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Classical Representation of a Quantum System at Equilibrium

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Overview

- Objective – exploit classical methods for description of correlations in quantum systems).
- Method – map quantum system thermodynamics and structure onto equivalent classical system.
- Approximate realization of the map – effective temperature, local chemical potential, pair potential.
- Limits of map – ideal Fermi gas; weak coupling (RPA)
- Target systems – uniform jellium correlations, shell structure of confined charges, DFT.

Can it work?

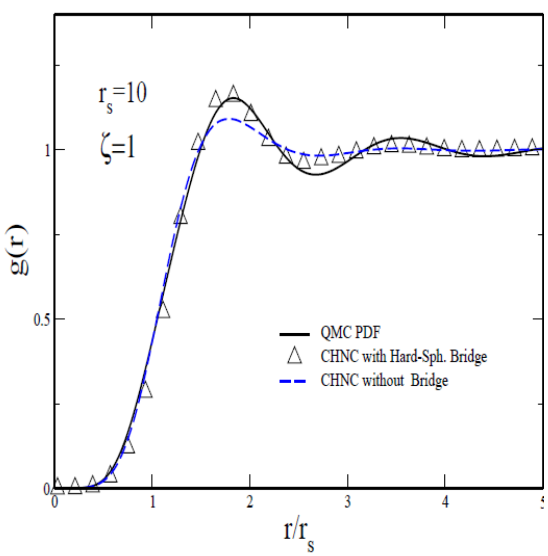
Dharma-wardana and Perrot, PRL 84, 959 (2000);
see review Dharma-wardana (2011), Arxiv: 1103 6070v1

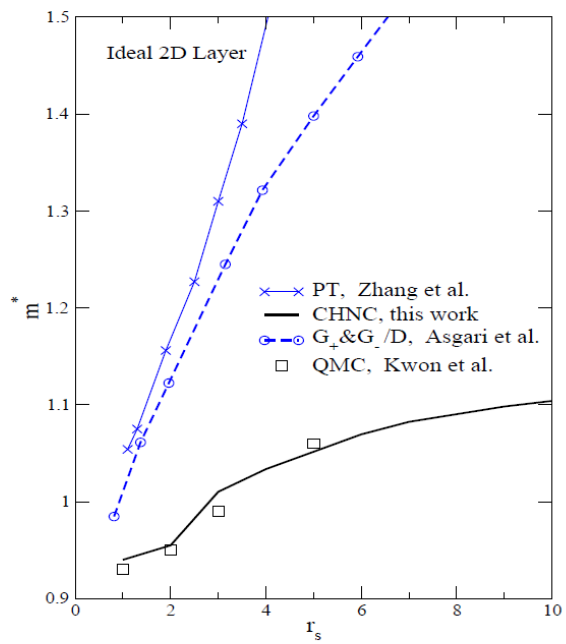
$$T_c = \sqrt{T^2 + T_0^2}$$

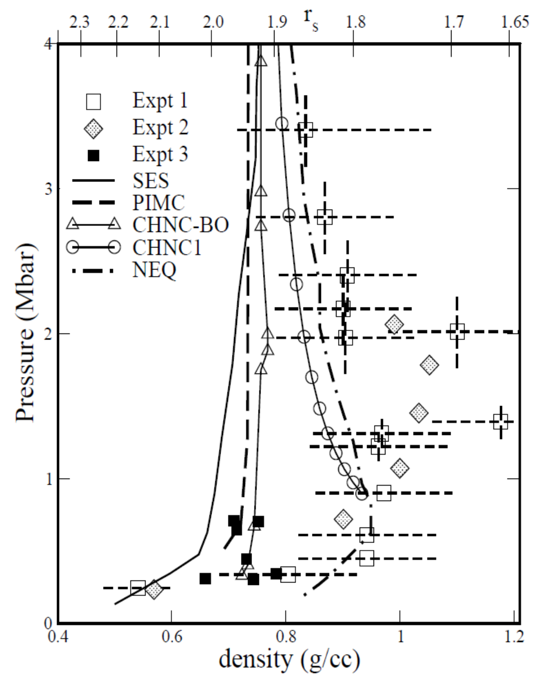
$$\phi_c(r) = \phi_c^{(0)}(r) + \frac{e^2}{r}(1 - e^{-\lambda r})$$

