

APPROACH TO MOLECULAR SOLVENTS

In the case of non-spherical solvent like water, the solvent particle carries a molecular structure described by a collection of distributed atomic interaction sites (LJ and Coulombic). The two theories mentioned in the previous section are now formulated in the molecular picture in which each solvent molecule is considered as a rigid body and characterized by its position \mathbf{r} (e.g. the position of center of mass), and its orientation $\mathbf{\Omega} \equiv (\Theta, \Phi, \Psi)$. In **MDFT!**, the solvent is characterized by an angle-dependent inhomogeneous density, $\rho(\mathbf{r}, \mathbf{\Omega})$; in **IET!**, an angle-dependent form of the pair distribution function $g(\mathbf{X}_1, \mathbf{X}_2)$ ($X \equiv (\mathbf{r}, \mathbf{\Omega})$) is proposed, while the molecular **OZ!** equation is expanded on rotational invariants. The reference interaction site model (RISM) [**hirata_molecular_2004**], which provides another way for **IET!** to treat molecular solvent, will not be discussed in this thesis.

1.1 MOLECULAR DENSITY FUNCTIONAL THEORY

In **MDFT!** (**MDFT!**), the grand potential is rewritten as:

$$\Omega[\rho(\mathbf{r}, \mathbf{\Omega})] = \Omega[\rho_0] + \mathcal{F}[\rho(\mathbf{r}, \mathbf{\Omega})] \quad (1.1)$$

where $\Omega[\rho_0]$ is the correspondent reference bulk fluid grand potential (with $\rho = \rho_0$ and $V_{\text{int}} = 0$). $\rho(\mathbf{r}, \mathbf{\Omega})$ is the angle-dependent fluid density function, depending on 3 variables for spatial coordinates \mathbf{r} , and also 3 for orientation $\mathbf{\Omega} \equiv (\Theta, \Phi, \Psi)$. In case of linear solvent, this number can reduce to 2, i.e. $\mathbf{\Omega} \equiv (\Theta, \Phi)$. The homogeneous bulk density ρ_0 is normalized to $n_0 / \int d\mathbf{\Omega}$, to keep coherent with the relation

$$\int d\mathbf{\Omega} \rho(\mathbf{r}, \mathbf{\Omega}) = \int d\cos\Theta d\Phi d\Psi \rho(\mathbf{r}, \mathbf{\Omega}) = n(\mathbf{r}) \quad (1.2)$$

which reduces eq. (1.1) to eq. (??) in §??.

According to the variation principle described in §??, the equilibrium density can be found by minimizing the free energy functional

$$\mathcal{F}[\rho] = \mathcal{F}_{\text{id}}[\rho] + \mathcal{F}_{\text{ext}}[\rho] + \mathcal{F}_{\text{exc}}[\rho] \quad (1.3)$$

regarding to $\rho(\mathbf{r}, \mathbf{\Omega})$:

$$\left. \frac{\delta \mathcal{F}[\rho]}{\delta \rho(\mathbf{r}, \mathbf{\Omega})} \right|_{\rho=\rho_0} = 0 \quad (1.4)$$

which remains exactly the same formalism with those in §??.

1.1.1 The ideal term

The ideal term $\mathcal{F}_{\text{id}}[\rho]$ deduced from the particle interaction-free condition is:

$$\mathcal{F}_{\text{id}}[\rho] = k_B T \int d\mathbf{r} d\mathbf{\Omega} \left[\rho(\mathbf{r}, \mathbf{\Omega}) \ln \left(\frac{\rho(\mathbf{r}, \mathbf{\Omega})}{\rho_0} \right) - \rho(\mathbf{r}, \mathbf{\Omega}) + \rho_0 \right] \quad (1.5)$$

(incoherent with §?? with an additional term ρ_0 , and disappeared Λ^3 .)

The differentiation of $\mathcal{F}_{\text{id}}[\rho]$ used for the minimization, which will be discussed later, has form:

$$\frac{\delta \mathcal{F}_{\text{id}}[\rho]}{\delta \rho(\mathbf{r}, \mathbf{\Omega})} = \beta^{-1} \ln \left(\frac{\rho(\mathbf{r}, \mathbf{\Omega})}{\rho_0} \right) \quad (1.6)$$

1.1.2 The external term

The solute, like the solvent, is described in microscopic detail by a molecular non-polarizable force field involving atomic Lennard-Jones and partial charge parameters, creating at each point in space an external potential $V_{\text{ext}}(\mathbf{r}, \mathbf{\Omega})$, containing two components:

$$V_{\text{ext}}(\mathbf{r}, \mathbf{\Omega}) = V_{\text{LJ}}(\mathbf{r}) + V_{\text{coul}}(\mathbf{r}, \mathbf{\Omega}) \quad (1.7)$$

The external potential term calculates the contribution of V_{ext} :

$$\mathcal{F}_{\text{ext}}[\rho] = \int d\mathbf{r} d\mathbf{\Omega} \rho(\mathbf{r}, \mathbf{\Omega}) (V_{\text{ext}}(\mathbf{r}, \mathbf{\Omega}) - \mu) \quad (1.8)$$

with μ the chemical potential.

