A WEIGHTED CORRELATION APPROACH OF THE DENSITY FUNCTIONAL THEORY FOR AN INHOMOGENEOUS FLUID AT AN INTERFACE

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Tryck: US-AB
To Yuanyuan
Abstract

This doctoral thesis presents a newly developed density functional theory (DFT), i.e., the weighted correlation approach (WCA), to study the structural and thermodynamic properties of an inhomogeneous fluid at an interface. The WCA approach provides a generic formulation to evaluate the change of the single-particle direct correlation function in terms of a series of pair direct correlation functions weighted by different correlation-weight functions with adjustable correlation-weight factors. When applied practically, however, an approximation of the pair direct correlation function has to be made, together with appropriate definitions of the weighted densities and the choices of the correlation-weight functions. Despite this seeming complexity, it is shown that the WCA approach can be regarded as a generalization of the classic density functional approaches and this enables us to develop and apply DFT methods in different ways. For demonstration purposes, several implementations of the WCA approach are proposed and applied to predict the density distribution of an inhomogeneous fluid at an interface. The WCA approach is also employed with a novel pressure expression to investigate the inhomogeneous fluid-mediated interaction pressure for different cases. The WCA calculations from the above applications suggest that it is a successful approach for describing the structural and thermodynamic properties of an inhomogeneous fluid at an interface, as compared to the published results of the Monte Carlo simulations, density functional methods and experimental data.
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This thesis is based on the following publications. The papers are referred to by their Roman numerals in the text.

I. The weighted correlation approach for density functional theory: a study on the structure of the electric double layer
Zhao Wang, Longcheng Liu and Ivars Neretnieks

II. Weighted correlation approach: an extended version with applications to the hard-sphere fluid
Zhao Wang and Longcheng Liu

III. A novel method to describe the interaction pressure between charged plates with application of the weighted correlation approach
Zhao Wang, Longcheng Liu and Ivars Neretnieks

IV. Hard-sphere fluid-mediated interaction: a novel pressure expression with application of the weighted correlation approach
Zhao Wang and Longcheng Liu
Submitted for publication (2013).

V. The swelling pressure of Na-bentonite: study with a density functional approach
Zhao Wang and Longcheng Liu

These papers are appended at the end of the thesis.

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Paper III: © 2011 American Institute of Physics
Paper V: © 2012 The Chemical Society of Japan
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The importance of understanding the structural and thermodynamic properties of inhomogeneous fluids was early emphasized in the field of theoretical physics. It has also been recognized in other modern disciplines such as chemical engineering, materials science and nanotechnology. The basis of such an understanding is sustained by statistical mechanics, which predict the physicochemical properties of meso- and macroscopic systems from the molecular perspective [1]. Although such a prediction is always very demanding, due to the significant variation of the molecular events in, e.g., the vicinity of the interface, rapid improvement in computing techniques promises, in principle, molecular simulation to be a robust approach to achieve the full potential of statistical mechanics [2, 3]. However, simulation cannot replace all the classic thermodynamic methods in the near future [4]. This is not only because of a much smaller computational effort based on the analytical nature of the conventional methods such as the van der Waals equation of state and Boltzmann’s distribution law, but more importantly due to the fact that interpretation of these simulation data could only be attained if the underlying physics are well understood.

Density functional theory (DFT) offers a compromise between simulation methods and conventional theories [3, 4]: on the one hand, DFT is able to describe the microscopic details of macroscopic systems at a more precise level than the conventional theories, with a numerical simplicity that decreases, to a large extent, the computational effort compared to that of the simulation methods; on the other hand, the superior physical clarity enables DFT, as an alternative to the conventional theories, to reasonably interpret the properties of macroscopic systems based on the understanding of their microscopic constituents.

A density functional theory appropriate to the non-uniform simple fluids was developed in 1976 by Ebner et al [5]. The foundation of the DFT is provided by the variational principle for the grand potential of the system under study [5, 6]. It was proven that a universal functional of the density exists, i.e., the intrinsic (Helmholtz) free energy \( F[n(r)] \), independent of the external potential \( u(r) \), such that the grand potential \( \Omega \) of the system under study has its minimum when the system reaches the equilibrium state at a fixed temperature \( T \) and chemical potential \( \mu \). A calculus of this principle is provided explicitly as the Euler–Lagrange equation, where the microscopic density profile can be solved by using different density functional approximations of the excess part of the functional \( F \) or its functional derivative. As a consequence, the full structural and thermodynamic properties of the system under study can be obtained.
Due to its physical clarity and numerical simplicity, the density functional theory is regarded as a powerful tool for treating problems varying from simple inhomogeneous fluids to complex systems including those containing polymers and biomacromolecules. Although this implies extensive usage of the density functional theory in a wide range of natural and industrial processes, the study of the behavior of inhomogeneous fluids, or particularly the ionic fluid at interfaces, is of considerable importance within the context of this thesis.

In particular, the ionic structure of a clay-water system has drawn many authors’ attention in the study of colloidal science. This is because of its great importance in determining the stability of, e.g., the smectite gel/sol in engineering applications, such as in a nuclear waste repository where natural bentonite clay is envisaged in several countries as the buffer and backfill material. In Sweden, the KBS-3 disposal concept for storing high-level nuclear waste is to enclose the nuclear waste in a copper canister, which is embedded by the compacted bentonite deep underground [7]. The success of such containment depends, therefore, crucially on the stability of the clay buffer material. The clay buffer material consists mainly of lamellar montmorillonite and has the characteristic property of swelling when it comes into contact with the groundwater. In this or similar situations, the electric double layer plays a decisive role in determining the swelling properties and the colloidal stability.

To study the structural and thermodynamic properties of the clay-water system, a weighted correlation approach is developed, within the framework of the density functional theory, to predict the microscopic density distribution of an inhomogeneous fluid at an interface. It is then applied to investigate an inhomogeneous fluid-mediated interaction pressure, based on a novel pressure equation formulated in this work. It is noteworthy that, by using a finite size for the microscopic particles of the inhomogeneous fluid, the weighted correlation approach properly addresses the correlation effects that have been entirely neglected in the conventional theories. Application of the weighted correlation approach on various cases suggests that it is very accurate and even has an advantage over the classic DFTs in studying the structural and thermodynamic properties of inhomogeneous fluids at an interface.

The rest of the thesis is organized as follows. In Chapter 2, the general formalism and the fundamental principle of the density functional theory are briefly introduced for the case of non-uniform fluids. Chapter 3 is devoted to a summary of the weighted correlation approach that is the theoretical basis of this thesis. The weighted correlation approach is then validated and implemented, respectively, in predicting the hard-sphere density profile between a pair of parallel planar hard walls and the ionic density profile of a single electric double layer in Chapter 4. In Chapter 5, a novel equation is formulated to describe the inhomogeneous fluid-mediated interaction pressure in a slit. The resulting expression can be applied to explicitly investigate the influence of the correlation effects on the interaction pressure between surfaces. For illustrative purposes, the pressure equation is implemented with the weighted correlation approach to study the medium-induced interaction pressure in different cases. The conclusions are given in Chapter 6.
In this chapter, the introduction to the density functional theory for an inhomogeneous fluid is based on the formalism of the grand canonical ensemble. The starting point is a Hamiltonian of a many-particle system in the presence of a spatially varying, external potential, in which a term representing the interaction energy between the particles and some external field is included. A complete description of the Hamiltonian is then used to construct the grand potential at static state through a link between statistics and thermodynamics. The fundamental importance in developing the density functional theory is the variational principle of the grand potential [5, 6]. This principle guarantees that the grand potential functional reaches its minimum (at fixed $\mu$ and $T$) and is equal to the exact grand potential of the system at the equilibrium state. Based on that, the so-called Euler-Lagrange equation explicitly provides the calculus for the variational principle, and it is the starting equation in the density functional theory. It should be mentioned that this chapter is committed to a brief summary of the fundamental concepts and definitions of classic density functional theory. The readers who are not familiar with this subject are, therefore, encouraged to refer to the standard textbooks [8-10].

2.1. Grand canonical ensemble

In statistic mechanics, an ensemble is a collection of an arbitrarily large number of imaginary systems as replicas of a many-particle physical system [1]. Although the macroscopic state of the ensemble is specified by a particular set of fixed macroscopic parameters, the microscopic state of each system can still differ in the assignment of the coordinates and momenta of the particles. To statistically realize each configuration of the microscopic states, an important quantity $p_s$ is used to denote the probability density of finding a randomly chosen system at a microscopic state $s$ of energy $E_s$, i.e., one can write [1]

$$p_s = \frac{e^{-\beta E_s}}{Q}$$

(2.1)

where $\beta = 1/k_B T$, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. $Q$ is a normalizing factor ensuring that the probability densities sum up to one; it is called the partition function.
If one considers a many-particle system where the number of particles $N$ may vary by interchange with the surroundings, the thermodynamic state of such an “open” system is determined by specifying the chemical potential $\mu$, the volume $V$ and $T$. The corresponding thermodynamic potential of the system is the grand potential $\Omega$, and it is defined as [8]

$$\Omega = H - N\mu$$  \hspace{1cm} (2.2)$$

where $H$ is the Helmholtz free energy.

To represent all possible configurations of this system, an ensemble of systems characterized by the same values of $\mu$, $V$ and $T$ is called a grand canonical ensemble. The constancy of $\mu$ and $T$ is ensured by the fact that the systems of the ensemble are allowed to be in equilibrium with a reservoir where they can exchange both matter and heat.