fit to T=0 xc energy **fit ideal gas g(r)** **thermal de Broglie**

Implement classical stat mech via HNC - examples







Non-uniform system thermodynamics - quantum

$$H = K + \Phi + \Phi_{ext} \qquad \Phi = \frac{1}{2}\sum_{ij}\phi\left(q_{ij}\right), \quad \Phi_{ext} = \sum_{i=1}^{N}\phi_{ext}\left(\mathbf{q}_i\right)$$

$$H - \mu N = K + \Phi - \int d\mathbf{r}\mu(\mathbf{r})\widehat{n}(\mathbf{r}) \qquad \widehat{n}(\mathbf{r}) = \sum_{i=1}^{N}\delta\left(\mathbf{r} - \mathbf{q}_i\right)$$

Grand potential - quantum

$$\Omega(\beta \mid \mu) = -\beta^{-1}\ln\sum_{N} Tr_N e^{-\beta\left(K+\Phi-\int d\mathbf{r}\mu(\mathbf{r})\widehat{n}(\mathbf{r})\right)}$$

temperature $\beta = 1/K_B T$

local chemical potential $\mu(\mathbf{r}) \equiv \mu - \phi_{ext}(\mathbf{r})$

pair potential $\phi\left(q_{ij}\right)$

Non-uniform system thermodynamics - classical

Grand potential - classical

$$\Omega_c(\beta_c \mid \mu_c) = -\beta_c^{-1} \ln \sum_N \frac{1}{\lambda_c^{3N} N!} \int d\mathbf{q}_1..d\mathbf{q}_N e^{-\beta_c \left(\Phi_c - \int dr \mu_c(r) \widehat{n}(r)\right)}$$

$$\lambda_c = \left(2\pi\beta_c\hbar^2/m\right)^{1/2}$$

effective temperature	β_c
effective local chemical potential	$\mu_c(\mathbf{r}) \equiv \mu - \phi_{c,ext}(\mathbf{r})$
effective pair potential	$\phi_c(q_{ij})$

Problem: how to define classical parameters to impose equivalence of thermodynamics and structure?

Definition of classical / quantum equivalence

$$\Omega_c(\beta_c \mid \mu_c) \equiv \Omega(\beta \mid \mu)$$

$$\frac{\delta\Omega_c(\beta_c \mid \mu_c)}{\delta\mu_c(\mathbf{r})}\Big|_{\beta_c,\phi_c} \equiv \frac{\delta\Omega(\beta \mid \mu)}{\delta\mu(\mathbf{r})}\Big|_{\beta} \qquad \frac{1}{\beta_c}\frac{\delta\Omega_c(\beta_c \mid \mu_c)}{\delta\phi_c(\mathbf{r},\mathbf{r}')} = \frac{1}{\beta}\frac{\delta\Omega(\beta \mid \mu)}{\delta\phi(\mathbf{r},\mathbf{r}')}$$

Interpretation (same thermodynamics and structure)

$$p_c(\beta_c \mid \mu_c) \equiv p(\beta \mid \mu)$$

$$n_c(\mathbf{r};\beta_c \mid \mu_c) \equiv n(\mathbf{r};\beta \mid \mu) \qquad g_c(\mathbf{r},\mathbf{r}';\beta_c \mid \mu_c) \equiv g(\mathbf{r},\mathbf{r}';\beta \mid \mu)$$

Problem: how to solve for

$$\beta_c = \beta_c(\beta \mid \mu), \qquad \mu_c = \mu_c(\mathbf{r};\beta \mid \mu), \qquad \phi_c = \phi_c(\mathbf{r},\mathbf{r}';\beta \mid \mu)$$

Relationship to density functional theory

Free energy (Legendre transform)

$$F(\beta \mid n) = \Omega\,(\beta \mid \mu) + \int d\mathbf{r}\mu(\mathbf{r})n(\mathbf{r})$$

$$n(\mathbf{r}) = -\frac{\delta\Omega(\beta \mid \mu)}{\delta\mu\,(\mathbf{r})}\,|_\beta$$

$$\frac{\delta F(\beta \mid n)}{\delta n\,(\mathbf{r})}\,|_\beta = \mu(\mathbf{r})$$

