

# The Density Functional Approach

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# Overview of previous lecture

- **Density-density correlation function**

$$H^{(2)}(\mathbf{r}, \mathbf{r}') = \langle [\rho(\mathbf{r}) - \langle \rho(\mathbf{r}) \rangle] [\rho(\mathbf{r}') - \langle \rho(\mathbf{r}') \rangle] \rangle$$

- **Pair distribution function**

$$g_N^{(2)}(|\mathbf{r}_2 - \mathbf{r}_1|) = g(r) = \rho^{(2)}(|\mathbf{r}_2 - \mathbf{r}_1|) / \rho^2 \quad (1)$$

- **Structure factor**

$$S(\mathbf{k}) = \langle \rho^*(\mathbf{k}) \rho(\mathbf{k}) \rangle \quad \text{where} \quad \rho(\mathbf{k}) = \sum_{i=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_i) \quad (2)$$

- **Grand potential:  $\Omega = \Omega[\psi(\mathbf{r})]$**

$$\delta\Omega = - \int \rho^{(1)}(\mathbf{r}) \delta\psi(\mathbf{r}) d\mathbf{r} - \frac{1}{2} \int \int \beta H^2(\mathbf{r}, \mathbf{r}') \delta\psi(\mathbf{r}) \delta\psi(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \dots \quad (3)$$

# Outline

- 1 Overview of previous lecture
- 2 **Response and correlation functions**
  - Density response function
  - Application: random phase approximation
- 3 Inhomogeneous fluids
  - Density functional theory
  - Approximate functionals
  - Application 1: liquid-vapor interface
  - Application 2: electrostatic double layer

# The density response function

A uniform fluid of density  $\rho_0$  is perturbed by a weak external field  $\delta\phi(\mathbf{r})$ . The Hamiltonian of the system is:

$$\mathcal{H} = \mathcal{H}_0 + \sum_{i=1}^N \delta\phi(\mathbf{r}_i) \quad (4)$$

and the induced density modulation:

$$\delta\rho^{(1)}(\mathbf{r}) = \rho^{(1)}(\mathbf{r}) - \rho_0 \quad (5)$$

For a weak perturbation the response is a **linear but non-local** function of  $\delta\phi(\mathbf{r})$

$$\delta\rho^{(1)}(\mathbf{r}) = \int \chi(\mathbf{r}, \mathbf{r}') \delta\phi(\mathbf{r}') d\mathbf{r}' \quad (6)$$

where the **linear response function or susceptibility** is give by:

$$\chi(\mathbf{r}, \mathbf{r}') = \left. \frac{\delta\rho^{(1)}(\mathbf{r})}{\delta\phi(\mathbf{r}')} \right|_{\phi=0} = \left. \frac{\delta\rho^{(1)}(\mathbf{r})}{\delta\psi(\mathbf{r}')} \right|_{\phi=0} \quad (7)$$

# The density response function

As shown before:  $\frac{\delta\rho^{(r)}(1)}{\delta\psi(\mathbf{r}')} = -\beta H^{(2)}(\mathbf{r}, \mathbf{r}')$  and,

## Linear response function:

$$\chi(\mathbf{r}, \mathbf{r}') = -\beta H^{(2)}(\mathbf{r}, \mathbf{r}') \quad \textit{Fluctuation dissipation theorem}$$

Within linear response: **The pair correlation function of the unperturbed system measures the response to an external field**

For an homogeneous system:

$$\chi(|\mathbf{r} - \mathbf{r}'|) = -\beta [\rho_0^2 h(|\mathbf{r} - \mathbf{r}'|) + \rho_0 \delta(|\mathbf{r} - \mathbf{r}'|)] \quad (8)$$

and the induced density change:

$$\delta\rho^{(1)}(\mathbf{r}) = -\beta\rho_0\delta\phi(\mathbf{r}) - \beta\rho_0^2 \int h(|\mathbf{r} - \mathbf{r}'|)\delta\phi(\mathbf{r}')d\mathbf{r}' \quad (9)$$