The Lennard-Jones potential is given by:

$$V_{\text{LJ}}(\mathbf{r}) = \sum_u \sum_v 4\epsilon_{uv} \left[\left(\frac{\sigma_{uv}}{r_{uv}} \right)^{12} - \left(\frac{\sigma_{uv}}{r_{uv}} \right)^6 \right] \quad (1.9)$$

where u stands for solute, v stands for solvent, $\epsilon_{uv} = \sqrt{\epsilon_u \epsilon_v}$ and $\sigma_{uv} = (\sigma_u + \sigma_v)$ are the geometric and arithmetic average Lennard-Jones parameters between solute and solvent, according to the Lorentz-Berthelot mixing rules. r_{ij} is the norm of relative site-site vector

$$\mathbf{r}_{uv} = \mathbf{r} + \mathbf{R}(\mathbf{\Omega})\mathbf{s}_v - \mathbf{r}_u \quad (1.10)$$

where \mathbf{r}_u and \mathbf{s}_v are the coordinates of solute/solvent molecules in the molecular frame, and $\mathbf{R}(\mathbf{\Omega})$ is the rotation matrix of the Euler angles $\mathbf{\Omega}$. In cases where the solvent site wears only one LJ centre, eq. (1.10) reduces to

$$\mathbf{r}_{uv} = \mathbf{r} - \mathbf{r}_u \quad (1.11)$$

which is actually what we use in the code as the solvent is SPC/E water.

The Coulomb interaction is calculated by solving the Poisson equation. The charge density of the solute is projected onto a space grid \mathbf{r} ,

$$\rho_q(\mathbf{r}) = \sum_u q_{ijk} / \Delta v \quad (1.12)$$

where q_{ijk} is the charge on the space grid distributed by its nearby point charge as shown in figure 1.1, and Δv the volume of the unit cube that this point charge situates in.

The electrostatic potential created by the charge distribution $\rho_q(\mathbf{r})$, $V_q(\mathbf{r})$, can be thus computed using a periodic Poisson Solver. The Poisson equation (??)

$$\nabla^2 V_q(\mathbf{r}) = -\frac{\rho_q(\mathbf{r})}{\epsilon_0} \quad (1.13)$$

(where is the $\epsilon(\mathbf{r})$?) gives in Fourier space

$$\hat{V}_q(\mathbf{k}) = \frac{\hat{\rho}_q(\mathbf{k})}{\epsilon_0 k^2} \quad (1.14)$$

where $\hat{V}_q(\mathbf{k})$ and $\hat{\rho}_q(\mathbf{k})$ are the Fourier transform of $V_q(\mathbf{r})$ and $\rho_q(\mathbf{r})$ respectively. These two equations provide a fast way to calculate $V_q(\mathbf{r})$ from $\rho_q(\mathbf{r})$.

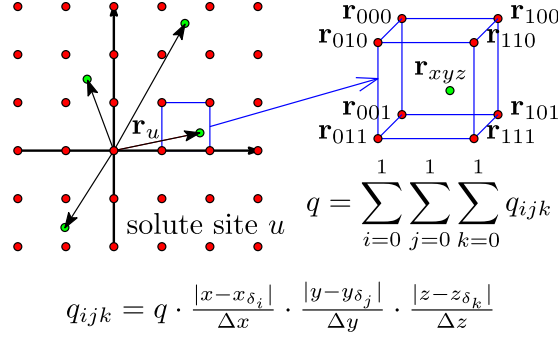


Figure 1.1: Solute charge density projected onto grids

The Coulomb potential is expressed as a sum of solvent partial charge contributions at each grid node:

$$V_{\text{coul}}(\mathbf{r}, \mathbf{\Omega}) = \sum_v q_v V_q(\mathbf{r}_v) \quad (1.15)$$

where q_v is the point charge of solvent, and

$$\mathbf{r}_v = \mathbf{r} + \mathbf{R}(\mathbf{\Omega})\mathbf{s}_v \quad (1.16)$$

is the cartesian coordinate of a solvent site v ; $V_q(\mathbf{r}_u)$ is the electrostatic potential, given by a linear interpolation of the nearby point of $V_q(\mathbf{r})$ obtained in the last step from the Poisson solver.