Euler equation of DFT determines density

$$F_c(\beta_c \mid n_c) = \Omega_c\,(\beta_c \mid \mu_c) + \int d\mathbf{r}\mu_c\,(\mathbf{r})\,n_c\,(\mathbf{r})$$

$$\frac{\delta F_c}{\delta n_c(\mathbf{r})} = \mu_c(\mathbf{r})$$

Classical DFT determines same density

Inversion of correspondence conditions

Classical density functional theory

$$\begin{pmatrix} n_c(\mathbf{r}) \\ g_c(\mathbf{r}) \end{pmatrix} = \begin{pmatrix} \mathcal{I}(\mathbf{r} \mid \beta_c\mu_c, \beta_c\phi_c) \\ \mathcal{J}(\mathbf{r} \mid \beta_c\mu_c, \beta_c\phi_c) \end{pmatrix}$$

$$\begin{pmatrix} \beta_c\mu_c(\mathbf{r}) \\ \beta_c\phi_c(\mathbf{r}) \end{pmatrix} = \begin{pmatrix} \mathcal{I}^{-1}(\mathbf{r} \mid n, g) \\ \mathcal{J}^{-1}(\mathbf{r} \mid n, g) \end{pmatrix}$$

quantum input

Examples of approximate functionals $\mathcal{I}(\mathbf{r} \mid \cdot, \cdot)$ *and* $\mathcal{J}(\mathbf{r} \mid \cdot, \cdot)$

Percus-Yevick, hypernetted chain, … better

Effective temperature – classical virial equation

$$\frac{\beta_c}{\beta} = \frac{\beta_c p_c}{\beta p} = \frac{\overline{n}}{\beta p}\left(1 - \frac{2\pi}{3}\overline{n}\int_0^\infty dr r^3 \left(g(r) - 1\right) \frac{d\left(\beta_c\phi_c(r)\right)}{dr}\right)$$

quantum input

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Application to Uniform Fermi Fluid

$$\beta_c \phi_c(\mathbf{r}) = \mathcal{J}^{-1}(\mathbf{r} \mid n, g) \rightarrow -\ln(g(\mathbf{r})) + g(\mathbf{r}) - 1 - c(\mathbf{r})$$

HNC

OZ $$c(\mathbf{r}) = g(\mathbf{r}) - 1 - n \int d\mathbf{r}' \left(g(\mathbf{r}') - 1\right) c(\mathbf{r} - \mathbf{r}')$$

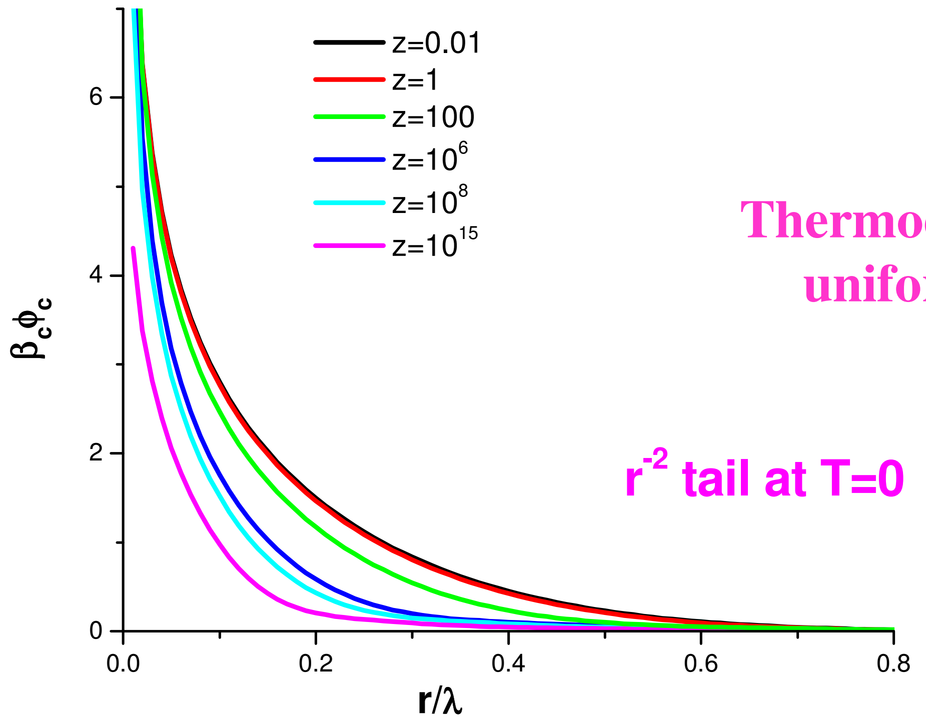
$$\frac{\beta_c}{\beta} = \frac{n}{\beta p} \left(1 - \frac{2\pi}{3} n \int_0^\infty dr r^3 \left(g(r) - 1\right) \frac{d\beta_c \phi_c(r)}{dr}\right)$$

