F_i^{id} + F_i^{el} + F_i^{xc}\right),}$$

$$\left\{\begin{array}{l}\lim\limits_{r\to\infty} n_{e_i}(\mathbf{r}) = n_e^0 = \textbf{invar} \;\Rightarrow\; \triangle n_{e_i}(\mathbf{r}) = n_{e_i}(\mathbf{r}) - n_e^0,\\ \lim\limits_{r\to\infty} n_i(\mathbf{r}) = n_i^0 \;\Rightarrow\; \triangle n_i(\mathbf{r}) = n_i(\mathbf{r}) - n_i^0 \left(\overline{n_i^0} \equiv \omega_i n_{tot} \neq n_i^0\right).\end{array}\right.$$

$$\boxed{F_i = \mathcal{F}_i + F_i^C} = \mathcal{F}_i + \int_{V_\infty} d\mathbf{r}\left(V^C_{N_i e_i}(\mathbf{r})\triangle n_{e_i}(\mathbf{r}) + V^C_{N_i i}(\mathbf{r})\triangle n_i(\mathbf{r})\right).$$

«non-Coulombic» contribution $\rightarrow \mathcal{F}_i = F_i^{id} + \mathcal{F}_i^{ex} = \left(F_{e_i}^{id} + F_{I_i}^{id}\right) + \mathcal{F}_i^{ex}$,

$$F_i^{el} + F_i^{xc} = \mathcal{F}_i^{ex} + F_i^C = \mathcal{F}_i^{ex} - Z_i\int_{V_\infty}\frac{d\mathbf{r}}{r}\underbrace{\left(\triangle n_{e_i}(\mathbf{r}) - Z_i^\star \triangle n_i(\mathbf{r})\right)}_{\equiv \mathcal{N}_{Ie_i}(\mathbf{r})}$$

Helmhotz free energy

The general scheme. «Ideal gas» (non-interacting) contributions

$$F_i = \underbrace{\left(F^{id}_{I_i} + F^{id}_{e_i}\right)}_{F^{id}_i} + \underbrace{\left(F^{el}_{0_i} + \triangle F^{el}_i\right)}_{F^{el}_i} + \underbrace{\left(F^{xc}_{0_i} + \triangle F^{xc}_{ie_i} + \triangle F^{xc}_{ii} + \triangle F^{xc}_{e_ie_i}\right)}_{F^{xc}_i}$$

Cluster expansion for the «ideal gas»-like «I» & «e» contributions:

$$F^{id}_{I_i} = \frac{1}{\beta}\ln\left|\frac{n^0_i\Lambda^3_i}{e}\right| + \frac{n^0_i}{\beta}\int_{V_\infty} d\mathbf{r}\left(g_{ii}(r)\ln\left|\frac{n^0_i g_{ii}(r)\Lambda^3_i}{e}\right| - \ln\left|\frac{n^0_i\Lambda^3_i}{e}\right|\right),$$

$$F^{id}_{e_i} = \frac{1}{n^0_I}\left[n^0_e\mu^{id}_{e_i} - \frac{2}{3\beta}C_{TF}I_{3/2}\left[\beta\mu^{id}_{e_i}\right]\right] +$$

$$+\int_{V_\infty} d\mathbf{r}\left[n_{e_i}(r)\frac{\Phi_i(r)}{\beta} - \frac{2}{3\beta}C_{TF}\left(I_{3/2}\left[\Phi_i(r)\right] - I_{3/2}\left[\beta\mu^{id}_{e_i}\right]\right) - n^0_e\mu^{id}_{e_i}\right],$$

$$C_{TF} = \frac{\sqrt{2}}{\pi^2\beta^{3/2}};\ \Phi_i(r) = \beta\left[\mu^{id}_{e_i} - V^{eff}_{N_ie_i}(r)\right],\ n_{e_i}(r) = C_{TF}I_{1/2}\left[\Phi_i(r)\right].$$

$\uparrow$ $\{e_i, i\}$ spatial correlated «gases» with non-interactive particles

Λ = const — ionic de Brogile wavelength, C_{TF} = const.