1.1.3 The excess term

The two terms $\mathcal{F}_{\text{id}}[\rho]$ and $\mathcal{F}_{\text{ext}}[\rho]$ are physically exact, while the excess term $\mathcal{F}_{\text{exc}}[\rho]$ depends on the exact correlation function, which is a priori unknown. As shown in §??, we invoke here the **HRF!** approximation which amounts to a second-order Taylor expansion around the homogeneous fluid at density ρ_0 :

$$\mathcal{F}_{\text{exc}}[\rho] = -\frac{k_B T}{2} \int d\mathbf{r}_1 d\mathbf{\Omega} \gamma(\mathbf{r}_1, \mathbf{\Omega}) \rho(\mathbf{r}_1, \mathbf{\Omega}) \quad (1.17)$$

where γ is the normalized gradient of the excess functional:

$$\gamma(\mathbf{r}_1, \mathbf{\Omega}_1) = -\frac{\delta \beta F_{\text{exc}}}{\delta \rho} = \int d\mathbf{r}_2 d\mathbf{\Omega}_2 \Delta \rho(\mathbf{r}_2, \mathbf{\Omega}_2) c(\mathbf{r}_{12}, \mathbf{\Omega}_1, \mathbf{\Omega}_2) \quad (1.18)$$

(attention the negative sign) which can be related to the solute-solvent 2-component **IET!** (**IET!**) with its definition:

$$\gamma(1, 2) = h_{\text{MS}}(1, 2) - c_{\text{MS}}(1, 2) \quad (1.19)$$

To evaluate the gradient γ for each $(\mathbf{r}, \mathbf{\Omega})$ in eq. (1.18), $N \equiv N_{\mathbf{r}} N_{\mathbf{\Omega}}$ function evaluations (**FE!**) are required. The total number of **FE!** is thus $N^2 = O(N^2)$, which, with typically $N_{\mathbf{r}} = 64^3$ and $N_{\mathbf{\Omega}} = 50 \sim 100$, is far too costly for current computing technology. For this reason, Fourier transform is used to treat the spatial convolution.

A convolution

$$h(x_1) \equiv f(x_2) \otimes g(x_2) \equiv \int_a^b f(x_2) g(x_1 - x_2) dx_2 \quad (1.20)$$

has the property that

$$\mathfrak{F}[h(x_1)] = \mathfrak{F}[f(x_2)] \mathfrak{F}[g(x_2)] \quad (1.21)$$

\mathfrak{F} being the Fourier transform operation. As $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$, eq. (1.18) is a 3D convolution, which leads to

$$\hat{\gamma}(\mathbf{k}, \boldsymbol{\Omega}_1) = \int d\boldsymbol{\Omega}_2 \Delta\hat{\rho}(\mathbf{k}, \boldsymbol{\Omega}_2) \hat{c}(\mathbf{k}, \boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2) \quad (1.22)$$

Therefore, the integral $\int d\mathbf{r}_2$ in eq. (1.18) is transformed into a simple product in eq. (1.22). To get $\hat{\gamma}(\mathbf{k}, \boldsymbol{\Omega}_1)$ with given $\Delta\hat{\rho}(\mathbf{k}, \boldsymbol{\Omega}_2)$, only $N_{\mathbf{r}} N_{\boldsymbol{\Omega}}^2$ **FE!** are needed. To this computational cost should be added the transform from $\Delta\rho(\mathbf{r}, \boldsymbol{\Omega})$ to $\Delta\hat{\rho}(\mathbf{k}, \boldsymbol{\Omega})$ and the backward transform from $\hat{\gamma}(\mathbf{k}, \boldsymbol{\Omega})$ to $\gamma(\mathbf{r}, \boldsymbol{\Omega})$ which are both of order $N_{\boldsymbol{\Omega}} \cdot O(N_{\mathbf{r}} \log_2 N_{\mathbf{r}})$ due to the properties of Fast Fourier Transforms (**FFT!**). The total number of **FE!** is thus reduced from quadratic complexity $O(N_{\mathbf{r}}^2 N_{\boldsymbol{\Omega}}^2)$ to $N_{\mathbf{r}} N_{\boldsymbol{\Omega}}^2 + 2N_{\boldsymbol{\Omega}} \cdot O(N_{\mathbf{r}} \log_2 N_{\mathbf{r}}) = O(N_{\mathbf{r}} \log_2 N_{\mathbf{r}} N_{\boldsymbol{\Omega}}^2)$. As the total number of spatial grid $N_{\mathbf{r}}$ is of magnitude $10^5 \sim 10^6$, this procedure, which is mathematically equivalent to the direct evaluation (1.18), offers a great advantage in terms of computational efficiency (figure ?? in section ??).