## Response in reciprocal space

Taking Fourier transforms:

$$\delta\hat{\rho}^{(1)}(\mathbf{k}) = \chi(\mathbf{k})\hat{\phi}(\mathbf{k}) = -\beta\rho_0\mathbf{S}(\mathbf{k})\delta\hat{\phi}(\mathbf{k}) \quad (10)$$

and

**Susceptibility:**

$$\chi(\mathbf{k}) = -\beta\rho_0\mathbf{S}(\mathbf{k}) \quad (11)$$

- $\mathbf{S}(\mathbf{k})$  measures the response of an unperturbed system to an external field of wavelength  $2\pi/k$
- At linear order the system responds only at the wave-vector of the perturbation
- For  $k \rightarrow 0$ :

$$\lim_{k \rightarrow \infty} \mathbf{S}(\mathbf{k}) = \rho k_B T \chi_T \quad (12)$$

Response and correlation functions

Density response function

Response in reciprocal space

Taking Fourier transforms:

$$\hat{\rho}^{(1)}(\mathbf{k}) = \chi(\mathbf{k})\hat{h}(\mathbf{k}) = -\beta\epsilon_0 S(\mathbf{k})\hat{h}(\mathbf{k}) \quad (10)$$

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**Susceptibility:**

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- $S(\mathbf{k})$  measures the response of an unperturbed system to an external field of wavelength  $2\pi/k$
- At linear order the system responds only at the wave-vector of the perturbation

- For  $k \rightarrow 0$ :  $\lim_{k \rightarrow 0} S(\mathbf{k}) = \rho_0 T_{11}$  (12)

- The Fourier components of  $\delta\hat{\phi}(\mathbf{k})$  are:

$$\delta\hat{\phi}(\mathbf{k}) = \int \exp(-i\mathbf{k} \cdot \mathbf{r}) \delta\phi(\mathbf{r}) d\mathbf{r} \quad (13)$$

- The structure factor was defined before as:

$$S(\mathbf{k}) = 1 + \rho_0 \hat{h}(\mathbf{k}) \quad (14)$$

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## Example: The random phase approximation (RPA)

**Aim:** To calculate the static susceptibility,  $\chi(\mathbf{k})$ , of a system of particles interacting via weak or long-range forces

- RPA: approximation based on a combination of linear response and mean field theories
- Separate interaction potential into short and weak/long-range parts

$$\begin{array}{ccccc}
 V_T(\mathbf{r}^N) & = & V^o(\mathbf{r}^N) & + & W(\mathbf{r}^N) \\
 \uparrow & & \uparrow & & \uparrow \\
 \textit{Total} & & \textit{Reference} & & \textit{Perturbation}
 \end{array}$$

- The total potential,  $\phi(\mathbf{r})$ , felt by a particle at point  $\mathbf{r}$  is a sum of an external plus a **mean** internal potential:

$$\phi(\mathbf{r}) = \phi_{\text{ext}}(\mathbf{r}) + \int w(\mathbf{r} - \mathbf{r}') \delta\rho(\mathbf{r}') d\mathbf{r}' \quad (15)$$

Response and correlation functions

Application: random phase approximation

Example: The random phase approximation (RPA)

**Aim:** To calculate the static susceptibility,  $\chi(\mathbf{k})$ , of a system of particles interacting via weak or long-range forces

- RPA: approximation based on a combination of linear response and mean field theories
- Separate interaction potential into short and weak/long-range parts

$$V_{\text{Total}}(r^{\text{th}}) = V_{\text{Reference}}(r^{\text{th}}) + W(r^{\text{th}})$$

- The total potential,  $\phi(r)$ , felt by a particle at point  $r$  is a sum of a external plus a **mean** internal potential:

$$\phi(r) = \phi_{\text{ext}}(r) + \int w(r-r') \rho(r') dr' \quad (15)$$

- RPA implies a Gaussian distribution,  $\mathcal{P}(\{\rho(\mathbf{k})\})$ , for the Fourier components of the density  $\rho(\mathbf{k}) = \sum_{i=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_i)$ . Such distribution implies that the phases of those complex numbers are uniformly and independently distributed.