Ideal Fermi Gas Limit

quantum input

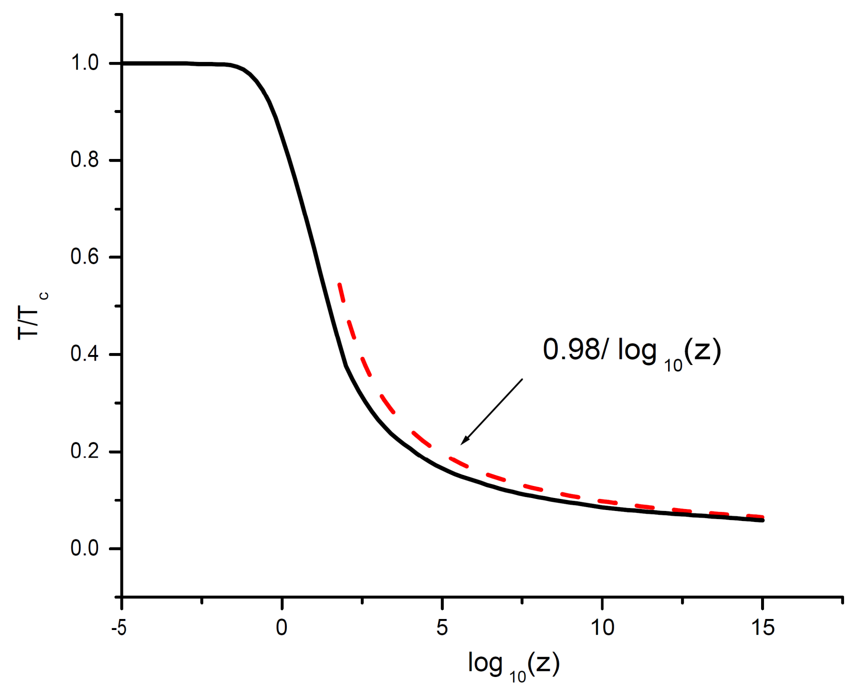
$$g^{(0)}(r) = 1 - \frac{1}{2s+1} \left(\frac{\eta(r)}{\eta(\mathbf{0})}\right)^2, \quad \eta\left(r, \beta, \mu^{(0)}\right) = \int \frac{d\mathbf{k}}{(2\pi)^3} e^{-i\mathbf{k}\cdot\mathbf{r}} \left(e^{\beta\left(\epsilon_k - \mu^{(0)}\right)} + 1\right)^{-1}$$

$$\beta p^{(0)}(\beta, \mu^{(0)}) = (2s+1) \int \frac{d\mathbf{k}}{(2\pi)^3} \ln\left(1 + e^{-\beta\left(\epsilon_k - \mu^{(0)}\right)}\right)$$



Thermodynamics requires uniform background

r^{-2} tail at T=0



$T_C(T=0) = 1.02\ T_F(n)$

Other Ideal Fermi Gas Properties – Internal Energy

By definition:

$$p_c(\beta_c \mid \mu_c)V = -\Omega_c(\beta_c \mid \mu_c) = p(\beta \mid \mu)V = -\Omega(\beta \mid \mu)$$