«Cluster expansion» — T. Blenski, B. Chichoki. Phys. Rev. E 75, 0056402 (2007).

Ion contribution (without the cluster expansion) F^{id}_I — J.-P. Hansen, I. R. McDonald. Theory of Simple Liquids. — N.-Y., «Acad. Press» (2006).

Electronic gas contribution (without the cluster expansion) F^{id}_e — J. Clérouin, E. L. Polloc, G. Zerah. Phys. Rev B 46, 5130 (1992).

Construction to the Helmholtz free energy

Second-order correlative theory

$$\triangle\mathcal{F}_i^{ex} = \mathcal{F}_i^{ex} - \left(\mathcal{F}_i^{ex}\right)^0 = \mathcal{F}_i^{ex} - \frac{f_i^0}{n_i^0} = \sum_{p=1}^{S}\frac{1}{p!}\sum_{\alpha_1=1}^{2}\dots\sum_{\alpha_p=1}^{2}\int\limits_{V_\infty} d\mathbf{r}_1\dots d\mathbf{r}_p\times$$

$$\times\left(\frac{\delta^p\mathcal{F}_i^{ex}}{\delta\triangle n_{\alpha_1}(\mathbf{r}_1)\dots\delta\triangle n_{\alpha_p}(\mathbf{r}_p)}\right)_{|0_{\alpha_1}\dots 0_{\alpha_p}}\prod_{t'=1}^{p}\triangle n_{\alpha_{t'}}(\mathbf{r}_{t'}),$$

$$0_{\alpha_p} \quad\Leftrightarrow\quad V^C_{N_i\alpha_p}(r) = \frac{1}{r}\begin{cases} Z_i Z_i^\star, & \alpha_p = 1,\\ -Z_i, & \alpha_p = 2\end{cases} \quad\to 0.$$

$$S\equiv 2 \;\Rightarrow\; \triangle\mathcal{F}_i^{ex} = \sum_{\alpha=1}^{2}\int\limits_{V_\infty} d\mathbf{r}\,\underbrace{\left(\frac{\delta\mathcal{F}_i^{ex}}{\delta\triangle n_\alpha(\mathbf{r})}\right)_{|0_\alpha}}_{\equiv\mu_\alpha^{ex}}\triangle n_\alpha(\mathbf{r}) +$$

$$+\frac{1}{2}\sum_{\alpha=1}^{2}\sum_{\beta=1}^{2}\int\limits_{V_\infty} d\mathbf{r}d\mathbf{r}'\,\underbrace{\left(\frac{\delta^2\mathcal{F}_i^{ex}}{\delta\triangle n_\alpha(\mathbf{r})\,\delta\triangle n_\beta(\mathbf{r}')}\right)_{|0_\alpha 0_\beta}}_{\equiv -c_{\alpha\beta}(|\mathbf{r}-\mathbf{r}'|)/\beta}\triangle n_\alpha(\mathbf{r})\triangle n_\beta(\mathbf{r}').$$

Direct corr. functions $\to$ $c_{\alpha\beta}(|\mathbf{r}-\mathbf{r}'|) = \widetilde{c_{\alpha\beta}}(|\mathbf{r}-\mathbf{r}'|) - \beta V^C_{\alpha\beta}(|\mathbf{r}-\mathbf{r}'|)$.

Exchange and correlative contributions to the Helmholtz energy

$$\boxed{F_i^{xc} = F_{0_i}^{xc} + \triangle F_{ii}^{xc} + \triangle F_{ie_i}^{xc} + \triangle F_{e_ie_i}^{xc}}$$

$$\triangle F_{ii}^{xc} = \frac{-1}{2\beta} \int\limits_{V_\infty} d\mathbf{r} d\mathbf{r}' \, \widetilde{c_{ii}} \left[(|\mathbf{r} - \mathbf{r}'|), n_e^0 \right] \triangle \, n_i(r) \triangle \, n_i(r') \, ,$$