# The random phase approximation (RPA)

- $\delta\rho(\mathbf{r}')$ : deviation of the local density from its mean
- The spatially modulated external potential can be written as:

$$\phi_{ext}(\mathbf{r}) = \frac{1}{V} \delta\phi_{ext}(\mathbf{k}) \exp(-i\mathbf{k} \cdot \mathbf{r}) \quad (16)$$

- Taking Fourier transform of previous equations:

$$\phi(\mathbf{k}) = \delta\phi_{ext}(\mathbf{k}) + w(\mathbf{k})\delta\rho(\mathbf{k}) \quad (17)$$

- According to linear response:

$$\begin{array}{ccccc}
 \delta\rho(\mathbf{k}) & = & \chi^0(\mathbf{k}) & \times & (\delta\phi_{ext}(\mathbf{k}) + w(\mathbf{k})\delta\rho(\mathbf{k})) \\
 \uparrow & & \uparrow & & \uparrow \\
 \text{Density} & & \text{Susceptibility} & & \text{Selfconsistent} \\
 \text{modulation} & & \text{ref. system} & & \text{potential}
 \end{array}$$

## The random phase approximation (RPA)

- Solving for  $\delta\rho(\mathbf{k})$ :

$$\delta\rho(\mathbf{k}) = \frac{\chi^o(\mathbf{k})}{1 - \chi^o(\mathbf{k})w(\mathbf{k})} \delta\phi_{\text{ext}}(\mathbf{k}) \quad (18)$$

- For the actual system, interacting through the full potential energy,  $\delta\rho(\mathbf{k}) = \chi^T(\mathbf{k})\delta\phi_{\text{ext}}(\mathbf{k})$ , and :

$$\chi^T(\mathbf{k}) = \frac{\chi^o(\mathbf{k})}{1 - \chi^o(\mathbf{k})w(\mathbf{k})} \quad (19)$$

- In terms of the structure factors  $S^T(\mathbf{k})$  and  $S^o(\mathbf{k})$ :

$$\frac{1}{S^T(\mathbf{k})} = \frac{1}{S^o(\mathbf{k})} + \frac{\rho w(\mathbf{k})}{k_B T} \quad (20)$$

- How does the previous expression look like when  $V^o = 0$  (ideal gas) ?

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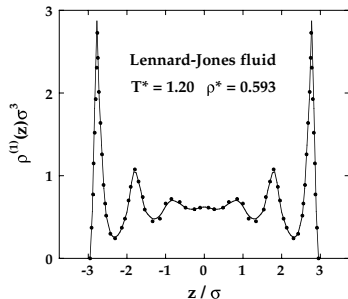
# Heterogeneous vs. Homogeneous Fluids

## ● Homogeneous fluid

- Invariant under translations
- Local density  $\rho(\mathbf{r}) \rightarrow \rho = N/V$
- $\rho$  uniquely determined by chemical potential  $\mu$
- $\Omega = \Omega(\rho)$

## ● Heterogeneous fluid

- External potential  $V_{ext}(\mathbf{r})$  break translational invariance
- Non-uniform local density  $\rho(\mathbf{r})$
- $\rho(\mathbf{r})$  uniquely determined by 'local' chemical potential  
 $\psi(\mathbf{r}) = \mu - V_{ext}(\mathbf{r})$
- $\Omega = \Omega[\rho(\mathbf{r})]$



# Density-Functional Theory

## Theorem 1:

For given choices of  $V_N$ ,  $T$  and  $\mu$ , the intrinsic free-energy functional

$$\mathcal{F}[\rho^{(1)}] = \text{Tr } f_0(K_N + V_N + k_B T \ln(f_0)) \quad (21)$$

is a unique functional of the equilibrium single-particle density  $\rho^{(1)}(\mathbf{r})$

There is only one external potential,  $\phi$ , that gives rise to a particular single-particle density,  $\rho(\mathbf{r})$

