Fundamentals of Density Functional Theory for T> 0 : Quantum meets Classical
CECAM, Lousanne, Switzerland, May 20-23

Thermodynamics for non-uniform systems and DFT

James Dufty
Department of Physics
University of Florida,
Gainesville, FL 32607, USA

Work supported under US DOE Grant DE-SC0002139

UF UNIVERSITY of FLORIDA

THANKS TO:

University of Florida Orbital Free DFT Group

Sam Trickey
Jim Dufty
Daniel Mejia Rodriguez
Kai Luo
Jeff Wrighton

Valentin Karasiev *
Lazaro Calderín *

* **no longer at UF but active collaboration**

Software and publications available from
www.qtp.ufl.edu/ofdft

Issues for group discussion

- Thermodynamics for non-uniform systems from statistical mechanics: criteria and functionals. Variational formulation and equivalence to DFT.

  Opportunities – Legendre transforms to new variables; first and second derivatives; bounds.

  Challenges – extensivity; charge neutrality (electrons and ions)

- Equilibrium structure (response) from Ornstein-Zernicke identity.

- Equivalent versions of classical and quantum DFT

Thermodynamics from statistical mechanics

Abstract thermodynamics

$$S = S(U, N, V) \quad \text{concave (stability)}$$

$$S(\lambda U, \lambda N, \lambda V) = \lambda S(U, N, V) \quad \text{(extensive)}$$

$$\frac{\partial S}{\partial U} \equiv \frac{1}{T} > 0 \quad \text{invertible} \qquad U = U(S, N, V)$$

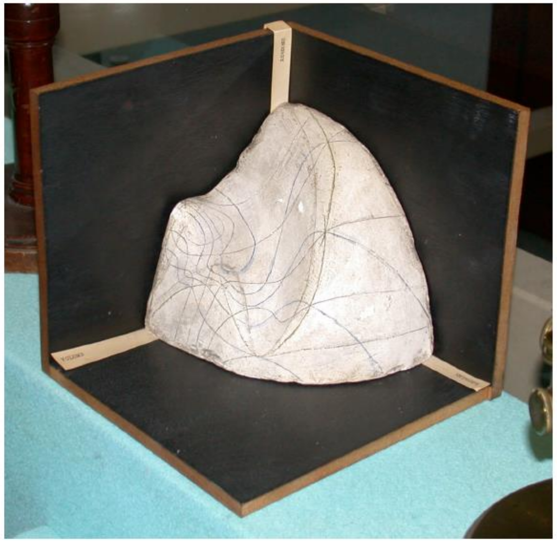


Figure 1. Plaster model of the equilibrium states of water constructed by James Clerk Maxwell and sent as a present to Josiah Willard Gibbs. (© The Cavendish Laboratory, University of Cambridge)

Abstract thermodynamics

$$S = S(U, N, V) \quad \text{concave (stability)}$$

$$S(\lambda U, \lambda N, \lambda V) = \lambda S(U, N, V) \quad \text{(extensive)}$$

$$\frac{\partial S}{\partial U} \equiv \frac{1}{T} > 0 \quad \text{invertible} \qquad U = U(S, N, V)$$

Legendre transform $U, N \;\rightarrow\; T, \mu \equiv -T\frac{\partial S}{\partial N}$

$$\frac{1}{T}p(T,\mu)V = -\frac{1}{T}\Omega(T,V,\mu) = S - \frac{\partial S}{\partial U}U - \frac{\partial S}{\partial N}N$$

Realization from statistical mechanics

$$-\frac{1}{T}\Omega(T, V \mid \mu) \equiv \ln \sum_N Tr^{(N)} e^{-\beta\left(H - \int d\mathbf{r}\mu(\mathbf{r})\widehat{n}(\mathbf{r})\right)}$$

$$\mu\left(\mathbf{r}\right) \equiv \mu - V_{ext}\left(\mathbf{r}\right), \qquad \widehat{n}\left(\mathbf{r}\right) = \sum_{\alpha=1}^{N} \Delta\left(\mathbf{r} - \mathbf{q}_\alpha\right)$$

$$\frac{\delta\Omega(T,V\mid\mu)}{\delta\mu(\mathbf{r})} = -\langle\widehat{n}(\mathbf{r})\rangle \equiv -n(\mathbf{r},T\mid\mu)$$

$\Omega(T,V\mid\mu)$ ***strictly* concave, so invertible:** $\mu(\mathbf{r}) = \mu(\mathbf{r},T\mid n)$