### 2.2. A fluid in an external potential

Now, the discussion is extended to the situation where the many-particle system, which consists of $N$ spherical particles of mass $m$ enclosed in a volume $V$, is subjected to an arbitrary external potential $u$. In classic mechanics, the dynamic state of the system at any instant is completely specified by the $3N$ coordinates $r^N = r_1,...,r_N$ and $3N$ momenta $p^N = p_1,...,p_N$ of the particles. Let $\mathcal{H}$ be the Hamiltonian of the grand canonical ensemble of the system, it can be written in a general form as [8-10]

$$\mathcal{H}(r^N,p^N) = K(p^N) + U(r^N) + \Phi(r^N)$$  \hspace{1cm} (2.3)$$

with

$$K(p^N) = \sum_{i=1}^{N} \frac{p_i^2}{2m}$$  \hspace{1cm} (2.4)$$

$$U(r^N) = U(r_1,...,r_N)$$  \hspace{1cm} (2.5)$$

and

$$\Phi(r^N) = \sum_{i=1}^{N} u(r_i)$$  \hspace{1cm} (2.6)$$
where \( K \) is the kinetic energy, \( U \) denotes the potential energy of interaction of the particles, and \( \Phi \) describes the total potential energy arising from the interaction between the particles and the spatially varying external field.

As a matter of fact, when the values of \( \mu \) and \( T \) are fixed and the interparticle potential energy is given, there is a unique external potential \( u \) that can give rise to a specific microscopic density of the particles [8]. This result implies that the external field is to be coupled to the “instantaneous” total density of the particles, which is simply given by a summation of the Dirac \( \delta \)-function for all the particles\(^\dagger\), i.e.,

\[
\hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \tag{2.7}
\]

In practice, however, the instantaneous total density is defined as an ensemble average, to give

\[
\langle \hat{\rho}(\mathbf{r}) \rangle = \rho^{(1)}(\mathbf{r}) \tag{2.8}
\]

where the angular brackets denote an average over a grand canonical ensemble. The average density \( \rho^{(1)}(\mathbf{r}) \) is called the density profile or the single-particle density.

Following this, the average value of the total potential energy due to the external field can also be defined, and it is written as

\[
\langle \Phi \rangle = \int \rho^{(1)}(\mathbf{r}) u(\mathbf{r}) \, d\mathbf{r} \tag{2.9}
\]

### 2.3. Connecting statistics to thermodynamics at equilibrium

The probability density \( p_s \) has already been discussed for randomly finding a system at a chosen microscopic state in any ensemble of distinguishable systems. For a probability density to be descriptive of a system at equilibrium state, an equilibrium probability density \( p_0 \) is normally used.

If one considers again the grand canonical ensemble of a many-particle system in the presence

\(^\dagger\)Given a spherical particle \( i \) at position \( \mathbf{r} \), the “instantaneous” local density can be described by a three-dimensional Dirac \( \delta \)-function as \( \hat{\rho}_i(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}_i) \). For a system containing \( N \) identical spherical particles, the total density is defined as a sum of the \( \delta \)-function for all the particles \( N \).
of an arbitrary external potential, the equilibrium probability density \( p_0 \) is defined as [8, 10]

\[
p_0 = \frac{\exp\left[-\beta(H - N\mu)\right]}{\Xi}
\]  

(2.10)

with \( \Xi \) being the grand partition function which is given by [8]

\[
\Xi = \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \iiint \exp\left[-\beta(H - N\mu)\right] d\mathbf{r}^N d\mathbf{p}^N
\]

(2.11)

where \( h \) is the Plank’s constant. The inclusion of \( 1/h^{3N} \) ensures that the grand partition function is a dimensionless quantity, while division by \( N! \) ensures that the microscopic states of the grand canonical ensemble are correctly counted.

The definition of Eq. (2.10) indicates that \( p_0 \) is normalized by [8]

\[
\sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \iiint p_0 d\mathbf{r}^N d\mathbf{p}^N = 1
\]

(2.12)

Having said this, the link between statistics and thermodynamics can be established through the relation [8]

\[
\Xi = \exp(-\beta\Omega)
\]

(2.13)

and it follows that Eq. (2.10) can be rewritten as

\[
p_0 = \exp\left[\beta(\Omega - H + N\mu)\right]
\]

(2.14)

By including explicitly the energy contributions of different types in \( H \), Eq. (2.14) becomes

\[
k_B T \ln p_0 = \Omega - K - U - \Phi + N\mu
\]

(2.15)

after taking the grand canonical ensemble average on both sides of Eq. (2.15), one can write

\[
\langle K + U + k_B T \ln p_0 \rangle = \Omega - \int \rho^{(1)}(\mathbf{r})\mu(\mathbf{r}) d\mathbf{r} + N\mu
\]

(2.16)
If, instead, a quantity $F$ is used to represent the ensemble average of $\langle K + U + k_B T \ln p_0 \rangle$, the grand potential can finally be expressed, via Eq. (2.16), as

$$\Omega = F + \int \rho^{(1)}(r) u(r) \, dr - N \mu$$  \hspace{1cm} (2.17)$$

Comparison between Eqs. (2.2) and (2.17) suggests that

$$F = H - \int \rho^{(1)}(r) u(r) \, dr$$  \hspace{1cm} (2.18)$$

Thus, $F$ is defined as an “intrinsic” (Helmholtz) free energy.

### 2.4 Variational principle of the grand potential functional

As stated above, for a given interparticle potential energy $U$ and fixed values of $\mu$ and $T$ in a grand canonical ensemble, only one external field can determine a specific density profile, i.e., $u(r)$ is uniquely coupled to $\rho^{(1)}(r)$. Since the equilibrium probability density $p_0$, defined by Eq. (2.10), is a functional of $u$, for any quantity that is wholly determined by $p_0$, at given $U$, $\mu$ and $T$, should also be a functional of $\rho^{(1)}$ and its functional dependence on $\rho^{(1)}$ is independent of the external potential [8]. To our particular interest, this result implies that the intrinsic free energy $F$, which is the ensemble average of $\langle K + U + k_B T \ln p_0 \rangle$, is a unique functional of $\rho^{(1)}$.

This statement corresponds to the statement of Ebner et al [5]: “the “intrinsic” Helmholtz free energy $F[n(r)]$ is a functional of the density $n(r)$ (not necessarily the equilibrium one), independent of $u(r)$” such that the grand potential, defined in Eq. (2.17), is also a functional of $n(r)$.

Given a density profile $n(r)$ of the microscopic particles, the grand potential can be written, via Eq. (2.17), as

$$\Omega[n(r)] = F[n(r)] + \int n(r) u(r) \, dr - \mu \int n(r) \, dr$$  \hspace{1cm} (2.19)$$

Based on Eq. (2.19), the variational principle of $\Omega$ [5, 6] shows that the functional $\Omega[n(r)]$ becomes minimal (at fixed $\mu$ and $T$) at the equilibrium state and equal to the exact grand potential $\Omega[\rho^{(1)}(r)]$ of the system, i.e.,

$$\Omega[n(r)] = \Omega[\rho^{(1)}(r)]$$  \hspace{1cm} (2.20)$$

---

†A functional is a function that depends on all values of an input variable $f(x)$, which is also a function of an infinite number of points in the relevant range of the variable $x$. 
where the equality applies only when \( n(\mathbf{r}) = \rho^{(1)}(\mathbf{r}) \).

Based on this, it allows the differentiation of \( \Omega[n(\mathbf{r})] \) with respect to \( n(\mathbf{r}) \), on both sides of Eq. (2.19), to yield

\[
\frac{\delta \Omega[n(\mathbf{r})]}{\delta n(\mathbf{r})}_{\rho^{(1)}} = \frac{\delta F[n(\mathbf{r})]}{\delta n(\mathbf{r})}_{\rho^{(1)}} + u(\mathbf{r}) - \mu = 0
\]

This equation provides explicitly the calculus for the variational principle and it is called the Euler-Lagrange equation. Given the external potential \( u(\mathbf{r}) \) and the chemical potential \( \mu \), evaluation of the variation of the intrinsic free energy functional \( F[n(\mathbf{r})] \) is the central problem in solving the equilibrium density profile \( \rho^{(1)}(\mathbf{r}) \) from the Euler-Lagrange equation. Eq. (2.21) is the fundamental equation in the theory of non-uniform fluids and approaches for finding solutions to it are categorized under the title of density functional theory.

### 2.5 Direct correlation functions

To make Eq. (2.21) tractable for practical use, the intrinsic free energy functional \( F[\rho^{(1)}(\mathbf{r})] \) can be split into an ideal part and an excess part,

\[
F[\rho^{(1)}(\mathbf{r})] = F^{\text{id}}[\rho^{(1)}(\mathbf{r})] + F^{\text{ex}}[\rho^{(1)}(\mathbf{r})]
\]

(2.22)

where the ideal contribution \( F^{\text{id}}[\rho^{(1)}(\mathbf{r})] \) represents a system of a non-interacting ideal-gas, and it is exactly given as [8, 9]

\[
F^{\text{id}}[\rho^{(1)}(\mathbf{r})] = k_B T \int \rho^{(1)}(\mathbf{r}) \left( \ln \left[ \Lambda \rho^{(1)}(\mathbf{r}) \right] - 1 \right) \, d\mathbf{r}
\]

(2.23)

with \( \Lambda \) as the thermal de Broglie wavelength.

To incorporate the effects of interactions between the particle in Eq. (2.22), the excess part of the intrinsic free energy functional \( F^{\text{ex}}[\rho^{(1)}(\mathbf{r})] \) provides a measure of the thermodynamic nonideality and it acts as a generating functional for a hierarchy of direct correlation functions \( c^{(n)}(\mathbf{r}) \) [8, 9]. More importantly, the direct correlation functions specify the response of the excess part of the intrinsic free energy functional with respect to the density variations, e.g., the first-order functional derivative of \( F^{\text{ex}} \) with respect to \( \rho^{(1)} \) gives
\[ c^{(1)}(r) = -\beta \frac{\delta F^{\text{ex}}}{\delta \rho^{(1)}(r)} \]  

(2.24)

where \( c^{(1)} \) is called the single-particle direct correlation function (DCF).