$$\triangle F_{ie_i}^{xc} = \frac{-1}{\beta} \int\limits_{V_\infty} d\mathbf{r} d\mathbf{r}' \, \widetilde{c_{e_i i}} \left[(|\mathbf{r} - \mathbf{r}'|), n_e^0 \right] \left(\triangle n_{e_i}(r) - n_{e_i}^{ion}(r) \right) \triangle n_i(r') \, ,$$

$$\triangle F_{e_ie_i}^{xc} = \frac{-1}{2\beta} \int\limits_{V_\infty} d\mathbf{r} d\mathbf{r}' \, \widetilde{c_{e_ie_i}} \left[(|\mathbf{r} - \mathbf{r}'|), n_e^0 \right] \triangle \, n_{e_i}(r) \triangle \, n_{e_i}(r') \, .$$

We usually use a «cluster expansion» for the electronic exchange contribution $\triangle F_{e_ie_i}^{xc}$ in our routine calculations:

$$\left(F_i^{xc} \right)^0 + \triangle F_{e_ie_i}^{xc} =$$

$$= \frac{-3}{4} \left(\frac{3}{\pi} \right)^{1/3} \left[\frac{\left(n_e^0 \right)^{4/3}}{n_i^0} - \int\limits_{V_\infty} d\mathbf{r} \left(n_{e_i}^{4/3}(r) - \left(n_e^0 \right)^{4/3} \right) \right] .$$

Problem: electrostatic contribution to the free energy

RFNC-VNIITF $\rightarrow$ F_i^{el} — from the Taylor expansion:

$$F_i^{el} = F_{0_i}^{el} + \triangle F_i^{el}, \quad F_{0_i}^{el} = \mu_{e_i}^{ex} \int_{V_\infty} d\mathbf{r} \triangle n_{e_i}(r) + \mu_i^{ex} \int_{V_\infty} d\mathbf{r} \triangle n_i(r),$$

$$\triangle F_i^{el} = -Z_i \int_{V_\infty} d\mathbf{r} \frac{\mathcal{N}_{Ie_i}(r)}{r} + \frac{1}{2} \int_{V_\infty} d\mathbf{r} d\mathbf{r}' \frac{\mathcal{N}_{Ie_i}(r) \mathcal{N}_{Ie_i}(r')}{|\mathbf{r} - \mathbf{r}'|},$$

$$\mathcal{N}_{Ie_i}(r) \equiv \triangle n_{e_i}(r) - n_e^0 \triangle n_i(r) / n_i^0.$$

LANL $\rightarrow$ F_i^{el} — from the averaging for sums in ionic pseudo-crystal:

$$F_i^{el} = \left(F_{NS}^{el}\right)_i + \langle F_S^{el} \rangle_i, \quad \left(F_{NS}^{el}\right)_i = \frac{1}{2} \int_{V_\infty} d\mathbf{r} n_{e_i}^{PA}(r) \left[\frac{-Z_i}{r} + V_i^{PA}(r)\right],$$

$$n_{e_i}^{PA}(r) \equiv n_{e_i}(r) - n_{e_i}^{\text{ion}}(r), \quad V_i^{PA}(r) \equiv \frac{-Z_i}{r} + \int_{V_\infty} d\mathbf{r}' \frac{n_{e_i}^{PA}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$\langle F_S^{el} \rangle_i = \frac{1}{2} \left[-Z_i V_{Ne_i}^{ext}(r=0) + \int_{V_\infty} d\mathbf{r} n_{e_i}^{PA}(r) V_{Ne_i}^{ext}(r)\right],$$

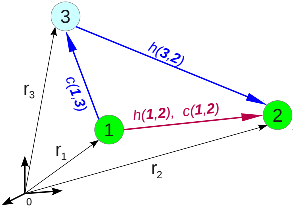
$$V_{Ne_i}^{ext}(r) = n_i^0 \int_{V_\infty} d\mathbf{r}' g_{ii}(|\mathbf{r} - \mathbf{r}'|) V_i^{PA}(r').$$

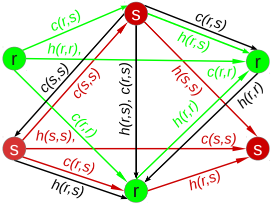
C. E. Starrett, D. Saumon. Phys. Rev. E 87, 013104 (2013), Phys. Rev. E 93, 063206 (2016).