By calculation:

$$E_c = \frac{\partial \beta_c p_c V}{\partial \beta_c}\Big|_{z_c,V} \neq \langle H \rangle_c$$

$$E_c \stackrel{?}{=} E = \frac{\partial \beta p V}{\partial \beta}\Big|_{z,V} = \left\langle \widehat{H} \right\rangle = \frac{3}{2}pV$$

$$E_c = \left(\frac{3}{2\beta_c} + n_c \frac{1}{2}\int d\mathbf{r} \frac{\partial \beta_c \phi_c(r)}{\partial \beta_{cl}}\Big|_{r,z_c} (g_c(r) - 1)\right)$$
$$= \frac{3}{2}p_c V$$

exact

Coulomb regularization via diffraction, exchange

$$\beta_c \phi_c(\mathbf{r}) = (\beta_c \phi_c(\mathbf{r}))^{(0)} + \Delta(\mathbf{r})$$

Coulomb effects

weak coupling limit:

$$c(\mathbf{r}) \rightarrow c^{RPA}(\mathbf{r}) = -\beta_c \phi_c(\mathbf{r}) = c^{(0)}(0) + \Delta^{RPA}(\mathbf{r})$$

$$c^{RPA}(\mathbf{r}) = g^{RPA}(\mathbf{r}) - 1 - n \int d\mathbf{r}' \left(g^{RPA}(\mathbf{r}') - 1 \right) c^{RPA}(\mathbf{r} - \mathbf{r}')$$

quantum input

Proposed approximate classical jellium potential

$$\beta_c \phi_c(\mathbf{r}) \simeq (\beta_c \phi_c(\mathbf{r}))^{(0)} - \left(c^{RPA}(\mathbf{r}) - c^{(0)}(\mathbf{r}) \right)$$

$$= -\ln(g^{(0)}(\mathbf{r})) + g^{(0)}(\mathbf{r}) - 1 - c^{RPA}(\mathbf{r})$$

Some properties of the RPA classical potential

Large r:

$$\beta_c \phi_c(r) \rightarrow \frac{1}{\frac{\beta\hbar\omega_p}{2}\coth(\frac{\beta\hbar\omega_p}{2})} \Gamma \frac{r_0}{r} \rightarrow \begin{cases} \Gamma \frac{r_0}{r}, & \beta\hbar\omega_p << 1 \\ 4\left(\frac{\pi}{3} r_s\right)^{1/2} \frac{r_0}{r}, & \beta\hbar\omega_p >> 1 \end{cases}$$