Legendre transform $T,V,\mu(\mathbf{r}) \to T,V,n(\mathbf{r})$

$$F(T,V\mid n) = \left[\Omega(T,V\mid\mu) - \int d\mathbf{r}\frac{\delta\Omega(T,V\mid\mu)}{\delta\mu(\mathbf{r})}\Big|_{V,T}\mu(\mathbf{r})\right]_{\mu(\mathbf{r},T|n)}$$

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

$F(T,V\mid n)$ ***strictly* convex, so invertible:** $n(\mathbf{r}) = n(\mathbf{r},T\mid\mu)$

Existence of $\Omega(T,V,\mu)$ **?**

H-stability (no collapse) $V(\mathbf{q}_1,..\mathbf{q}_N) > -BN$ (classical) $\Longrightarrow$ $E_0 > -BN$ (quantum)

Tempering (no explosion) $V(N_a,N_b) - V(N_a) - V(N_b) \leq Cr^{-(3+\epsilon)}N_aN_b$

Extensive $\lim\Omega(T,V\mid\mu) \to V\omega(T\mid\mu)$

Variational formulation

$$\Omega_\mu (T,V \mid n) \equiv F(T,V \mid n) - \int d\mathbf{r} n(\mathbf{r}) \mu(\mathbf{r})$$

(independent)

Convex in n

Euler eq. $$\frac{\delta \Omega_\mu (T,V \mid n)}{\delta n(\mathbf{r})} = 0 \Longrightarrow \frac{\delta F(T,V \mid n)}{\delta n(\mathbf{r})} = \mu(\mathbf{r})$$

solution $n(\mathbf{r}) = n_e(\mathbf{r}, T \mid \mu) \Longrightarrow \Omega_\mu (T,V \mid n_e) = \Omega(T,V \mid \mu)$

(Same as DFT)

Dual variational formulation

$$F_n (T,V \mid \mu) \equiv \Omega(T,V \mid \mu) + \int d\mathbf{r} n(\mathbf{r}) \mu(\mathbf{r})$$

Concave in $\mu(\mathbf{r})$

Euler eq. $$\frac{\delta \Omega (T,V \mid \mu)}{\delta \mu(\mathbf{r})} = -n(\mathbf{r})$$

Opportunities from thermodynamic connections

New functionals, properties

$$\frac{d\Omega(T,V\mid\mu)}{dT}\mid_{\mu,V}=-S(T,V\mid\mu)$$

$$U(S,V\mid n)=\Omega(T,V\mid\mu)-\int d\mathbf{r}\mu\left(\mathbf{r}\right)\frac{\delta\Omega\left(T,V\mid\mu\right)}{\delta\mu\left(\mathbf{r}\right)}-T\frac{d\Omega(T,V\mid\mu)}{dT}\mid_{\mu,V}$$

Convexity constraints (stability)

$$\frac{d^2F(\beta,V\mid n)}{dT^2}=-\frac{dS(\beta,V\mid n)}{dT}<0. \qquad \frac{d^2U(S,V\mid n)}{dS^2}\mid_{n,V}=\frac{dT}{dS}\mid_{n,V}>0.$$

Structure / fluctuations from functional derivatives

Response from free energy functional

Response function

$$\frac{\delta^2\Omega\left(\beta,V\mid\mu\right)}{\delta\mu\left(\mathbf{r}\right)\delta\mu\left(\mathbf{r}'\right)}\Big|_{T,V} = -\frac{\delta n\left(\mathbf{r}\right)}{\delta\mu\left(\mathbf{r}'\right)} \equiv -\chi(\mathbf{r},\mathbf{r}';\beta,V\mid\mu)$$

$$\chi(\mathbf{r},\mathbf{r}';T,V\mid\mu) = T\int_0^{1/T} d\beta'\left\langle e^{\beta' H}\delta\widehat{n}(\mathbf{r})e^{-\beta' H}\widehat{n}(\mathbf{r}');T\mid\mu\right\rangle$$

(classical) $$\to n\left(\mathbf{r}'\right)\left[\delta\left(\mathbf{r}-\mathbf{r}'\right)+n\left(\mathbf{r}\right)\left(g\left(\mathbf{r},\mathbf{r}';T,V\mid\mu\right)-1\right)\right]$$

Inverse response

$$\frac{\delta^2 F\left(T,V\mid n\right)}{\delta n\left(\mathbf{r}\right)\delta n\left(\mathbf{r}'\right)}\Big|_{\beta,V} = \frac{\delta\mu\left(\mathbf{r}\right)}{\delta n\left(\mathbf{r}'\right)} = \chi^{-1}(\mathbf{r},\mathbf{r}';T,V\mid\mu)$$

$$F\left(T,V\mid n\right) = F^{(0)}\left(T,V\mid n\right) + F_{ex}\left(T,V\mid n\right)$$

$$c\left(\mathbf{r}_1,\mathbf{r}_2;T,V\mid n\right) \equiv -\frac{1}{T}\frac{\delta^2 F_{ex}\left(T,V\mid n\right)}{\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)}$$