## Theorem 2:

If  $n(\mathbf{r})$  is some average microscopic density. Then the functional

$$\Omega[n] = \mathcal{F}[n] + \int n(\mathbf{r})\phi(\mathbf{r})d\mathbf{r} - \mu \int n(\mathbf{r})d\mathbf{r} \quad (22)$$

has its minimum value when  $n(\mathbf{r})$  coincides with the equilibrium single-particle density  $\rho^{(1)}(\mathbf{r})$

# Variational principle

- Theorem 2 implies: at equilibrium  $n(\mathbf{r}) = \rho^{(1)}(\mathbf{r})$  and  $\Omega[\rho^{(1)}] = \Omega$
- Differentiation of  $\Omega$  with respect to  $n(\mathbf{r})$  gives:

$$\left. \frac{\delta \Omega_\phi}{\delta n(\mathbf{r})} \right|_{n=\rho^{(1)}} = \left. \frac{\delta \mathcal{F}[n]}{\delta n(\mathbf{r})} \right|_{n=\rho^{(1)}} - \mu + \phi(\mathbf{r}) = 0$$

which implies that  $\Omega_\phi$  is stationary with respect to variations in  $n(\mathbf{r})$  around the equilibrium density

- In addition  $\Omega_\phi$  has a lower bound given by the exact grand potential of the system:

$$\Omega_\phi[n] \geq \Omega$$

## Exact expression for $\mathcal{F}[\rho]$

An exact expression for  $\mathcal{F}^{\text{ex}}[\rho]$  can be obtained when  $V_N$  is a sum of pair potentials

- Re-write grand canonical partition function in terms of  $e(i, j) = \exp(-\beta v(i, j))$

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \int \cdots \int \left( \prod_{i,j}^N e(i, j) \right) \left( \prod_{i=1}^N z^*(i) \right) d1 \cdots dN$$

- Calculate first functional derivative with respect to  $v(1, 2)$  at constant  $T$  and  $\psi$

$$\begin{aligned} \frac{\delta \Omega}{\delta v(1, 2)} &= \frac{\delta \ln \Xi}{\delta \ln e(1, 2)} = \frac{e(1, 2)}{\Xi} \frac{\delta \Xi}{\delta e(1, 2)} \\ &= \frac{1}{\Xi} \sum_{N=2}^{\infty} \frac{N(N-1)}{2N!} \int \cdots \int \left( \prod_{i,j}^N e(i, j) \right) \left( \prod_{i=1}^N z^*(i) \right) d1 \cdots dN \end{aligned}$$

## Exact expression for $\mathcal{F}[\rho]$

- Use definition of (see next note)

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}') = 2 \frac{\delta \Omega}{\delta v(\mathbf{r}, \mathbf{r}')} \quad (23)$$

- Since:  $\Omega = \mathcal{F} + \int \rho^{(1)}(\mathbf{r})\phi(\mathbf{r})d\mathbf{r} - N\mu$

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}') = 2 \frac{\delta \mathcal{F}^{(ex)}[\rho^{(1)}]}{\delta v(\mathbf{r}, \mathbf{r}')} \quad (24)$$

- Express potential as a sum of a **reference** part,  $v_0$ , and a **perturbation**,  $w$ , and define a family of intermediate potentials by:

$$v_\lambda(\mathbf{r}, \mathbf{r}') = v_0(\mathbf{r}, \mathbf{r}') + \lambda w(\mathbf{r}, \mathbf{r}') \quad \text{with} \quad 0 \leq \lambda \leq 1 \quad (25)$$

- Use definition of (see next note)

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}') = 2 \frac{\delta \Omega}{\delta \rho(\mathbf{r}, \mathbf{r}')} \quad (23)$$

- Since:  $\Omega = \mathcal{F} + \int \rho^{(1)}(\mathbf{r}) \mu(\mathbf{r}) d\mathbf{r} - N\mu$

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}') = 2 \frac{\delta \mathcal{F}^{(2)}[\rho^{(1)}]}{\delta \rho(\mathbf{r}, \mathbf{r}')} \quad (24)$$