The L. S. Ornstein – F. Zernike scheme

An approximate method for many-particle interaction treatment

One-component system case: **Two-component system case:**





$$(1) \to h\left(\mathbf{r}\right) = c\left(\mathbf{r}\right) + n_I^0 \int\limits_{V_\infty} d\mathbf{r}' h\left(\mathbf{r}'\right) c\left(\left|\mathbf{r}-\mathbf{r}'\right|\right)$$

$$(2) \to h_{rs}\left(\mathbf{r}\right) = c_{rs}\left(\mathbf{r}\right) + n_s^0 \int\limits_{V_\infty} d\mathbf{r}' h_{rs}\left(\mathbf{r}'\right) c_{ss}\left(\left|\mathbf{r}-\mathbf{r}'\right|\right) +$$

$$+ n_r^0 \int\limits_{V_\infty} d\mathbf{r}' h_{rr}\left(\mathbf{r}'\right) c_{rs}\left(\left|\mathbf{r}-\mathbf{r}'\right|\right)$$

c — direct pair correlative function;

h — full pair correlative function.

Ornstein-Zernike-Chihara system of equations

Reducted form for the plasmas with N various kinds of ion

OZ equations matrix form for the classical (non-quantum) ions:

$$\widehat{h}(k) = \widehat{c}(k) + \widehat{c}(k)\widehat{D}\widehat{h}(k), \; D_{ij} = \delta_{ij}\overline{n_j^0}, \; \begin{cases} \widehat{h}(k) = \{h_{ij}\}_{i,j=1}^N : \; \widehat{h} = \widehat{h}^T, \\ \widehat{c}(k) = \{c_{ij}\}_{i,j=1}^N : \; \widehat{c} = \widehat{c}^T. \end{cases}$$

System of closure equiations for the OZ system:

$$h_{ij}(r) + 1 = \exp\left(-\beta V_{ij}(r) + h_{ij}(r) - c_{ij}(r) + E_{ij}(r)\right), \quad i, j \leqslant N,$$

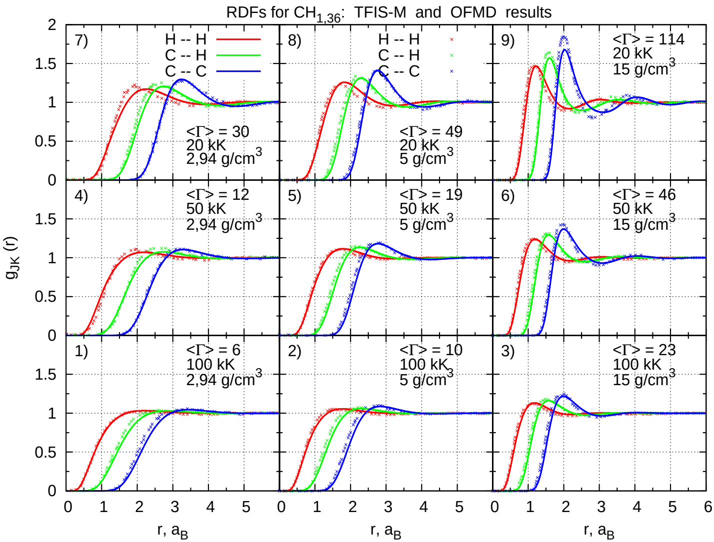
An effective ion-ion potential finding scheme:

$$V_{ij}(k) = 4\pi \frac{\overline{Z_i} \cdot \overline{Z_j}}{k^2} - \frac{c_{e_i i}(k)}{\beta} n_{e_j}^{\text{scr}}(k), \quad c_{e_i i}(k) = -\beta n_{e_i}^{\text{scr}}(k)/\chi'_{ee}(k),$$

$$\overline{Z}_i = \int\limits_{V_\infty} d\mathbf{r} n_{e_i}^{\text{scr}}(r), \qquad \chi'_{ee}(k) = \frac{\chi_{ee}^0(k)}{1 + \chi_{ee}^0(k) c_{ee}(k)/\beta},$$

$$n_{e_i}^{\text{scr}}(r) = n_{e_i}^{\text{PA}}(r) - n_{e_i}^{\text{ion}}(r) = n_{e_i}(r) - n_{e_i}^{\text{ext}}(r) - n_{e_i}^{\text{ion}}(r).$$