Weak coupling, low density

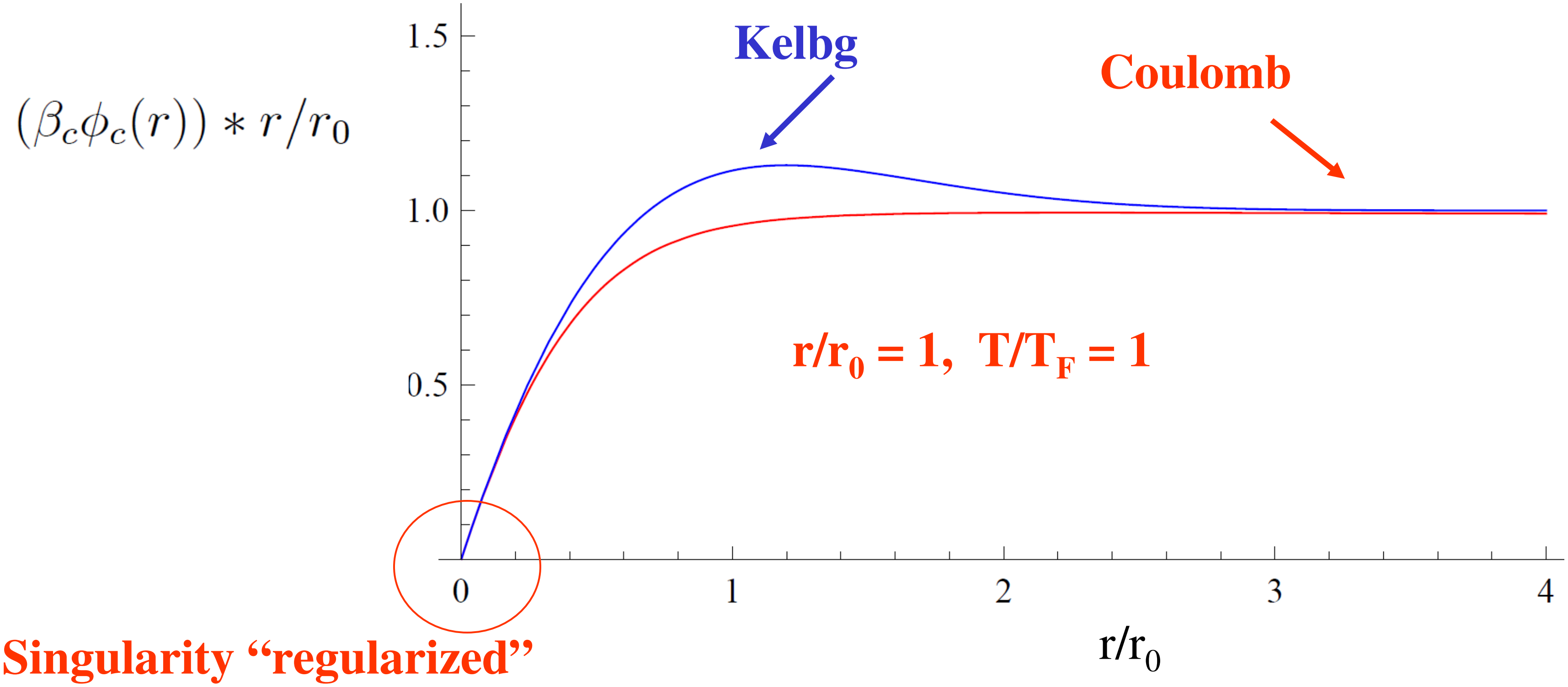
$$\beta_c \phi_c(r) \rightarrow (\beta_c \phi_c(r))^{(0)} + \int d\mathbf{r}' \phi(r') G(|\mathbf{r} - \mathbf{r}'|)$$

$$G(|\mathbf{r} - \mathbf{r}'|) = \frac{1}{(2\pi)^3} \int d\mathbf{k} e^{-i\mathbf{k}.\mathbf{r}} \left(\frac{\delta}{\delta\phi(\mathbf{r}')} \frac{1}{n\widetilde{S}^{RPA}(k)} \right) |_{\phi=0}$$

(diffraction, exchange)

$$\underset{z<<1}{\rightarrow} \quad \mathrm{Kelbg}$$

(low density – diffraction only)



Singularity "regularized"

Aside: $\lim_{k \to 0} \widetilde{S}(kr_0, q, t, r_s)$ non-analytic about $q = 0, T = 0$

$$\lim_{k \to 0} \widetilde{S}(kr_0, q, t, r_s) \to c_1(q, t, r_s)\,(kr_0)^2$$

$$\lim_{k \to 0} \widetilde{S}(kr_0, q = 0, T) \to c_2(t, r_s) + c_3(t, r_s)\,(kr_0)^2$$

$$\lim_{k \to 0} \widetilde{S}(kr_0, q = 0, T = 0) \to c_4\,(r_2)\,kr_0 + c_5(r_s)\,(kr_0)^3$$