Ornstein-Zernicke

$$\chi_{ex} = -\chi^{(0)} * c * \chi^{(0)} - \chi^{(0)} * c * \chi_{ex}$$

Useful ?

$$F_{ex}\left(T,V\mid n\right) \to c\left(\mathbf{r}_1,\mathbf{r}_2;T,V\mid n\right) \to \chi(\mathbf{r},\mathbf{r}';T,V\mid\mu)$$

$$\chi(\mathbf{r},\mathbf{r}';T,V\mid\mu) \to c\left(\mathbf{r}_1,\mathbf{r}_2;T,V\mid n\right) \to F_{ex}\left(T,V\mid n\right)$$

Challenges – extensivity, ensemble equivalence

$$\beta p_G V = \ln \sum_{N=0}^{\infty} Tr_N \, e^{-\beta(H_N - \mu N)}$$

$$\beta f_C = -\frac{1}{N} \ln Tr_N \, e^{-\beta H_N}$$

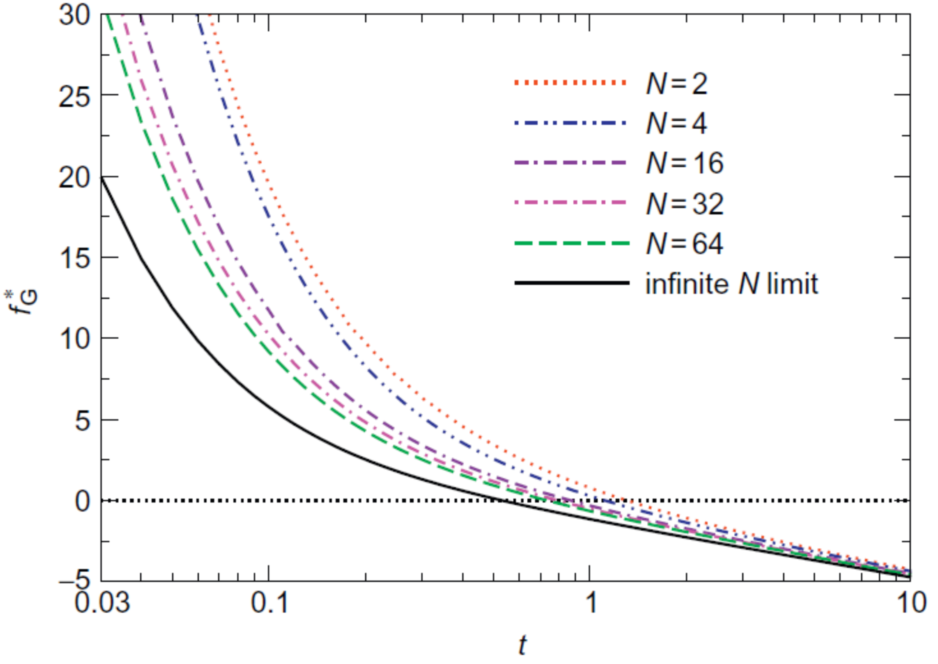
$$e^{-\beta f_C(\beta, n, V) N} = \frac{1}{2\pi} \int_0^{2\pi} d\theta e^{i\theta N} e^{\beta p_G(\beta, \mu = -i\theta/\beta, V) V}$$