Following this, one can also define a pair direct correlation function \( c^{(2)} \) as the functional derivative of \( c^{(1)} \), i.e.,

\[ c^{(2)}(r, s) = \frac{\delta c^{(1)}(r)}{\delta \rho^{(1)}(s)} = -\beta \frac{\delta^2 F^{\text{ex}}}{\delta \rho^{(1)}(r) \delta \rho^{(1)}(s)} \]  

(2.25)

and similarly for higher-order correlation functions.

Having introduced \( c^{(1)} \) through Eq. (2.24), the Euler-Lagrange equation, i.e., Eq. (2.21), can be written in a variant form as a description of the chemical potential \( \mu \), due also to Eqs. (2.22) and (2.23),

\[ \mu = k_b T \ln \left[ \lambda^3 \rho^{(1)}(r) \right] + u(r) - k_b T c^{(3)}(r) \]  

(2.26)

This equation indicates that the chemical potential \( \mu \) of an inhomogeneous system consists of three terms: the ideal contribution arising from the kinetic motion of the particles in the fluid; the external potential, which is a density independent but position dependent part of the chemical potential; the last term is the excess part of the chemical potential resulting from the particle interactions in the fluid, and it is the amount of work that has to be done to overcome the interactions from all existing particles, if we transfer a particle from infinity to the inhomogeneous system at position \( r \).
As a novel approach to the density functional theory, the weighted correlation approach is presented in this chapter for a single-component hard-sphere fluid† and it is the theoretical basis of this thesis.

In order to solve the equilibrium density profile of an inhomogeneous hard-sphere fluid, it is argued that the change of the single-particle direct correlation function can be exactly expressed in terms of a weighted pair direct correlation function (Paper I). The formulation of the weighted pair direct correlation function is still formally exact and it involves the use of the pair direct correlation function, the correlation-weight function and the correlation-weight factor. When applied in practice, the evaluation of the pair direct correlation function is made on the homogeneous fluid with some weighted density, which can be defined as an average of the density profile of the inhomogeneous fluid under study. Despite its seeming complexity, the WCA approach provides a very generic way of describing the single-particle direct correlation function or the excess part of the intrinsic free energy functional of an inhomogeneous fluid. As a result, it is shown that the classic density functional approaches are all special cases of the WCA approach; these DFTs manifest the difference mainly in the description of the pair direct correlation function, the expression of the weighted density and the choice of the correlation-weight function.

3.1. The change of single-particle direct correlation function

In a DFT, the equilibrium density profile can be obtained based on the Euler-Lagrange equation, and subsequently used to determine the thermodynamic properties of the system of interest. Towards that end, a formally exact expression for the single-particle density of an inhomogeneous hard-sphere fluid at equilibrium is written, from Eq. (2.26), as

\[
\rho^{(1)}(r) = \frac{\exp(\beta\mu)}{\mathcal{N}^1} \exp[-\beta u(r) + c^{(1)}(r)]
\]

†For the sake of simplicity, the formulation is restricted to the case of a single-component inhomogeneous hard-sphere fluid. The expression obtained can, however, be easily extended to multi-component mixtures without loss of generality.
For an ideal-gas system, \( c^{(1)}(r) = 0 \), and Eq. (3.1) reduces to the well-known barometric law \[8\],

\[
\rho^{(1)}(r) = \left[ \exp(\beta u)/\mathcal{A} \right] \exp[-\beta u(r)] \quad \text{(ideal gas)} \tag{3.2}
\]

Comparison between Eqs. (3.1) and (3.2) shows that the effects of particle interactions on the single-particle density distribution are wholly contained in the function \( c^{(1)} \) for a non-uniform system. Unfortunately, Eq. (3.1) cannot directly be applied, since no exact information is available concerning the single-particle direct correlation function of the system under study. To tackle this problem, a reference state at the same chemical potential as that of the system under study can always be selected, as discussed in the following.

Let \( \rho^{(1)}(r; 0) \) and \( c^{(1)}(r; 0) \) be, respectively, the single-particle density and the single-particle direct correlation function at a reference state. One may define, by using a coupling parameter \( \lambda \) \[8\],

\[
\rho^{(1)}(r; \lambda) = \rho^{(1)}(r; 0) + \lambda \Delta \rho^{(1)}(r), \quad (0 \leq \lambda \leq 1) \tag{3.3}
\]

with

\[
\Delta \rho^{(1)}(r) = \rho^{(1)}(r) - \rho^{(1)}(r; 0) \tag{3.4}
\]

Equation (3.3) denotes a continuous set of density profiles resulting from the imposition of an external potential \( u(r; \lambda) \) without any change in \( \mu \) so that \( \rho^{(1)}(r; 1) \) leads back to \( \rho^{(1)}(r) \), which is the density profile in the presence of the external potential \( u(r) \).

Since Eq. (3.1) also holds for the reference state, it follows that the equilibrium density profile of an inhomogeneous hard-sphere fluid, based on a preselected reference state, can be written as

\[
\frac{\rho^{(1)}(r)}{\rho^{(1)}(r; 0)} = \exp[-\beta \Delta u(r) + \Delta c^{(1)}(r)] \tag{3.5}
\]

with

\[
\Delta u(r) = u(r) - u(r; 0) \tag{3.6}
\]
and

$$\Delta c^{(1)}(\mathbf{r}) = c^{(1)}(\mathbf{r}) - c^{(1)}(\mathbf{r}; 0)$$  \hspace{1cm} (3.7)$$

Once the reference state is selected, \(\Delta u(\mathbf{r})\) can easily be obtained through Eq. (3.6). To evaluate \(\Delta c^{(1)}(\mathbf{r})\), one may use a formally exact expression to describe the change of the single-particle direct correlation function \([8, 9]\), to give

$$c^{(1)}(\mathbf{r}) = c^{(1)}(\mathbf{r}; 0) + \int_0^1 \frac{\partial c^{(1)}(\mathbf{r}; \lambda)}{\partial \lambda} d\lambda$$  \hspace{1cm} (3.8)$$

following the chain rule of differentiation,

$$\frac{\partial c^{(1)}(\mathbf{r}; \lambda)}{\partial \lambda} = \int \frac{\partial c^{(1)}(\mathbf{r}; \lambda)}{\partial \rho^{(1)}(\mathbf{s}; \lambda)} \frac{\partial \rho^{(1)}(\mathbf{s}; \lambda)}{\partial \lambda} d\mathbf{s}$$  \hspace{1cm} (3.9)$$

one can write, with the definition of the pair direct correlation function as given in Eq. (2.25) and the help of Eq. (3.3)

$$\frac{\partial c^{(1)}(\mathbf{r}; \lambda)}{\partial \lambda} = \int c^{(2)}(\mathbf{r}, \mathbf{s}; \lambda) \Delta \rho^{(1)}(\mathbf{s}) d\mathbf{s}$$  \hspace{1cm} (3.10)$$

and subsequently Eq. (3.8) becomes

$$\Delta c^{(1)}(\mathbf{r}) = \int \Delta \rho^{(1)}(\mathbf{s}) d\mathbf{s} \int_0^1 c^{(2)}(\mathbf{r}, \mathbf{s}; \lambda) d\lambda$$  \hspace{1cm} (3.11)$$

It should be pointed out that the second integral in Eq. (3.11) is, however, not integration path dependent \([8, 9]\), because the excess part of the intrinsic free energy \(F^{\text{ex}}\) and consequently the single-particle direct correlation function \(c^{(1)}(\mathbf{r})\), as defined in Eq. (2.24), are state functions of thermodynamics. They depend only on the state of the system, not on the way in which the system reaches that state, i.e., both are unique functionals of \(\rho^{(1)}(\mathbf{r})\), as detailed theoretically in the textbook of Hansen and McDonald \([8]\).

In spite of the path-independency, it is impossible to obtain an exact solution of Eq. (3.11) due to the lack of information concerning \(c^{(2)}(\mathbf{r}, \mathbf{s}; \lambda)\). As a result, an immediate approximation on \(c^{(2)}(\mathbf{r}, \mathbf{s}; \lambda)\) is commonly applied in many density functional approaches to make the coupling integral in Eq. (3.11) performable. In this study, however, an alternative is developed to
describe the change of the single-particle direct correlation function based on a better understanding of the coupling parameter $\lambda$, as detailed in the following.

It has been clearly shown that the derivation of Eq. (3.11) is only constrained by these requirements: the coupling parameter $\lambda$ must satisfy the densities $\rho^{(1)}(r; \lambda)$ becoming $\rho^{(1)}(r; 0)$, the density in the reference state, when $\lambda = 0$, and $\rho^{(1)}(r)$, the density in the final state, when $\lambda = 1$, and the chemical potential $\mu$ has to be kept constant along the integration path from $\lambda = 0$ to $\lambda = 1$. As long as the above conditions are fulfilled, the integration path for Eq. (3.11) can be chosen arbitrarily, as schematically shown in Fig. 3.1a.