Application to Charges in a Trap

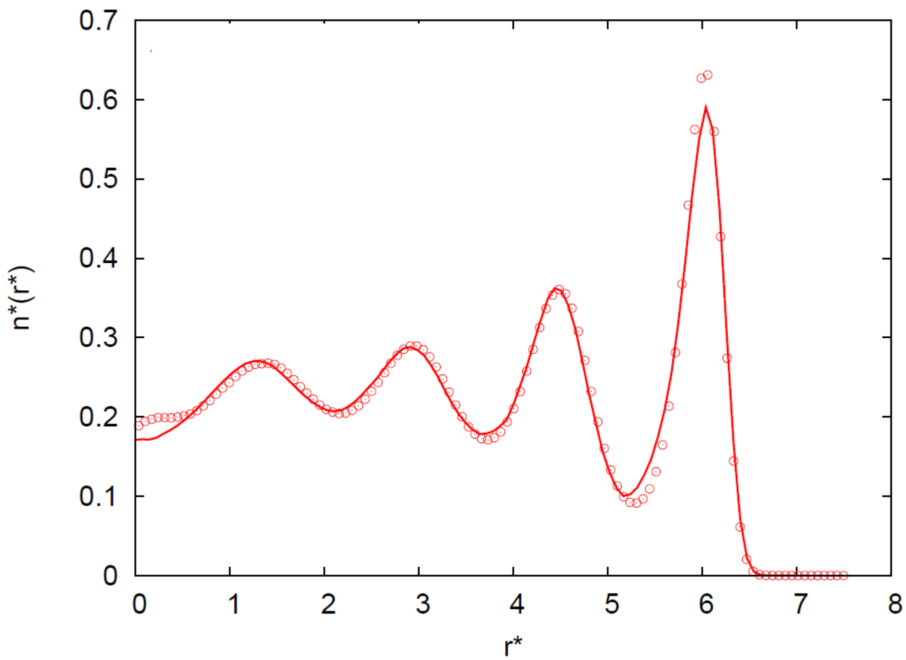
$$H = K + \Phi + \sum_{i=1}^{N} \phi_{ext}(q_i), \qquad \phi_{ext}(q_i) = \frac{1}{2} m\omega^2 q_i^2$$

$$\ln\left(n_c(\mathbf{r})\lambda_c^3\right) \simeq \beta_c \mu_c(\mathbf{r}) + \int d\mathbf{r}' c_c(|\mathbf{r} - \mathbf{r}'|)\, n_c(\mathbf{r}')$$

HNC

OCP correlations (see Wrighton poster)

(classical – no quantum effects)



$$\mu(\mathbf{r}) = \mu\left(\beta, n\right) - \phi_{ext}(\mathbf{r}) \quad \xrightarrow{\text{(map)}} \quad \mu_c(\mathbf{r}) = \mu_c - \phi_{ext,c}(\mathbf{r})$$

$$\beta_c\mu_c(\mathbf{r}) = \frac{3}{2}\ln\left(\frac{\beta_c}{\beta}\right) + \ln\left(n\left(\mathbf{r}\right)\lambda^3\right) + \int d\mathbf{r}' c\left(\left|\mathbf{r} - \mathbf{r}'\right|\right) n\left(\mathbf{r}'\right)$$

quantum input

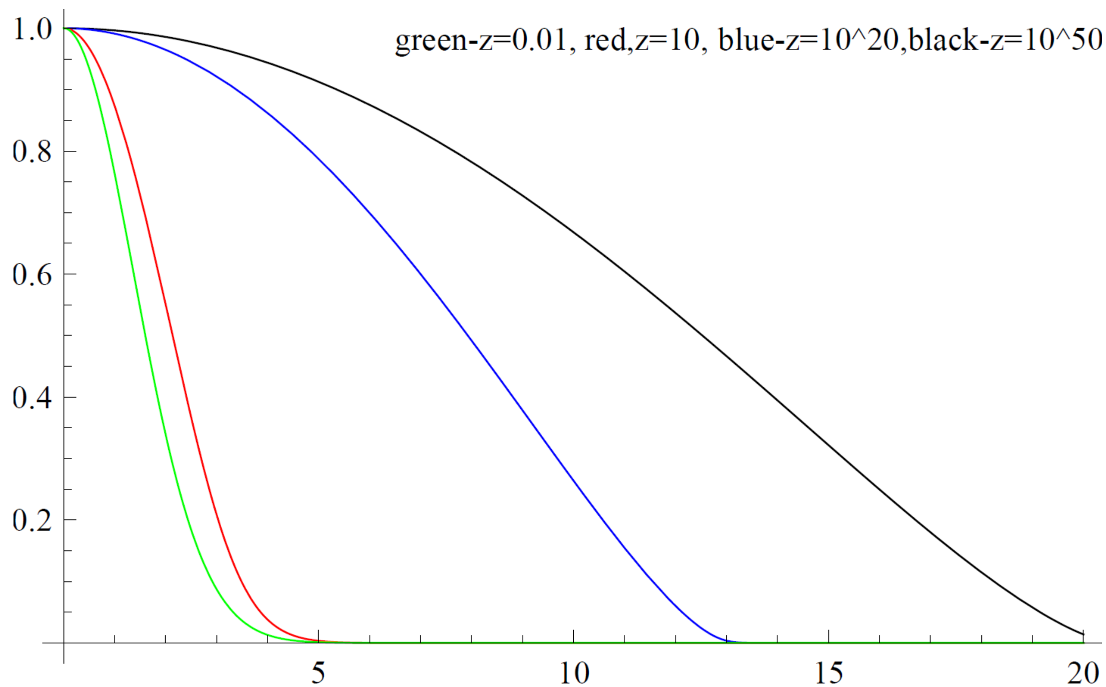
Lowest order map – inhomogeneous ideal Fermi gas