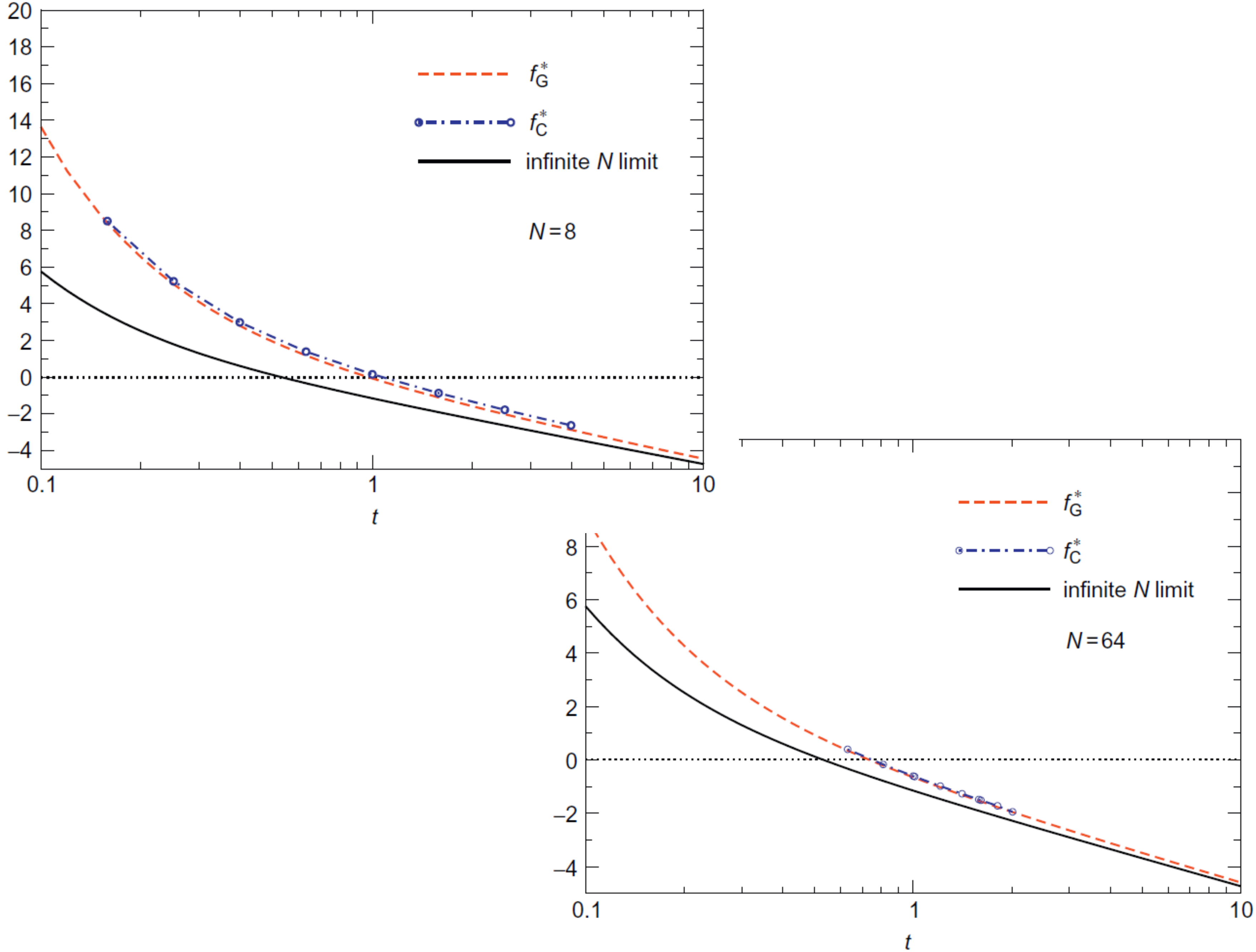
Example: ideal Fermi gas

$$\beta p_G = \frac{2}{V} \sum_{\mathbf{k}} \ln \left(1 + e^{\beta\mu} e^{-\left(\frac{k}{\ell}\right)^2}\right)$$

$$n_G = \frac{2}{V} \sum_{\mathbf{k}} \left(e^{-\beta\mu} e^{(k/\ell)^2} + 1\right)^{-1}$$

$$\ell^2 = \frac{4}{\pi} \left(\frac{L}{\lambda}\right)^2 \quad \lambda = \left(2\pi\beta\hbar^2/m\right)^{1/2}$$





f_G^*
f_C^*
infinite N limit
N = 8
t
f_G^*
f_C^*
infinite N limit
N = 64
t

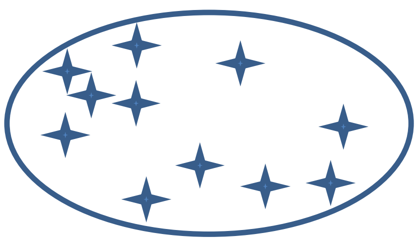
Electrons and ions

H for electrons and ions not bounded; Coulomb interaction not tempered; systems with net charge not extensive (no thermodynamics)

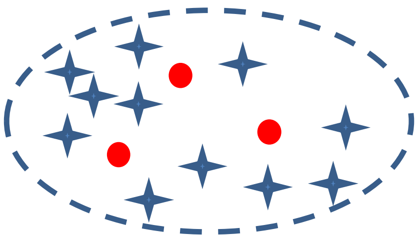
Problems solved for charge - neutral quantum electrons – ion systems

How to do DFT for electrons in external potential of ions?