Partial ionic RDFs for the $CH_{1.36}$ plasmas

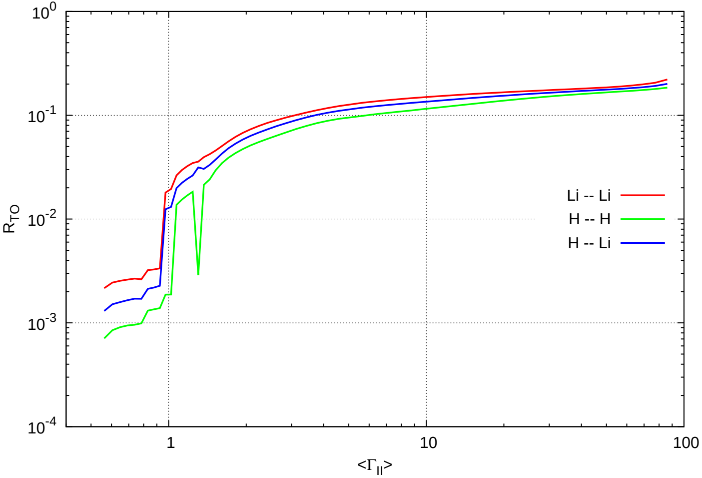


TFIS-M vs OFMD. E_D : $T_{H-H} \sim 20$ kK, $T_{C-H} \sim T_{C-C} \sim 50$ kK

× — OFMD data: C. E. Starrett, D. Saumon et al. Phys. Rev. E 90, 033110 (2014).

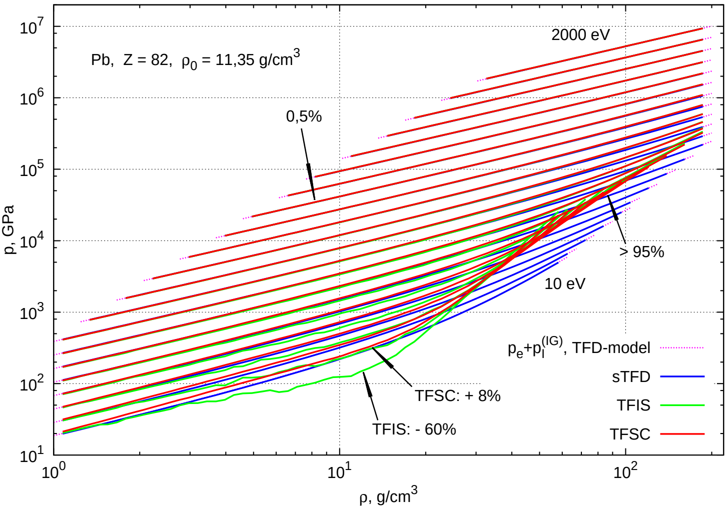
R_{TO} — a translational order parameter along isochores

Note! About the range of applicability of the method ^{7}LiH, $\rho = 0{,}78$ g/cm^3