$$\left(\beta_c\mu_c(\mathbf{r})\right)^{(0)} = \frac{3}{2}\ln\left(\frac{\beta_c^{(0)}}{\beta}\right) + \ln\left(n^{(0)}\left(\mathbf{r}\right)\lambda^3\right) - \int d\mathbf{r}' c^{(0)}\left(\left|\mathbf{r} - \mathbf{r}'\right|\right) n^{(0)}\left(\mathbf{r}'\right)$$

quantum input

LDA (Thomas-Fermi) $n^{(0)}(\mathbf{r}) = \int \frac{d\mathbf{k}}{(2\pi)^3} e^{-i\mathbf{k}\cdot\mathbf{r}} \left(e^{\beta\left(\epsilon_k - \mu^{(0)}(r)\right)} + 1 \right)^{-1}$

$$\frac{n^{(0)}(\mathbf{r})}{n^{(0)}(\mathbf{0})} = \frac{f_{3/2}(ze^{-\frac{1}{2}\Gamma r^2})}{f_{3/2}(z)} \rightarrow \begin{cases} \frac{z}{f_{3/2}(z)} e^{-\frac{1}{2}\Gamma r^2}, & ze^{-\frac{1}{2}\Gamma r^2} << 1 \\ \left(1 - \frac{1}{2\ln(z)}\Gamma r^2\right)^{3/2}, & ze^{-\frac{1}{2}\Gamma r^2} >> 1 \end{cases}$$



How to use an approximate classical mapping?

With quantum properties embedded approximately in classical temperature, local chemical potential, and pair potential:

1. **Implement classical statistical mechanics via molecular dynamics**

2. **Implement classical statistical mechanics via classical non-perturbative, non-local, orbital free density functional theory**

3. **Implement classical statistical mechanics via integral equations ("bootstrap").**

$$\begin{pmatrix} n_c(\mathbf{r}) \\ g_c(\mathbf{r}) \end{pmatrix} = \begin{pmatrix} \mathcal{I}(\mathbf{r} \mid \beta_c\mu_c, \beta_c\phi_c) \\ \mathcal{J}(\mathbf{r} \mid \beta_c\mu_c, \beta_c\phi_c) \end{pmatrix}$$

Example of bootstrap – HNC equations

Jellium:

$$g_c(\mathbf{r}) = \exp\left(-\beta_c\phi_c(\mathbf{r}) + g_c(\mathbf{r}) - 1 - c_c(\mathbf{r})\right)$$

+ Ornstein – Zernicke equation for $c_c(\mathbf{r})$

Harmonic trap:

$$n_c(\mathbf{r}) = n^{(0)}(\mathbf{r})\left(\frac{\beta_c^{(0)}}{\beta_c}\right)^{3/2}\exp\int d\mathbf{r}'\left(c_c(|\mathbf{r}-\mathbf{r}'|)\,n_c(\mathbf{r}') - c^{(0)}(|\mathbf{r}-\mathbf{r}'|)\,n^{(0)}(\mathbf{r}')\right)$$

Results – 2013 in Kiel / Tahoe

Summary

- Quantum – Classical map defined for thermodynamics and structure
- Implementation of map with two exact limits
- Application to jellium via HNC integral equation - in progress (need finite T simulation data for benchmark!)
- Application to shell structure for charges in trap – in progress
- Extension to orbital free density functional theory