Having understood these mathematical constraints on $\lambda$, one may define it in terms of, e.g., the spatial variation of the density profile of the system under study, although it originally has no physical meaning. Given that in the final state, one can find a position $r_0$ at which $\rho^{(1)}(r_0)$ equals $\rho^{(1)}(r; 0)$ as shown in Fig. 3.1b, the integration path can be chosen as a spatial path $L$ between $r_0$ and $r$, along which the density $\rho^{(1)}(r')$ changes continuously. This is, of course, always possible because $\rho^{(1)}(r; 0)$ is preselected. Thus, along the path one may define

$$d\lambda = w(s)\,ds$$  \hspace{1cm} (3.12-a)

with the requirement of

$$\int_L w(s)\,ds = 1$$  \hspace{1cm} (3.12-b)

Likewise, it may be envisaged that numerous paths around $L$ may form a tube element continuing from $r_0$ to $r$. Then, it is possible to extend Eqs. (3.12) in three dimension to give,
\[ d\lambda = w(r') \, dr' \]  \hspace{1cm} (3.13-a)

and

\[ \int w(r') \, dr' = 1 \]  \hspace{1cm} (3.13-b)

where \( w(r') \) denotes that \( w \) itself is a spatially variable function and it may be \( \rho^{(1)}(r') \)-dependent. In addition, it should be noted that the integral has been extended over the whole space rather than being limited to a single tube element between \( r_0 \) and \( r \), due to the fact that numerous tube elements of such a type would fill the whole space of the system.

As a result, Eq. (3.11) becomes (Paper I)

\[
\Delta c^{(1)}(r) = \int \Delta \rho^{(1)}(s) \, ds \int \tilde{c}^{(2)}(r,s;w) \, w(r') \, dr'
\]  \hspace{1cm} (3.14)

where \( w \) in place of \( \lambda \) implies that the density profile of the system will continuously change as \( w \) changes along a tube element such as \( \rho^{(1)}(r;w) \), which has a similar meaning as \( \rho^{(1)}(r;\lambda) \) but depends implicitly on \( \rho^{(1)}(r') \), and \( \rho^{(1)}(r;w) \) will become \( \rho^{(1)}(r) \) when \( r' \) reaches \( r \). Thus, the correlation function \( \tilde{c}^{(2)}(r,s;w) \) for an inhomogeneous fluid depends not only on the physical positions \( r \) and \( s \), but also on the densities \( \rho^{(1)}(r;w) \) everywhere in the system under study (Paper I).

Note that Eq. (3.14) is still exact, but together with Eq. (3.13-b) it highlights the fact that \( w(r') \) is nothing else than a weight function over the space. With this understanding, it is generally defined that (Paper I)

\[
w(r') = \frac{f(r')}{\int f(r') \, dr'}
\]  \hspace{1cm} (3.15)

where the sub-function \( f \) represents a spatial function that may be \( \rho^{(1)}(r') \)-dependent.

Consequently, Eq. (3.14) can be rewritten as

\[
\Delta c^{(1)}(r) = \int \tilde{c}^{(2)}(r,s) \Delta \rho^{(1)}(s) \, ds
\]  \hspace{1cm} (3.16)

where the weighted pair direct correlation function is given by (Paper I),
and it has been extended, in a subsequent work (Paper II), to give,

$$
\bar{c}^{(2)}(\mathbf{r}, \mathbf{s}) = \sum_m \alpha_m \frac{\int c^{(2)}(\mathbf{r}, \mathbf{s}; f_m) f_m(\mathbf{r'}) \, d\mathbf{r'}}{\int f_m(\mathbf{r'}) \, d\mathbf{r'}}
$$

(3.17)

with

$$
\sum_m \alpha_m = 1
$$

(3.18)

where $f_m$ represents a correlation-weight function that may depend spatially on the local densities of the inhomogeneous fluid. The replacement of $w$ by $f$ also highlights the fact that the pair direct correlation function $c^{(2)}(\mathbf{r}, \mathbf{s}; f_m)$ of the inhomogeneous fluid for a particle at $\mathbf{r}$ and a particle at $\mathbf{s}$ separated by a distance $r = |\mathbf{r} - \mathbf{s}|$ depends explicitly on the $f_m$ function. $\alpha_m$ denotes a correlation-weight factor that should be closely related to the choice of the $f_m$ function.

In this manner, to evaluate $\bar{c}^{(2)}(\mathbf{r}, \mathbf{s})$ or equivalently $\Delta c^{(1)}(\mathbf{r})$ in the WCA approach, one has to estimate $c^{(2)}(\mathbf{r}, \mathbf{s}; f_m)$ since its exact solution is not available for the inhomogeneous fluid. For this reason, one may simply approximate $c^{(2)}(\mathbf{r}, \mathbf{s}; f_m)$ with its counterpart of a homogeneous fluid $c_b^{(2)}$ at a weighted density of $\bar{\rho}_m(\mathbf{r'})$, inspired by the weighted density approximation [11, 12]. That is, one can write for each of the weighted densities

$$
c^{(2)}(\mathbf{r}, \mathbf{s}; f_m) \approx c_b^{(2)}[|\mathbf{r} - \mathbf{s}|; \bar{\rho}_m(\mathbf{r'})]
$$

(3.19)

where $\bar{\rho}_m(\mathbf{r'})$ refers to a weighted density evaluated at $\mathbf{r'}$, and each of the weighted densities can generally be written as

$$
\bar{\rho}_m(\mathbf{r'}) = \sum_n \lambda_{m,n} \frac{\int \rho^{(1)}(\mathbf{r}) w_{m,n}(\mathbf{r'}, \mathbf{r}) \, d\mathbf{r}}{\int w_{m,n}(\mathbf{r'}, \mathbf{r}) \, d\mathbf{r}}
$$

(3.20)

To ensure that Eq. (3.20) is exact in the uniform bulk fluid, the weight factors are required to satisfy
\[ \sum_n \lambda_{m,n} = 1 \]  \hspace{1cm} (3.21)

where \( w_{m,n} \) is a density-weight function and \( \lambda_{m,n} \) signifies a density-weight factor.

Since the physical picture describing the weighted density is easily established, the similarity between Eqs. (3.17) and (3.20) helps to understand the roles of the correlation-weight factors \( \alpha_m \) and the correlation-weight functions \( f_m \) in defining the weighted pair DCF \( \bar{c}^{(2)}(r, s) \). It should be noted that Eq. (3.20) aims to construct a new system that is more homogeneous than the system under study while Eq. (3.17) tries to approximate \( \bar{c}^{(2)}(r, s) \) as accurately as possible by use of the structural properties of numerous homogeneous systems that are piecewisely close to the newly generated system via Eq. (3.19). This suggests that, although there is no limitation in the number and in the definitions of the weight factors and the weight functions, certain restrictions on \( \alpha_m \) and \( f_m \) or \( \lambda_{m,n} \) and \( w_{m,n} \) should be imposed in order to keep the consistency of the structural and thermodynamic properties of the system, as detailed later.

To summarize, the WCA evaluation of \( \Delta c^{(1)}(r) \) can be regarded as a functional integral of a weighted pair DCF, i.e. \( \bar{c}^{(2)}(r, s) \), which is exactly expressed in the form of a series of pair DCFs weighted by their correlation-weight functions. When applied in practice, however, approximations of the pair direct correlation functions have to be made on a homogeneous fluid together with appropriate definitions of the weighted densities.

### 3.2 Generalization of the classic DFTs

It has been shown in the previous section that the WCA approach focuses on the evaluation of the change of the single-particle direct correlation \( \Delta c^{(1)}(r) \) or, equivalently, the inhomogeneous single-particle direct correlation function \( c^{(1)}(r) \)\(^1\). It is essentially the same strategy as described in the literature for constructing different classic density functional approaches. Generally speaking, one may categorize different versions of the DFTs into several types.

The first one is the density-expansion approach and it is based on the functional Taylor expansion of the single-particle DCF of the inhomogeneous fluid around a uniform bulk system, in powers of the difference between the non-uniform density and the bulk density. Due to the lack of information on higher orders of the DCFs of even a uniform fluid, the Taylor expansion is always truncated at the first order, with the lowest order derivative as the pair direct correlation function evaluated at the bulk fluid, leading to the uniform pair DCF approach [13, 14].

The second type of DFTs also relies on the usage of a uniform representation of the pair DCF.

---

\(^1\)Evaluation of \( c^{(1)}(r) \) is equivalent to the approximation of the excess part of the intrinsic free energy functional \( F^e[\rho^{(1)}(r)] \), since the functional derivative of \( F^e \) with respect to the density profile yields the single-particle direct correlation function \( c^{(1)} \) as given by Eq. (2.24).
but replaces the bulk density by a weighted density averaged from the inhomogeneous density through some density-weight functions. For this reason, these DFT approaches are referred to as the weighted density approximations (WDA). Different WDA approaches are mainly distinguished by the choice of density-weight functions. Among many possibilities, the simplest one is the Heaviside step function, as suggested by Nordholm et al [11]. A more sophisticated choice from Denton and Ashcroft [12] is to use the analytical solution of the single-particle and pair DCFs of the bulk fluid at an averaged smooth density. The calculation of the weight function is, then, coupled with the weighted density, and therefore it is numerically sluggish. To tackle this problem, Zhou [15] introduced a decoupling formalism, and it has later been well applied in the DFTs [16, 17].

The third type of classic DFTs is the fundamental measure theory (FMT), originally proposed by Rosenfeld [18] and later modified by Roth and Wu [19, 20], where the thermodynamic condition of the bulk fluid is utilized to construct the excess part of the intrinsic free energy or equivalently the single-particle DCF of the hard-sphere fluid. Although this theory does not need an analytical pair DCF as an input, it is still along the lines of the WDA [21] due to the use of the weighted density based on the geometrical considerations of the hard-sphere particles to approximate the single-particle DCF.