1) One component (electrons) in external potential. *Electron functionals are not thermodynamic.*

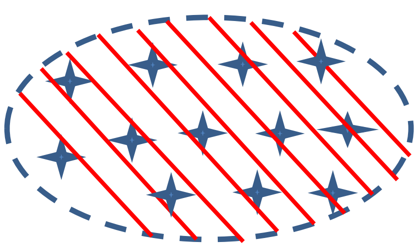


Electron gas

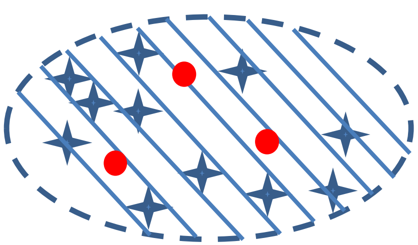


Inhomogeneous electron gas

Solution: add positive and negative uniform backgrounds



Jellium



Inhomogeneous jellium

2) Two component (charge neutral electrons and ions) in external potential. Electron-ion functionals are thermodynamic. (Dharma-wardan/Perrot (1982))

$$\Omega(T,V \mid \mu) \rightarrow \Omega(T,V \mid \mu_e,\mu_i)$$

$$F(T,V \mid n_e,n_i) = \Omega(T,V \mid \mu_e,\mu_i) - \int d\mathbf{r} \left(\frac{\delta\Omega(T,V \mid \mu_e,\mu_i)}{\delta\mu_e(\mathbf{r})} |_{V,T}\, \mu_e(\mathbf{r}) + \frac{\delta\Omega(T,V \mid \mu_e,\mu_i)}{\delta\mu_e(\mathbf{r})} |_{V,T}\, \mu_e(\mathbf{r}) \right)$$

Coupled set of Euler equations

$$\frac{\delta F(T,V \mid n_e,n_i)}{\delta n_e(\mathbf{r})} = \mu_e(\mathbf{r}), \qquad \frac{\delta F(T,V \mid n_e,n_i)}{\delta n_i(\mathbf{r})} = \mu_i(\mathbf{r})$$

but, charge neutrality constraint

$$\int d\mathbf{r} \left(\frac{\delta\Omega(T,V \mid \mu_e,\mu_i)}{\delta\mu_e(\mathbf{r})} - Z\frac{\delta\Omega(T,V \mid \mu_e,\mu_i)}{\delta\mu_e(\mathbf{r})} \right) = 0$$

Exact classical map

(Dharma-wardana/Perrot (2000); Dufty/Dutta (2012))

$$H-\mu N=K+\sum_{i,j}\phi(\mathbf{r}_i,\mathbf{r}_j')-\int d\mathbf{r}\mu\left(\mathbf{r}\right)n\left(\mathbf{r}\right) \qquad H_c-\mu N=K+\sum_{i,j}\phi_c(\mathbf{r}_i,\mathbf{r}_j')-\int d\mathbf{r}\mu_c\left(\mathbf{r}\right)n\left(\mathbf{r}\right)$$

$$T,\mu\left(\mathbf{r}\right),\phi\left(\mathbf{r},\mathbf{r}'\right)\rightarrow T_c,\mu_c\left(\mathbf{r}\right),\phi_c\left(\mathbf{r},\mathbf{r}'\right)$$

The map

$$\Omega_c\left(T_c,V\mid\mu_c,\phi_c\right)=\Omega\left(T,V\mid\mu,\phi\right)$$

$$\frac{\delta\Omega\left(T_c,V\mid\mu_c,\phi_c\right)}{\delta\mu_c(\mathbf{r})}=\frac{\delta\Omega\left(T,V\mid\mu\left(T,V\mid\mu,\phi\right)\right)}{\delta\mu(\mathbf{r})}$$

$$\frac{\delta\Omega\left(T_c,V\mid\mu_c,\phi_c\right)}{\delta\phi_c(\mathbf{r},\mathbf{r}')}=\frac{\delta\Omega\left(T,V\mid\mu\left(T,V\mid\mu,\phi\right)\right)}{\delta\phi(\mathbf{r},\mathbf{r}')}$$

or equivalently

$$\Omega_c\left(T_c,V\mid\mu_c,\phi_c\right)=-p\left(T,V\mid\mu,\phi\right)V$$

$$\frac{\delta\Omega\left(T_c,V\mid\mu_c,\phi_c\right)}{\delta\mu_c\left(\mathbf{r}\right)}=-n\left(\mathbf{r}\right),$$

$$\frac{\delta\Omega\left(T_c,V\mid\mu_c,\phi_c\right)}{\delta\phi_c(\mathbf{r},\mathbf{r}')}=g\left(\mathbf{r},\mathbf{r}';T,V\mid\mu,\phi\right)$$

How to invert? These are the Euler equations of the classical *dual* variational theory above !

Questions?

Comments?

Complaints?