- Express potential as a sum of a **reference part**,  $v_0$ , and a **perturbation**,  $w$ , and define a family of intermediate potentials by:

$$v_\lambda(\mathbf{r}, \mathbf{r}') = v_0(\mathbf{r}, \mathbf{r}') + \lambda w(\mathbf{r}, \mathbf{r}') \quad \text{with } 0 \leq \lambda \leq 1 \quad (25)$$

- In general:

$$\begin{aligned} \rho_N^{(n)}(\mathbf{r}^n) &= \frac{N!}{(N-n)!} \frac{1}{h^{3N} N! Q_N} \int \int \exp(-\beta V_N) d\mathbf{r}^{(N-n)} d\mathbf{p}^N \\ &= \frac{N!}{(N-n)!} \frac{1}{Z_N} \int \exp(-\beta V_N) d\mathbf{r}^{(N-n)} \end{aligned}$$

## Exact expression for $\mathcal{F}[\rho]$

Integrating  $\rho^{(2)}(\mathbf{r}, \mathbf{r}') = 2 \frac{\delta \mathcal{F}^{(ex)}[\rho^{(1)}]}{\delta v(\mathbf{r}, \mathbf{r}' )}$  at constant single particle density:

$$\begin{aligned} \mathcal{F}^{(ex)}[\rho^{(1)}] &= \mathcal{F}_0^{(ex)}[\rho^{(1)}] + \frac{1}{2} \int_0^1 d\lambda \int \int \rho^{(2)}(\mathbf{r}, \mathbf{r}'; \lambda) w(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ &= \mathcal{F}_0^{(ex)}[\rho^{(1)}] + \frac{1}{2} \int \int \rho^{(1)}(\mathbf{r}) \rho^{(1)}(\mathbf{r}') w(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' + \mathcal{F}_{corr}[\rho^{(1)}] \end{aligned}$$

$$\mathcal{F}_{corr}[\rho^{(1)}] = \frac{1}{2} \int_0^1 d\lambda \int \int \rho^{(1)}(\mathbf{r}) \rho^{(1)}(\mathbf{r}') h^{(2)}(\mathbf{r}, \mathbf{r}'; \lambda) w(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (26)$$

**Starting point for approximations**

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# Long range forces and mean field methods

In previous equation:

- Discard correlation effects, i.e.  $\mathcal{F}_{corr}[\rho^{(1)}] = 0$
- Take reference system as a uniform ideal gas with density  $\rho^{(-1)}$

$$\mathcal{F}[\rho^{(1)}] = \mathcal{F}^{(id)}[\rho^{(1)}] + \frac{1}{2} \int \int \rho^{(1)}(\mathbf{r}) \rho^{(1)}(\mathbf{r}') w(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

## Mean field approximation

- Useful for low density systems interacting via long range potentials
- Limited for systems where long wavelength fluctuations play a role

## Quadratic approximation

- Consider a weakly inhomogeneous density  $\rho(\mathbf{r}) = \rho_0 + \delta\rho(\mathbf{r})$  with  $\delta\rho(\mathbf{r})/\rho_0 \ll 1$  everywhere.
- Expand  $\mathcal{F}$  up to second order in  $\delta\rho(\mathbf{r})$ :

$$\mathcal{F}[\rho_0 + \delta\rho(\mathbf{r})] = V f_0(\rho_0) + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \delta\rho(\mathbf{r}) A(\mathbf{r} - \mathbf{r}') \delta\rho(\mathbf{r}') + \dots \quad (27)$$

- That written in terms of the Fourier components becomes:

$$\mathcal{F}[\rho_0 + \delta\rho(\mathbf{r})] = V f_0(\rho_0) + \frac{1}{2V} \sum_{\mathbf{k}} \delta\rho(\mathbf{k}) A(\mathbf{k}) \delta\rho(-\mathbf{k}) + \dots \quad (28)$$