In short, there are different approaches in the density functional theory and unequally satisfactory results have been noted for some specific problems among those DFTs. A recent review on this topic can be found in, e.g., a paper by Wu and Li [22]. However, the connections between different DFT approaches are not obvious; the reasons for their different performance are less clear. Since all the classic DFTs attempt to estimate the inhomogeneous single-particle DCF at the root, the WCA formulated above, as a novel DFT approach, not only provides an optional formulation for \( c^{(1)} \) but also generalizes the previously developed DFT approaches in a consistent manner. To justify this, it shall be briefly discussed, one by one, three of the commonly used DFT approaches showing that they all can be written in the language of the WCA approach.

### 3.2.1 The uniform pair DCF approach

If the bulk fluid is selected as the reference state, as is commonly done in the classic DFTs [23-26], the external potential of the reference fluid should vanish, i.e., \( u(\mathbf{r}; 0) = 0 \). This leads Eq. (3.5) to become

\[
\frac{\rho^{(1)}(\mathbf{r})}{\rho_b} = \exp\left[-\beta u(\mathbf{r}) + \Delta c^{(1)}(\mathbf{r})\right]
\]

(3.22)

where \( \rho_b \) refers to the bulk density.

To evaluate the change of the single-particle DCF, \( \Delta c^{(1)} \), the uniform pair DCF approach [13, 14] applies the functional Taylor expansion of the non-uniform single-particle DCF around the bulk fluid and truncates at the first order to give
\[ \Delta c^{(1)}(r) = \int c^{(2)}_b \left[ (r - s); \rho_b \right] \Delta \rho^{(1)}(s) \, ds \] (3.23)

Comparison with Eqs. (3.16), (3.17) and (3.19) indicates that this result is equivalent to defining, within the framework of the WCA approach, a single density-weight function,

\[ w_{m,n}(r', r) = \delta(|r - r_\infty|) \] (3.24)

with the density-weight factor

\[ \lambda_{m,n} = 1 \] (3.25)

and a single correlation-weight function,

\[ f_m(r') = \delta(|r' - r_\infty|) \] (3.26)

with the correlation-weight factor

\[ \alpha_m = 1 \] (3.27)

where \( \delta(x) \) is the Dirac delta function, and \( r_\infty \) stands for an infinity position where the fluid becomes homogeneous, i.e., the bulk fluid.

Equations (3.24) and (3.25) ensure that the weighted density \( \bar{\rho}_m(r') \), as defined in Eq. (3.20), amounts to the bulk density \( \rho_b \), while Eqs. (3.26) and (3.27) make the combination of Eqs. (3.16), (3.17) and (3.19) become exactly Eq. (3.23). Thus, the uniform pair DFC approach [13, 14] is a special case of the WCA approach.

### 3.2.2 The WDA approach

By also selecting the bulk fluid as the reference state and truncating the functional Taylor expansion of the non-uniform single-particle DCF around the bulk fluid at the first order, Zhou’s WDA approach [17] arrives at the expression

\[ \Delta c^{(1)}(r) = \int c^{(2)}(r, s; [\rho_b + \lambda (\rho^{(1)}(r) - \rho_b)]) \Delta \rho^{(1)}(s) \, ds \] (3.28)
where $\lambda$ is an adjustable parameter between 0 and 1 [17].

When $\lambda = 0$, Eq. (3.28) reduces to Eq. (3.23), the result of the uniform pair DCF approach that makes the pair DCF independent of the density of the inhomogeneous fluid itself. Otherwise it describes the change of the single-particle DCF in terms of a non-uniform pair DCF with a mixed density.

When applying Eq. (3.28) in practice, the non-uniform pair DCF is approximated in the WDA approach [17] by its counterpart, the uniform fluid with a weighted density $\bar{\rho}$, i.e.,

$$c_b^{(2)}(r, s; b^{(1)}(r) - \rho_b) \approx c_b^{(2)}(|r - s|; \bar{\rho}((r + s)/2))$$

(3.29)

and

$$\bar{\rho}(r') = \int \rho_b + \lambda (\rho^{(1)}(r) - \rho_b) w^{\text{WDA}}(r', r) \, dr$$

(3.30)

where the WDA density-weight function is given by [12]

$$w^{\text{WDA}}(r', r) = \frac{c_b^{(2)}(|r - r'|; \rho_b)}{\int c_b^{(2)}(r, \rho_b) \, dr}$$

(3.31)

The spirit of Zhou’s WDA approach [17] lies, therefore, in the approximation of the pair DCF by its counterpart, the homogeneous fluid at a weighted density, which is defined as an average of some “constructed” density such as $\rho_b + \lambda (\rho^{(1)}(r) - \rho_b)$, with an adjustable parameter $\lambda$ between 0 and 1.

This weighted density can, noticeably, be defined in the WCA approach by utilizing two density-weight functions,

$$w_{m,1}(r', r) = c_b^{(2)}(|r - r'|; \rho_b)$$

(3.32)

and

$$w_{m,2}(r', r) = \delta(|r' - r_c|)$$

(3.33)
The corresponding density-weight factors are then given as: \( \lambda_{m,1} = \lambda \) and \( \lambda_{m,2} = 1 - \lambda \). These definitions would make Eq. (3.20) become exactly Eq. (3.30).

Subsequently, comparison of Eqs. (3.29) and (3.19) suggests that one can define, in the WCA approach, a single correlation-weight function that considers the symmetry condition, i.e.,

\[
f_m(r') = \delta(\frac{r' - (r + s)}{2})
\]  

(3.34)

with the correlation-weight factor \( a_m = 1 \).

The set of definitions from Eqs. (3.32) to (3.34) gives, then, the WCA version of Zhou’s WDA approach [17] where \( \lambda \) is determined by the contact theorem [27] of a hard-sphere fluid in contact with a hard wall.

Thus, it may be concluded that the classic DFTs that use the uniform pair DCF as input can conveniently be generalized by the WCA approach to solve the density distribution equation based on a bulk reference state. These arguments show, however, those DFTs are special cases of the WCA approach where a single weighted density is involved, with few (one or two) definitions of the density weight-functions. Defining more weighted densities is also possible within the framework of the WCA approach, leading to another set of DFT approaches such as the fundamental measure theory [18-20].

### 3.2.3 The FMT approach

If, instead, an ideal fluid of non-interacting hard spheres is employed as reference state [8], which has the same chemical potential as that of the inhomogeneous fluid under study, both the external potential and the single-particle DCF of the reference state should vanish, i.e., \( u(r; 0) = 0 \) and \( c^{(1)}(r; 0) = 0 \). As a result, the FMT version of Eq. (3.5) becomes [20]

\[
\frac{\rho^{(1)}(r)}{\rho^*} = \exp[\beta u(r) - c^{(1)}(r)]
\]  

(3.35)

with the density \( \rho^* \) of the hard spheres in the ideal fluid given by [8]

\[
\rho^* = A^3 \exp(\beta \mu)
\]  

(3.36)

To make Eq. (3.35) well applicable, the FMT approach further gives an expression to explicitly describe the single-particle DCF of the inhomogeneous hard-sphere fluid as [18]
\[ c^{(1)}(\mathbf{r}) = - \sum_{m} \frac{\partial \Phi}{\partial \bar{\rho}^\text{FMT}_m}(s) w^\text{FMT}_m(\mathbf{r} - \mathbf{s}) d\mathbf{s} \]  

where \( w^\text{FMT}_m \) represents six weight functions (\( m = 0, 1, 2, 3, V1 \) and \( V2 \)) that have been well defined to characterize the fundamental geometries of the hard spheres comprising the fluid [18]. \( \Phi \) is the reduced excess part of the intrinsic free energy density and it is a function of six weighted densities, defined as

\[ \bar{\rho}^\text{FMT}_m(\mathbf{r}) = \int \rho^{(1)}(s) w^\text{FMT}_m(\mathbf{r} - \mathbf{s}) d\mathbf{s} \]  

Based on an ansatz for \( \Phi \), the scaled particle theory [28], and the Percus-Yevick solution of the pair DCF of a homogeneous fluid [29], Rosenfeld [18] and his successors [19, 20] proposed several formulations for the \( \Phi \) function, one of which can be written as [19]

\[ \Phi = -\bar{\rho}_0 \ln(1 - \bar{\rho}_3) + \bar{\rho}_1 \bar{\rho}_2 - \bar{\rho}_1 \bar{\rho}_V \bar{\rho}_2 + \left( \bar{\rho}_2^3 - 3 \bar{\rho}_2 \bar{\rho}_V \bar{\rho}_V \right) \frac{(1 - \bar{\rho}_3)^2 \ln(1 - \bar{\rho}_3)}{36 \pi \bar{\rho}_3^2 (1 - \bar{\rho}_3)^2} \]  

where the superscript FMT on the weighted densities has been omitted for simplicity.

This or alike analytical solutions [20] of the \( \Phi \) function enables the partial derivative of \( \Phi \) with respect to \( \bar{\rho}^\text{FMT}_m \), and thus \( c^{(1)}(\mathbf{r}) \), to be easily evaluated by Eq. (3.37), which makes the FMT approach very accurate and attractive in the study of liquid states. Within the context of this thesis it is interesting to note that Eq. (3.37) also can be written in the form of the WCA approach, on the condition that \( c^{(1)}(\mathbf{r}; 0) = 0 \), as

\[ \Delta c^{(1)}(\mathbf{r}) = - \sum_{m} \frac{\partial \Phi}{\partial \bar{\rho}^\text{FMT}_m}(s) w^\text{FMT}_m(\mathbf{r} - \mathbf{s}) \Delta \rho^{(1)}(s) d\mathbf{s} \]  

with

\[ \Delta \rho^{(1)}(s) = \rho^{(1)}(s) - \rho^* \]  

since an ideal fluid has been selected as the reference state.