Once $\gamma(\mathbf{r}, \boldsymbol{\Omega})$ is obtained by inverse Fourier transform of $\hat{\gamma}(\mathbf{k}, \boldsymbol{\Omega})$, the excess functional can be calculated as eq. (1.17).

The input $\hat{c}(\mathbf{k}, \boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2)$ is an angular-dependent **DCF!** of the homogeneous solvent which depends on the relative position of two molecules r_{12} and their orientations (two in the initial code [Zhao_2011], and three developed in this thesis). This quantity is provided with high precision and in different representations by Luc Belloni, using a mixture of **MC!** simulations and inversion of the angular-dependent **MOZ!** equation within a rotational invariant expansion [puibasset_bridge_2012]. A detailed comparison of some **DCF!**s is in appendix [ref].

1.2 ANGULAR DEPENDENT INTEGRAL EQUATION THEORY

To extend the **IET!** formalism to molecular cases, Blum [Blum_I, Blum_II] proposed an angular-dependent form of the pair distribution function, which is then used in the **IET!** formalism. Fries & Patey [Fries_Patey_1985] proposed the numerical solution of the full **HNC!** theory using angle-dependent pair potentials. The description below is based on these articles.

1.2.1 Expansion of angular-dependent distribution functions

The angular-dependent **PDF!** is defined as

$$g(\mathbf{X}_1, \mathbf{X}_2) \equiv g(\mathbf{r}_1, \mathbf{r}_2, \boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2) \quad (1.23)$$

which possesses the translational invariance if the fluid is homogeneous:

$$g(\mathbf{X}_1, \mathbf{X}_2) = g(\mathbf{r}_{12}, \boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2) \quad (1.24)$$

and the rotational invariance (attention indices): (Non, cette équation mélange tous les **R** possibles et n'a pas encore imposé l'invariance par rotation de l'ensemble. C'est la condition d'invariance qui impose alors 4.24 avec 4.23.)

$$g(\mathbf{X}_1, \mathbf{X}_2) = \sum_{m,n,l=0}^{\infty} \sum_{|\mu,\mu'| \leq m, |\nu,\nu'| \leq m, |\lambda| \leq l} g_{\mu,\mu'\nu\nu'\lambda}^{mnl}(\|\mathbf{r}_{12}\|) R_{\mu\mu'}^m(\boldsymbol{\Omega}_1) R_{\nu\nu'}^m(\boldsymbol{\Omega}_2) R_{\lambda 0}^l(\hat{\mathbf{r}}_{12}) \quad (1.25)$$

The suggestion of Wigner gives a set of rotation invariant: (Pourquoi as-tu échanger les indices $\mu\nu\lambda$ et $\mu'\nu'\lambda$?' Il faut rester cohérent le plus possible avec

la notation de la littérature existante. Cette remarque s'applique à toutes les équations suivantes.)

$$\Phi_{\mu'\nu'}^{mnl}(\hat{\mathbf{r}}_{12}, \mathbf{\Omega}_1, \mathbf{\Omega}_2) = f^{mnl} \sum_{\mu\nu\lambda} \begin{pmatrix} m & n & l \\ \mu & \nu & \lambda \end{pmatrix} R_{\mu\mu'}^m(\mathbf{\Omega}_1) R_{\nu\nu'}^m(\mathbf{\Omega}_2) R_{\lambda 0}^l(\hat{\mathbf{r}}_{12}) \quad (1.26)$$

such that

$$g(\mathbf{X}_1, \mathbf{X}_2) = \sum_{mnl} \sum_{\mu'\nu'} g_{\mu'\nu'}^{mnl}(\|\mathbf{r}_{12}\|) \Phi_{\mu'\nu'}^{mnl}(\hat{\mathbf{r}}_{12}, \mathbf{\Omega}_1, \mathbf{\Omega}_2) \quad (1.27)$$

and

$$g_{\mu'\nu'}^{mnl} = \sum_{\mu\nu\lambda} \begin{pmatrix} m & n & l \\ \mu & \nu & \lambda \end{pmatrix} g_{\mu, \mu'\nu\nu'\lambda}^{mnl} \quad (1.28)$$