- Using the variational formula:  $\frac{\delta\mathcal{F}[\eta]}{\delta n(\mathbf{r})} - \mu + \phi(\mathbf{r}) = 0$  one finds:

$$A(\mathbf{k}) \delta\rho(\mathbf{k}) = -\delta\phi(\mathbf{k}) \quad (29)$$

- Comparing with linear response:

$$A(\mathbf{k}) = -\frac{1}{\chi(\mathbf{k})} = \frac{k_B T}{\rho_0 S(\mathbf{k})} \quad (30)$$

# Quadratic approximation

## Quadratic approximation:

$$\mathcal{F}[\rho_0 + \delta\rho(\mathbf{r})] \approx V f_0(\rho_0) + \frac{1}{2V} \sum_{\mathbf{k}} \delta\rho(\mathbf{k}) \frac{k_B T}{\rho_0 S(\mathbf{k})} \delta\rho(-\mathbf{k})$$

The free energy cost in creating a density modulation with wavevector  $\mathbf{k}$  is proportional to  $1/S(\mathbf{k})$

## Local density approximation

- We consider a free energy density  $f = F/V$  to be a function of  $\rho^{(1)}$  and its lower order derivatives:

$$\mathcal{F}[\rho^{(1)}] = \int_{-\infty}^{+\infty} dz f(\rho^{(1)}(z), \frac{d\rho^{(1)}}{dz}, \frac{d^2\rho^{(1)}}{dz^2}) \quad (31)$$

- Assuming the gradient is small the integrand can be expanded as:

$$f = f_0(\rho^{(1)}) + f_1(\rho^{(1)}) \frac{d\rho^{(1)}}{dz} + f_2'(\rho^{(1)}) \left( \frac{d\rho^{(1)}}{dz} \right)^2 + f_2''(\rho^{(1)}) \frac{d^2\rho^{(1)}}{dz^2}$$

- Inserting into the integral and truncating at first order:

$$\mathcal{F}[\rho^{(1)}] = \int_{-\infty}^{+\infty} dz f_0(\rho^{(1)}(z)) \quad \text{Local Density Approximation (LDA)}$$

## Square gradient approximation

- Truncating previous expression at second order. We get:

$$\mathcal{F}[\rho^{(1)}] = \int_{-\infty}^{+\infty} dz \left[ f_0(\rho^{(1)}(z)) + f_2(\rho^{(1)}) \left( \frac{d\rho^{(1)}}{dz} \right)^2 \right]$$

### Square Gradient Functional (SGF)

- Use of the variational principle leads to the the following differential equation for  $\rho^{(1)}(z)$ :

$$f_0' + f_2' \left( \frac{d\rho^{(1)}(z)}{dz} \right)^2 - 2f_2 \frac{d^2\rho^{(1)}(z)}{dz^2} = \mu - \phi(z)$$

- With:

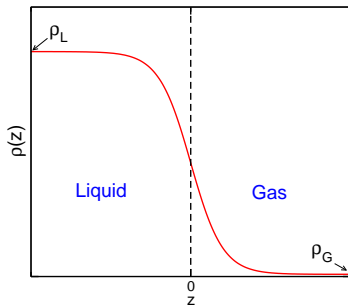
$$f_2(\rho^{(1)}) = \frac{1}{12} k_B T \int c(r) r^2 dr$$

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# Liquid-vapor interface

- Consider a liquid in equilibrium with its vapor  $\rightarrow$  **interface**
- $\rho_L$  and  $\rho_G$  are the liquid and gas densities
- Weak external field:  $\phi(z) = mgz$
- Interface parallel to the  $xOy$  plane and density is a function of  $z$
- Questions:
  - How does the interfacial profile,  $\rho(z)$ , look like at any  $T$  ?
  - How to calculate surface tension ?



# Free energy model

## Square gradient approximation:

$$\mathcal{F}[\rho] = \int_{-\infty}^{+\infty} \left( f_0 + f_2 \left( \frac{d\rho}{dz} \right)^2 \right) dz \quad (32)$$

where  $f_0$  is free energy density of uniform system.