This is equivalent to define, by comparison with Eq. (3.16),
\begin{equation}
\tilde{c}^{(2)}(\mathbf{r}, \mathbf{s}) = -\sum_{m} \frac{\partial \Phi}{\partial \rho_{m}^{\text{FMT}}(\mathbf{s})} \frac{w_{m}^{\text{FMT}}(\mathbf{r} - \mathbf{s})}{\Delta \rho^{(1)}(\mathbf{s})} \tag{3.42}
\end{equation}

It follows, in analogue to Eq. (3.17), that six different correlation-weight functions may be defined in the WCA approach,

\begin{equation}
f_{m}(\mathbf{r}') = w_{m}^{\text{FMT}}(\mathbf{r} - \mathbf{r}') \tag{3.43}
\end{equation}

with the correlation-weight factor

\begin{equation}
\alpha_{m} = \frac{1}{6} \tag{3.44}
\end{equation}

and the definition of the pair DCF,

\begin{equation}
c^{(2)}(\mathbf{r}, \mathbf{s}; f_{m}) = -6 \frac{\partial \Phi}{\partial \rho_{m}^{\text{FMT}}(\mathbf{r}')} \frac{\delta(|\mathbf{r}' - \mathbf{s}|)}{\Delta \rho^{(1)}(\mathbf{s})} \tag{3.45}
\end{equation}

where the weighted density of the WCA approach $\bar{\rho}_{m}$ is related to $\rho_{m}^{\text{FMT}}$ by

\begin{equation}
\bar{\rho}_{m}(\mathbf{r}) = \frac{\rho_{m}^{\text{FMT}}(\mathbf{r})}{\int w_{m}^{\text{FMT}}(\mathbf{r} - \mathbf{s}) d\mathbf{s}} \tag{3.46}
\end{equation}

This highlights the fact that it is also possible to define several weighted densities in the WCA approach, as discussed previously. In practice, using the nomenclature of the WCA approach, one may write Eq. (3.46) in the same form as given in Eq. (3.20) with

\begin{equation}
w_{m,n} = w_{m}^{\text{FMT}}(\mathbf{r} - \mathbf{s}) \tag{3.47}
\end{equation}

in the case of the density-weight factor $\lambda_{m,n} = 1$.

For each of the weighted densities $\bar{\rho}_{m}$, the pair DCFs $c^{(2)}(\mathbf{r}, \mathbf{s}; f_{m})$ as given in Eq. (3.45) would be different. Noticeably, they are also different from the commonly used one, i.e. Eq. (3.19), illustrating that alternative approximations of $c^{(2)}(\mathbf{r}, \mathbf{s}; f_{m})$ are possible in the WCA approach. Likewise, the use of the associated $f_{m}$ functions, as defined by Eq. (3.43), demonstrates that
multiple choices of the $f_m$ functions are available in the WCA approach. In addition, Eq. (3.35) shows that it is not necessary to restrict the reference state to the bulk fluid. Hence, the FMT approach is not only a special case of the WCA approach, as it describes the single-particle DCF of the inhomogeneous hard-sphere fluid in terms of a weighted pair DCF, but also helps understand the spirit of the WCA approach.
THE STRUCTURE OF AN INHOMOGENEOUS FLUID AT AN INTERFACE: A WCA STUDY

Having introduced the WCA approach and demonstrated its versatility in generalizing the classic density functional approaches, specific DFT methods can be formulated within the framework of the WCA to study the structural properties of an inhomogeneous fluid at an interface. Although, in principle, several possibilities for implementing the WCA approach for various applications are allowed, in this chapter two WCA methods are discussed. These are the WCA-N method and the FMT/WCA-\(k^2\) method, together with their validation and application in, respectively, predicting the hard-sphere density profile between a pair of parallel planar hard walls and the ionic density profile of a single electric double layer.

4.1 Hard-sphere density profile between a pair of parallel planar hard walls

The structural properties of an inhomogeneous fluid at interfaces are of considerable importance, since they are closely linked to varieties of interfacial phenomena such as coagulation [30, 31], adsorption [32] and wetting transition [33, 34], etc. As a result, numerous approaches [8, 10] using statistic mechanics or thermodynamics have been devoted to the study of the microscopic density distribution of inhomogeneous fluids. Since such predictions are always very demanding, due to the significant variation of the density over molecular dimensions in the vicinity of the interface, any developed approach has to be tested at the first stage on the simplest representation possible of inhomogeneous fluids, i.e., the hard-sphere fluid, before it can be applied for practical use with confidence (Paper II).

The hard-sphere fluid is often regarded as the fundamental system of more complex fluids that establishes an important ground for molecules or colloids with soft repulsive or attractive interactions in addition to the hard-core repulsion at short distances. It is commonly used as the model system when studying the microscopic structures of a wide range of inhomogeneous fluids [35-37], and taken as the starting point for testing the validity of theories of fluids. For the reasons above, a new DFT method is proposed in the following to study the density distribution of the hard-sphere fluid between two parallel planar hard walls. To validate the newly proposed WCA approach, the performance of this specific WCA method is investigated by comparisons with both the Monte Carlo (MC) simulations [38] and the results from the WDA and the FMT approaches.
4.1.1 WCA formulation for a hard-sphere fluid

To start with, one considers the walls to be located, respectively, at \( z = 0 \) and \( z = H \) (with \( H \) defined as the separation between the surfaces). The walls are assumed to be infinitely large and smooth. The density distribution of the hard spheres would, then, only be a function of \( z \), i.e., \( \rho^{(1)}(r) = \rho^{(1)}(z) \), and the external potential for the interaction between the walls and the hard spheres would depend solely on the distance \( z \) from the surfaces, given by

\[
u(z) = \begin{cases} 
0, & d/2 < z < H - d/2 \\
\infty, & \text{otherwise}
\end{cases}
\]  

(4.1)

where \( d \) denotes the diameter of the hard spheres.

Thus, by selecting the bulk fluid as the reference state, as is commonly done in the DFTs [23-26], the external potential of the reference fluid should vanish, i.e., \( u(r; 0) = 0 \). This allows Eq. (3.5) to be rewritten in one-dimensional form as

\[
\frac{\rho^{(1)}(z)}{\rho_b} = \exp\left[-\beta u(z) + \Delta c^{(1)}(z)\right]
\]  

(4.2)

To evaluate \( \Delta c^{(1)} \), the WCA approach can be applied in different ways by following the procedures discussed in chapter 3. In this study, however, only one implementation of the WCA approach is given to be illustrative rather than exhaustive. To start with, the pair DCF for a particle at \( z \) and a particle at \( z' \), separated by a distance \( r \), is approximated by its counterpart of the bulk fluid with the Percus-Yevick (PY) equation [29], evaluated at a weighted density of \( \bar{\rho}_m(z') \), i.e.,

\[
c^{(2)}(z, z', r; f_m) \approx c^{(2)\text{(PY)}}[r; \bar{\rho}_m(z')]
\]  

(4.3)

where \( \bar{\rho}_m(z') \) is defined through Eq. (3.20), by using, however, only one density-weight function \( w_{m,n} \) as the Heaviside step function, as suggested by Nordholm et al [11], i.e.,

\[
w_{m,n}(r) = \Theta(d - r)
\]  

(4.4)

Together with the fact that the density-weight factor \( \lambda_{m,n}=1 \), \( \bar{\rho}_m(z') \) can be written explicitly as

\[
\bar{\rho}_m(z') = \frac{3}{4d^3} \int_{z - d}^{z + d} \rho^{(1)}(z') \left[d^2 - (z' - z)^2\right] dz
\]  

(4.5)
Moreover, to close the WCA approach for describing $\tilde{c}^{(2)}$ or $\Delta c^{(1)}$, one may define two correlation-weight functions $f_m$ as follows

$$f_1(z') = \delta \left[ z' - \left( z + z^* / 2 \right) \right]$$

(4.6)

and

$$f_2(z') = \delta \left[ |z' - z_\infty| \right]$$

(4.7)

where $z_\infty$ stands for an infinity position from the surfaces where the fluid becomes homogeneous, i.e., the bulk fluid.

In this manner, the $f_1$ function ensures the symmetry property of $\tilde{c}^{(2)}$, and it also takes into account the heterogeneity of the hard-sphere distribution around $z$. The $f_2$ function makes $\tilde{c}^{(2)}$ go easily to the pair DCF of the bulk fluid in the limiting case of $H \to \infty$, in addition to giving compensation for any possible discrepancy of $\tilde{c}^{(2)}$ from the real value of the pair DCF of the inhomogeneous hard-sphere fluid.

As a result, the correlation-weight factors in Eq. (3.17), due to the requirement of Eq. (3.18), are simply related to each other by

$$\alpha_2 = 1 - \alpha_1$$

(4.8)

Following this, a natural constraint on the definition of $\alpha_1$ or $\alpha_2$ for the problem at hand, is to make sure that the resulting density distribution of the hard-sphere fluid should fulfill the exact contact theorem [27] in the limiting case as $H \to \infty$, i.e.,

$$P_b = k_B T \rho^{(1)}(d/2; \infty)$$

(4.9)

where $P_b$ is the pressure of the bulk fluid, which can be calculated by the PY compressibility equation [39]. The contact density $\rho^{(1)}(d/2; \infty)$, on the right-hand side of Eq. (4.9), is obtained by the WCA approach in the case of $H \to \infty$. After each calculation, the result from the right-hand side of Eq. (4.9) is compared with $P_b$, and this iteration continues until the relative error between the two sides is below 0.1%.