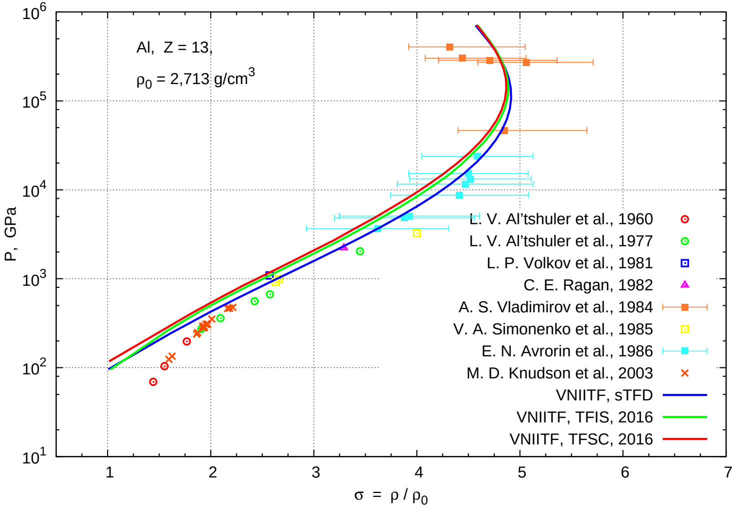
$$R_{TO}^{(i,j)} = \frac{1}{r_{\mathsf{max}}^{(i,j)}} \int\limits_0^{r_{\mathsf{max}}^{(i,j)}} dr\,\left(g_{ij}(r) - 1\right)$$

Intersection of the total pressure isotherms
obtained in the model with realistic description of ionic correlations



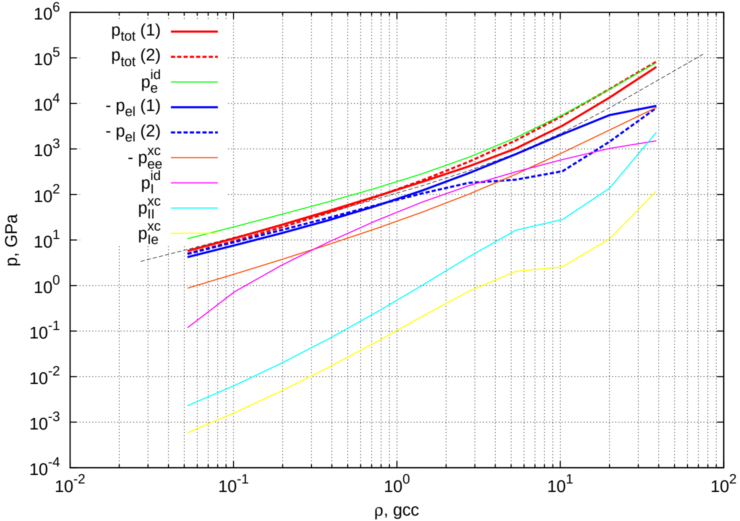
sTFD vs TFIS/TFSC (models with ionic correlations)

Shock Hugoniot (σ, P) for the normal-density Al



Partial contributions in the total pressure

Example for Al at $\mathrm{T} = 5$ eV isotherm



All the problems lie in the equations for p_{el} and p_{ee}^{xc} wich have been constructed with the «cluster expansion» principles

Results of investigation. The most essential results

Microstructure of matter. Thermodynamical functions

1. RDFs for single-element warm and hot dense matter done with the TFIS/TFSC/QMIS ELEGIA code implementing a semiclassical (TFD-like) version of the Starrett & Saumon average-atom model with ion correlations agree well with first-principle quantum or orbital-free molecular dynamics simulations.
2. The first iteration of the model in the TFIS-M case allows us to reproduce partial ion-ion RDFs up to $\langle \Gamma_{II} \rangle \sim 10^3$ with a good accuracy.
3. An appropriate account of ion disordering and correlations in the predicted EOS was performed with the «infinite» version of the average-atom semiclassical model.
4. Inclusion of ionic correlations increases the calculated pressure by as much as $\sim 45\%$ along the $\simeq 10$ eV isotherms and by as much as $\simeq 65\%$ along the shock Hugoniots for doubly compressed state as compared to the TFD data.
5. As the electronic «ideal» F_i and exchange-correlation contributions $(F_i^{xc})^0 + \triangle F_{e_i e_i}^{xc}$ to the Helmholtz free energy are strongly modulated by the ion-ion RDFs. The corrections in thermodynamics are evidently due to the use of the «cluster expansion». At the moment, we see no accurate alternative to the pseudoatomic MD simulations (PAMD) in themodynamic prorepties calculation.

Thank you for your time and attention!

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