Using the variational principle:

$$\left. \frac{\delta \mathcal{F}[n]}{\delta n(z)} \right|_{n=\rho^{(1)}} - \mu + \phi(z) = 0 \quad (33)$$

One finds:

## Euler-Lagrange equation:

$$f_0' + f_2' \left( \frac{d\rho}{dz} \right)^2 - 2f_2 \frac{d^2\rho}{dz^2} = \mu - \phi(z)$$

## Statistical Mechanics

## Inhomogeneous fluids

## Application 1: liquid-vapor interface

## Free energy model

## Free energy model

Square gradient approximation:

$$\mathcal{F}[\rho] = \int_{-\infty}^{+\infty} \left( \xi + \xi \left( \frac{d\rho}{dz} \right)^2 \right) dz \quad (32)$$

where  $\xi$  is free energy density of uniform system.

Using the variational principle:

$$\frac{\delta \mathcal{F}[\rho]}{\delta \rho(z)} \Big|_{\rho=\rho^{(0)}} = -\mu + \psi(z) = 0 \quad (33)$$

One finds:

Euler-Lagrange equation:

$$\xi + \xi \left( \frac{d\rho}{dz} \right)^2 - 2\xi \frac{d^2\rho}{dz^2} = \mu - \psi(z)$$

- Boundary conditions:  $\rho(z) \rightarrow \rho_G$  for  $z \rightarrow +\infty$  and  $\rho(z) \rightarrow \rho_L$  for  $z \rightarrow -\infty$

## Using the square gradient approximation

Using a mean field approximation:

$$f_2(\rho_0) = -\frac{1}{3}\pi \int w(r)r^4 dr = \frac{1}{2}m \quad (34)$$

and in the limit  $\phi(z) = mgz \rightarrow 0$

$$f'_0 - m \frac{d^2 \rho}{dz^2} = \mu$$

Defining

$$W(\rho) = \frac{-\Omega}{V} = -f_0(\rho) + \mu \rho \quad \frac{dW(\rho)}{d\rho} = -f'_0(\rho) + \mu \quad (35)$$

## Using the square gradient approximation

### Euler-Lagrange equation:

$$m \frac{d^2 \rho}{dz^2} = - \frac{dW(\rho)}{d\rho} \quad (36)$$

Boundary conditions:

$$\lim_{z \rightarrow \pm \infty} W(\rho) = -f_0(\rho_{bulk}) + \mu \rho_{bulk} = P \quad (37)$$

with

$$\rho_{bulk} = \begin{cases} \rho_G & z \rightarrow +\infty \\ \rho_L & z \rightarrow -\infty \end{cases} \quad (38)$$

Integrating previous equation:

$$\frac{d\rho}{dz} = \left[ \frac{2}{m} (P - W(\rho)) \right]^{1/2} \quad (39)$$

# The density profile

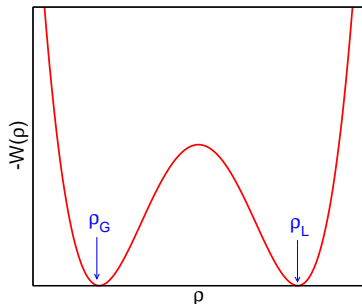
- A second integration yields the density profile:

$$z = \left(\frac{m}{2}\right)^{1/2} \int_{\rho(0)}^{\rho(z)} d\rho [P - W(\rho)]^{1/2}$$

- Last ingredient: model for  $W(\rho)$ :

**At liquid-gas coexistence**

$$-W(\rho) = P_T - \frac{1}{2} c_T (\rho - \rho_L)^2 (\rho - \rho_G)^2$$



# The density profile

Using the previous model for  $W(\rho)$ :

$$z = - \left( \frac{m}{c_T} \right)^{1/2} \int_{\rho(0)}^{\rho(z)} \frac{d\rho}{(\rho - \rho_L)(\rho - \rho_G)} \quad (40)$$

$$= -\xi \ln \left( \frac{\rho(z) - \rho_G}{\rho_L - \rho(z)} \right) \quad (41)$$