It should, however, be pointed out that although the value of $\alpha_1$ or $\alpha_2$ is specified through the contact theorem which is only valid for the special case interested in this thesis, i.e., the planar hard walls, it can be used for other geometries such as cylindrical or spherical walls at the
same thermodynamic condition of the bulk fluid. This can be understood by the inherent characteristic of the weighted pair DCF $\tilde{c}^{(2)}$ that is independent of the external potential.

In this manner, the WCA approach ensures the accuracy of the weighted pair DCF $\tilde{c}^{(2)}$, and consequently $\Delta c^{(1)}$ from Eq. (3.16). It addresses not only the structures but also the thermodynamics of the hard-sphere fluid, as the contact theorem of Eq. (4.9) essentially connects the contact density of the fluid or the inhomogeneous structure near the hard wall in the limiting case as $H \to \infty$ to the bulk pressure. For ease of reference, this specific WCA is named as the WCA-N method since the recipe for the density-weight function of Eq. (4.4) was originally proposed by Nordholm et al [11].

### 4.1.2 Validation and discussion

To validate the WCA-N method for inhomogeneous hard-sphere fluids, and to investigate the difference between the WCA-N predictions and those from the WDA and the FMT approaches, the hard-sphere density distribution equation as given in Eq. (4.2) is solved by using the standard Picard iteration method with the bulk density as the initial guess. The iteration continues until the relative error of the calculated densities is below 0.1%.

Figure 4.1 shows the density profiles of a hard-sphere fluid in the case of $\rho_b d^3 = 0.6$, with a surface separation $H$ of $2d$, $3d$, $4d$ and $9d$, respectively. In this figure, the calculated hard-sphere density distributions from DFT methods are plotted as function of a dimensionless distance $z/d$ between the surfaces, while the MC results [38] are given by the solid circles.

It is seen that the WCA-N results are well compatible with the MC simulations of the hard-sphere density profiles in all cases shown in Fig. 4.1. Such a good agreement with the MC data is also found by the WDA and the FMT results in each case. The difference between these DFT predictions, particularly in a whole picture of the hard-sphere density distribution, is too small to be resolved. This is expected as an outcome of the WCA generalization of classic DFTs as discussed in chapter 3. Additionally, it should be pointed out that, in most cases in Fig. 4.1, the WDA and FMT approaches yield identical predictions of the contact values as compared to the WCA-N results since these DFT approaches fulfill the contact theorem [27].

On the other hand, it is interesting to observe that, as the surface separation extends from (a) to (d) in Fig. 4.1, the MC results suggest an increase of layers in the hard-sphere distribution between the walls. Such a phenomenon is referred to as the layering effect and it has been well understood as a result of the excluded volume effect of the hard spheres: an extensive amount of hard spheres in contact with the wall prevent distant spheres from moving towards the surface, those precluded spheres then pack themselves into a second layer and will successively induce more layers, if a high bulk density is provided for some large surface separations.
Due also to the layering effect, in Fig. 4.1(d) the MC results near the surface reveal the period of the oscillating behavior of the hard-sphere density profile as one diameter $d$ of the hard sphere. In the middle region between the surfaces, however, the MC results maintain a constant value as the bulk reduced density. The reason for this is that, provided with an abundant space between the walls, the effect from the walls is no longer felt by the hard spheres far from the surface, giving rise to a non-interacting, bulk fluid-like density distribution in that region.

Hence, from the above discussion, the present WCA method is well validated by comparing with the MC simulations of the structural properties of a hard-sphere fluid confined between two parallel planar hard walls (Paper II). It should also be stressed that, from the overall good agreement between the WCA, WDA and FMT results, the WCA is capable of generalizing the classic DFTs. These findings suggest that the WCA provides a reliable, yet flexible, option for studying the structural properties of an inhomogeneous hard-sphere fluid. Consequently, an extension can be made to apply the WCA in, e.g., the case of an inhomogeneous ionic fluid, where electrostatic interaction is present in addition to the hard-sphere repulsion at short distances.

\[\text{FIG. 4.1 (Color in Paper II) Density profile of a hard-sphere fluid confined by two parallel, planar hard walls at a bulk reduced density } \rho_b d^3 = 0.6. \text{ Surface separations are (a) } H = 2d, \text{ (b) } H = 3d, \text{ (c) } H = 4d \text{ and (d) } H = 9d. \text{ The density profiles are plotted with different colors corresponding to each method stated in the legend. Solid circles indicate the Monte Carlo data}^\dagger [38].\]

\[\text{\[38\]}\]
4.2 Ionic density profile of a single electric double layer

Study of the electric double layer (EDL) is a long-standing problem in the entire domain of interface and colloidal science. The EDLs form spontaneously in an aqueous system, where ions of opposite sign are released from the charged surface into the solvent, which generally contains additional microscopic cations and anions. As a result, these micro-ions all act together as counter-ions and co-ions to compensate the surface charge [40, 41].

Since the thermodynamic properties of the systems involving EDLs crucially depend on the ion distribution in the electrolyte, understanding the ionic structures of EDLs is essential in describing the interfacial phenomena. Historically, the Poisson-Boltzmann (PB) equation provides the benchmark for treating the problems concerning EDLs with different geometries. Based on this equation, the modified Gouy-Chapman (MGC) theory [42, 43] has been demonstrated to represent the ionic structure of planar EDLs in very dilute monovalent electrolytes, but is not capable of reproducing the MC results in other cases [44-46]. For instance, the charge inversion phenomenon predicted by the MC simulations, where the co-ion density is higher than that of the counter-ion in a portion of the EDL, cannot appear in the MGC results. It is believed that the ion-ion correlations should take the main responsibility for this discrepancy, and such correlations are entirely neglected in the conventional theories.

In contrast, by satisfactorily addressing the correlations between ions, the DFT is a powerful alternative for describing the EDLs. Although different DFTs have been reported in the literature, they all have a similar strategy in common, i.e., these approaches focus on the evaluation of the single-particle DCF of the ionic fluid and divide the ion-ion correlation function into the direct Coulomb contribution, the hard-sphere contribution and the electric residual contribution, respectively [24, 47, 48]. The difference between these approaches lies, in essence, mainly in the methods of evaluation of the electric residual correlation as discussed briefly in Paper III.

4.2.1 WCA formulation for a charged hard-sphere fluid near a charged wall

To study the structural properties of a single EDL, the so-called primitive model (PM) of electrolyte solutions [49] is utilized, where the micro-ions are treated as charged hard spheres with either unequal diameter or different charge, and the solvent (e.g. the water) is considered as structureless dielectric continuum with \( \varepsilon_r \) being the relative dielectric constant of the medium and \( \varepsilon_0 \) the permittivity of vacuum. The macro-ion, in the case of planar EDLs, is assumed to be an infinitely large, impenetrable hard wall containing uniform charges on the surface. Although the molecular nature of the solvent is not included, this model incorporates the key features of EDLs, such as the hard-sphere repulsion and the electrostatic interaction between ions [50, 51].

Furthermore, one considers that the charged hard wall is placed at \( z = 0 \), with a homogeneous charge density \( \sigma \) on the surface. As a result, the density profile of an ion species \( i \) would only be a function of \( z \), i.e., \( \rho_i^{(1)}(\mathbf{r}) = \rho_i^{(1)}(z) \), and consequently Eq. (3.5) can be rewritten for a multi-component mixture in one-dimensional form as
Following this, it is convenient to decompose the single-particle DCF into the following form, as generally defined in the DFTs [24, 47, 48],

\[ c^{(i)}_i(z) = c^{\text{CO}}_i(z) + c^{\text{HS}}_i(z) + c^{\text{EL}}_i(z) \]  

(4.11)

The first term on the right-hand side is the direct Coulomb (CO) contribution, the second term is the hard-sphere (HS) contribution due to the excluded volume effect, and the last one is the electric residual (EL) contribution. Since the direct Coulomb correlation describes only the Coulomb interaction between point charges, the combination of this correlation term with the external potential gives nothing but the mean electrostatic potential \( \psi \) [40], i.e., one can write

\[ \beta u_i(z) - c^{\text{CO}}_i(z) = \beta z_i e \psi(z) \]  

(4.12)

where \( z_i \) is the valence of the ionic species \( i \), \( e \) is the elementary charge, and hence \( z_i e \) are the point charges assumed to be located at the center of the hard spheres.

This allows Eq. (4.10) to be rewritten as

\[ \frac{\rho^{(i)}_i(z)}{\rho^{(i)}_i(z;0)} = \exp\left[ -\beta z_i e \Delta \psi(z) + \Delta c^{\text{HS}}_i(z) + \Delta c^{\text{EL}}_i(z) \right] \]  

(4.13)

with

\[ \Delta \psi(z) = \psi(z) - \psi(z;0) \]  

(4.14)

The mean electrostatic potential \( \psi \) is given by [40]

\[ \psi(z) = \frac{1}{\varepsilon_i \varepsilon_r} \sum_j \int_z \rho^{(i)}_j(z') d z' (z - z') \rho^{(i)}_j(z') z_j e \]  

(4.15)

with the overall electroneutrality condition
In writing Eq. (4.15), it has been taken that $\psi(z; 0) = 0$, implying the zero level of the mean electrostatic potential has been placed at the reference state which is conventionally selected as the bulk fluid. As a result, Eq. (4.13) becomes

$$
\frac{\rho_i^{(1)}(z)}{\rho_{i,b}} = \exp\left[-\beta z_e \psi(z) + \Delta \epsilon_i^{\text{HS}}(z) + \Delta \epsilon_i^{\text{EL}}(z)\right]
$$

(4.17)

The MGC theory would then be recovered, if one neglects the ion-ion correlations, by setting both $\Delta \epsilon_i^{\text{HS}}$ and $\Delta \epsilon_i^{\text{EL}}$ equal to zero.