1.2.2 Blum's reduction of molecular OZ equation

The molecular Ornstein-Zernike **MOZ!** equation is defined as (rester cohérent dans la notation: il s'agit de la fonction gamma et non eta. a changer dans toutes les eq. qui suivent.)

$$h(\mathbf{X}_1, \mathbf{X}_2) - c(\mathbf{X}_1, \mathbf{X}_2) = \frac{\rho}{8\pi^2} \int d\mathbf{X}_3 h(\mathbf{X}_1, \mathbf{X}_3) c(\mathbf{X}_3, \mathbf{X}_2) \quad (1.29)$$

which can be both expanded as

$$h(\mathbf{X}_1, \mathbf{X}_2) = \sum_{mnl} \sum_{\mu'\nu'} h_{\mu'\nu'}^{mnl}(\|\mathbf{r}_{12}\|) \Phi_{\mu'\nu'}^{mnl}(\hat{\mathbf{r}}_{12}, \mathbf{\Omega}_1, \mathbf{\Omega}_2) \quad (1.30)$$

$$c(\mathbf{X}_1, \mathbf{X}_2) = \sum_{mnl} \sum_{\mu'\nu'} c_{\mu'\nu'}^{mnl}(\|\mathbf{r}_{12}\|) \Phi_{\mu'\nu'}^{mnl}(\hat{\mathbf{r}}_{12}, \mathbf{\Omega}_1, \mathbf{\Omega}_2) \quad (1.31)$$

$$\eta(\mathbf{X}_1, \mathbf{X}_2) = h(\mathbf{X}_1, \mathbf{X}_2) - c(\mathbf{X}_1, \mathbf{X}_2) = \sum_{mnl} \sum_{\mu'\nu'} \eta_{\mu'\nu'}^{mnl}(\|\mathbf{r}_{12}\|) \Phi_{\mu'\nu'}^{mnl}(\hat{\mathbf{r}}_{12}, \mathbf{\Omega}_1, \mathbf{\Omega}_2) \quad (1.32)$$

As an analog to the **FFT!** the fast Hankel transform can deal these rotational invariant projections into k -space, such that

$$\hat{c}_{\mu\nu}^{mnl}(k) = 4\pi i^l \int dr r^2 j_l(kr) c_{\mu\nu}^{mnl}(r) \quad (1.33)$$

$$\hat{\eta}_{\mu\nu}^{mnl}(k) = 4\pi i^l \int dr r^2 j_l(kr) \eta_{\mu\nu}^{mnl}(r) \quad (1.34)$$

where $j_l(kr)$ are the spherical Bessel functions.

The χ -transform defined by Blum gives (Je vois que tu as ajouté un prime pour les fonctions dans le repère moléculaire indicées par khi. Ce n'est pas la notation historique de Blum mais tu as voulu te rapprocher de la nôtre pour soluté+solvant. Comme je l'ai dit dans des mails et utilisé dans l'article, je conseillerais de coller le plus possible à la notation de Blum, donc pas de prime, mais khi en indice après une virgule.)

$$\hat{c}_{\mu\nu,\chi}^{mn}(k) = \sum_{l=|m-n|}^{m+n} \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \hat{c}_{\mu\nu}^{mnl}(k) \quad (1.35)$$

$$\hat{\eta}_{\mu\nu,\chi}^{mn}(k) = \sum_{l=|m-n|}^{m+n} \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \hat{\eta}_{\mu\nu}^{mnl}(k) \quad (1.36)$$

If $\Phi_{\mu'\nu'}^{mnl}(\hat{\mathbf{r}}_{12}, \boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2)$ is defined with the factor $f^{mnl} = [(2m+1)(2n+1)]^{1/2}$, the **MOZ!** equation can be reduced by Blum's reduction such that

$$\hat{\eta}_{\mu\nu,\chi}^{mn}(k) = \rho \sum_{n_1} \sum_{\nu_1=-n_1}^{n_1} (-)^{\chi+\nu_1} \left[\hat{\eta}_{\mu\nu_1,\chi}^{mn_1}(k) + \hat{c}_{\mu\nu_1,\chi}^{mn_1}(k) \right] \hat{c}_{\underline{\nu_1}\nu,\chi}^{n_1n}(k) \quad (1.37)$$

which reduces the calculation of $(\mathbf{X}_1, \mathbf{X}_3)$ for $(\mathbf{X}_3, \mathbf{X}_2)$ to a sum of n_1, ν_1 .

(The part of HNC has non need in this thesis.)