with:  $\xi = (m/c_T)^{1/2}/(\rho_L - \rho_G) \rightarrow$  **Interface width**

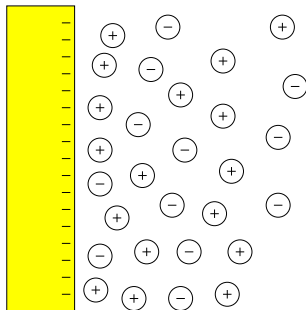
$$\rho(z) = \frac{1}{2}(\rho_L + \rho_G) - \frac{1}{2}(\rho_L - \rho_G) \tanh \left( \frac{z}{2\xi} \right)$$

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# A single charged plane

- Infinite planar surface
  - Position  $z = 0$
  - Uniform charge density,  $\sigma < 0$
- Ionic solution in contact with the surface
- We aim at calculating the ionic density profiles  $\rho_{\pm}(z)$



## A single charged plane

$$F[\rho_+, \rho_-] = - \sum_{s=+,-} k_B T \int_0^\infty \rho_i(z) [\ln(\rho_i(z)\Delta^3) - 1] dz \quad (42)$$

$$\frac{e}{2} \int_0^\infty \Phi(z) \rho_c(z) dz \quad (43)$$

$$\frac{d^2\Phi(z)}{dz^2} = -\frac{e}{\epsilon_0} \rho_c(z) \quad \text{with} \quad \rho_c(z) = \rho_+(z) - \rho_-(z) \quad (44)$$

and

$$\rho(z) = \rho_\pm^0 \exp(\mp\beta\Phi(z)) \quad (45)$$

Two considerations:

- In the bulk  $\rho_+^0 = \rho_-^0 = \rho^0$
- Overall charge neutrality requires:  $e \int_0^\infty \rho_c(z) dz = -\sigma$

## A single charged plane

Using the variational principle:

$$\frac{\delta\Omega[\rho^+, \rho^-]}{\delta\rho^\pm} = 0 \quad (46)$$

we arrive at:

**Poisson-Boltzmann equation:**

$$\frac{d^2\Phi(z)}{dz^2} = \frac{2e\rho_0}{\epsilon_0} \sinh(\beta e\Phi(z)) \quad (47)$$

or

$$\frac{d^2\Phi^*(z)}{dz^2} = \kappa_D^2 \sinh[\Phi^*(z)] \quad \text{with} \quad \kappa_D = \sqrt{\frac{2\rho_0 e^2}{\epsilon_0 k_B T}} \quad (48)$$

Boundary conditions:

$$\frac{d\Phi(z)}{dz} = 0 \quad \text{and} \quad \left. \frac{d\Phi(z)}{dz} \right|_{z=0} = -\frac{\sigma}{\epsilon_0} \quad (49)$$

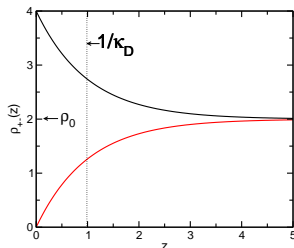
# A single charged plane

Linearising with respect to  $\Phi^*(z)$ :

$$\frac{d^2\Phi(z)}{dz^2} \approx \kappa_D^2 \Phi(z)$$

with solution: 
$$\Phi(z) = \frac{\sigma}{\epsilon_0 \kappa_D} \exp(-\kappa_D z)$$

$\sigma/\Phi(0) = \epsilon \kappa_D \rightarrow$  **Capacitance**



The linearised densities are:

$$\rho_{\pm}(z) = \rho_{\pm}^0 \mp \frac{e\Phi(z)}{k_B T} = \rho_{\pm}^0 \pm \frac{\kappa_D |\sigma|}{2e} \exp(-\kappa_D z)$$

# Bibliography

- "*Theory of Simple Liquids* ", by Jean Pierre Hansen , Ian R. McDonald, Academic Press, Third Edition, 2005
- "*Principles of Condensed Matter Physics* ", by P. M. Chaikin and T. C. Lubensky, Cambridge University Press, 1995