To evaluate $\Delta \epsilon_i^{\text{HS}}$ and $\Delta \epsilon_i^{\text{EL}}$ in Eq. (4.17) in this study, the FMT [18-20] is adopted to describe the hard-sphere single-particle DCF. The change of the electric residual single-particle DCF is approximated by the WCA as discussed in chapter 3. The pair DCF thus involved, i.e. $c_{ij}^{\text{EL}}$, is specified by the mean spherical approximation (MSA) [52] of a homogeneous fluid with, however, a local density $\rho_i^{(1)}(z')$ of the fluid under study, i.e.,

$$
c_{ij}^{\text{EL}}(z, z', r; \rho_m) \approx c_{ij}^{\text{EL(MSA)}}(r; \rho_i^{(1)}(z'))
$$

(4.18)

where a “real” density of the inhomogeneous fluid $\rho_i^{(1)}(z')$ is used instead of the weighted density $\bar{\rho}_m(z')$.

Following this, only one correlation-weight function $f$ is defined as (Paper I)

$$
f(z') = \kappa^2(z') \Theta(|z' - z| - d)
$$

(4.19)

where $\kappa$ is the Debye parameter, given by

$$
\kappa^2(z') = \frac{\beta e^2}{\epsilon_0 \epsilon_r} \sum_i \rho_i^{(1)}(z') z_i^2
$$

(4.20)

To summarize, this DFT scheme is essentially a combination of the FMT and the WCA approaches, where the estimation of the electric residual pair DCF is made on the MSA solution of a homogeneous fluid at a local density of the fluid under study and only one
The correlation-weight function is defined through Eq. (4.19). One may, thus, refer to this DFT scheme as the FMT/WCA-$k^2$ method, where $\kappa^2$ highlights the use of the Debye parameter in defining $f$.

If Eq. (4.7) is used, instead, as the only definition of the correlation-weight function, the so-called FMT/MSA method would result. This method has been applied in many density functional studies [25, 26, 48].

Comparison between Eqs. (4.7) and (4.19) suggests that the FMT/WCA-$k^2$ evaluation of $\bar{c}_{ij}^{\text{EL}}$ would be much closer to the real value of the electric residual contribution to the pair DCF, since now the heterogeneity of the ionic structure and the important contributions to $\bar{c}_{ij}^{\text{EL}}$ from the surrounding ions around $z$ have been taken into account.

It should, however, be noted that the FMT/WCA-$k^2$ method has not been enforced to the exact contact theorem [27], due to its specific use of a local density and a single correlation-weight function. As a result, there would be no need to determine the density-weight factor or the correlation-weight factor through the contact theorem in the case of $H \to \infty$, i.e., Eq. (4.9), as is imposed in the WCA-N method. Nevertheless, the thermodynamic self-consistency of the FMT/WCA-$k^2$ method should be assessed by following the contact theorem of ionic fluids [27], as presented in the following.

4.2.2 Simulation and discussion

To perform the thermodynamic self-consistency test for a DFT, a standard contact value condition method [53] is used. Towards that end, the exact expression of the contact theorem, in the case of an ionic fluid in contact with a charged wall, takes the form [27]

$$P_b = \kappa T \sum_i \rho_i^{(x)} \left( \frac{d}{2} ; \infty \right) - \frac{\sigma^2}{2\varepsilon_0\varepsilon_r}$$

(4.21)

where $P_b$ is the pressure of the bulk ionic fluid.

With this contact theorem, the thermodynamic expressions given by Lebowitz et al. [54] are applied to compute $P_b$, while the right-hand side of Eq. (4.21) is calculated, respectively, through Eq. (4.17) by the FMT/WCA-$k^2$ method and the FMT/MSA method with a standard Picard iteration method. The results with respect to the left-hand side and the right-hand side of Eq. (4.21) are shown, respectively, on the $x$-axis and $y$-axis in Fig. 4.2 for all simulations listed in Table 4.1. To facilitate comparisons, the pressures have been normalized by $RT$ ($R$ is the gas constant). Only when Eq. (4.21) is exactly satisfied, can the data points fall on the straight line as $y = x$. 
It is seen, in the entire range of the investigated bulk pressures, that the FMT/WCA-\(k^2\) method is always closer to the self-consistent contact densities than the FMT/MSA method, particularly under conditions when the bulk electrolyte is not too concentrated. This in turn suggests that the FMT/WCA-\(k^2\) method, with a better WCA approximation of the \(f\)-function as defined in Eq. (4.19), actually achieves a better self-consistency and gives a more accurate prediction of the chemical potential of the bulk fluid (Paper I).

Having performed the thermodynamic self-consistency test, the ionic density profile near a charged surface from simulations using the FMT/WCA-\(k^2\) and FMT/MSA methods will be presented and discussed in the following.

**Table. 4.1** Thermodynamic self-consistency test. The valence of the counter- and co-ions are given, respectively, in the columns of \(z^+\) and \(z^-\); \(d\) indicates the ion diameter; \(\sigma\) specifies the surface charge density; the bulk fluid concentration is given in M. Results from the left-hand side (l.h.s) of Eq. (4.21) are listed under \(P_b\), while calculations from the right-hand side (r.h.s) of Eq. (4.21) are presented, respectively, for the FMT/MSA method and the FMT/WCA-\(k^2\) method (Paper I).

<table>
<thead>
<tr>
<th>Test</th>
<th>(z^+)</th>
<th>(z^-)</th>
<th>(d) (nm)</th>
<th>(\sigma) (C/m(^2))</th>
<th>Bulk conc. (M)</th>
<th>(P_b) (l.h.s/RT) (M)</th>
<th>FMT/MSA (r.h.s/RT) (M)</th>
<th>FMT/WCA-(k^2) (r.h.s/RT) (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>0.425</td>
<td>0.267</td>
<td>0.2</td>
<td>0.38</td>
<td>0.6314</td>
<td>0.3832</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-1</td>
<td>0.46</td>
<td>0.224</td>
<td>0.5</td>
<td>1.03</td>
<td>1.253</td>
<td>1.046</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>-1</td>
<td>0.425</td>
<td>0.3725</td>
<td>1</td>
<td>2.1945</td>
<td>2.65</td>
<td>2.237</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>-1</td>
<td>0.425</td>
<td>0.3513</td>
<td>2</td>
<td>5.478</td>
<td>6.207</td>
<td>5.826</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>-2</td>
<td>0.84</td>
<td>0.24</td>
<td>0.05</td>
<td>0.151</td>
<td>1.01</td>
<td>0.1579</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>-2</td>
<td>0.84</td>
<td>0.24</td>
<td>0.2</td>
<td>0.8830</td>
<td>1.827</td>
<td>0.8858</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>-2</td>
<td>0.425</td>
<td>0.267</td>
<td>0.4</td>
<td>1.05</td>
<td>1.887</td>
<td>1.077</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>-2</td>
<td>0.425</td>
<td>0.267</td>
<td>0.4</td>
<td>3.2386</td>
<td>4.5</td>
<td>3.616</td>
</tr>
</tbody>
</table>

It is seen, in the entire range of the investigated bulk pressures, that the FMT/WCA-\(k^2\) method is always closer to the self-consistent contact densities than the FMT/MSA method, particularly under conditions when the bulk electrolyte is not too concentrated. This in turn suggests that the FMT/WCA-\(k^2\) method, with a better WCA approximation of the \(f\)-function as defined in Eq. (4.19), actually achieves a better self-consistency and gives a more accurate prediction of the chemical potential of the bulk fluid (Paper I).

Having performed the thermodynamic self-consistency test, the ionic density profile near a charged surface from simulations using the FMT/WCA-\(k^2\) and FMT/MSA methods will be presented and discussed in the following.

**FIG. 4.2** (Color in Paper I) Thermodynamic self-consistency test. DFT results from the right hand-side of Eq. (4.21) are symbolized in different colors. The exact equality of Eq. (4.21) is given by the straight line as \(y = x\) (Paper I).
To start with, the case of a 1-1 electrolyte is considered where the counter- and co-ions have the same valence with, however, different signs. The diameter of these ions is treated uniformly as 0.425 nm, being consistent with the one used in the MC simulations [44]. Figure 4.3 shows the calculated densities of counter-ions and co-ions, respectively, as function of the dimensionless distance $z/d$ in the case of 1 M electrolyte, where the surface charge is uniformly distributed with a surface charge density $\sigma = 0.3725$ C/m$^2$.

It is seen that the MC results display, though not very prominently, a fluctuation of the ionic density profile near the region around 1.5 $d$ from the surface. This actually indicates the existence of a second layer of counter-ions near the surface whereas the first “peak” is located at the closest distance 0.5 $d$ to the wall, and it is referred to as the layering effect. The reasons for its formation have the same origin as that of the hard-sphere layering effect, which has been discussed in Fig. 4.1.

In Fig. 4.3, the MGC theory gives only monotonic density distributions of counter-ions and co-ions; both significantly deviate from the MC data. In practice, the MGC always fails to reproduce the ion oscillation when the concentration and ionic strength increase [44, 45]. It is successful only in the description of the ionic structure of planar EDLs in very dilute solutions with low surface charge density. By comparison, the FMT/MSA results have a reasonable agreement with the MC data; however, they cannot reproduce the fine feature of the counter-ion distribution near the region around 1.5 $d$ from the surface. In contrast, the FMT/WCA-$k^2$ method very nicely captures the layering effect, and it also yields results matching the MC points better in other regions than the FMT/MSA does, not only in the counter-ion distribution but also in the co-ion distribution.

**FIG. 4.3** (Color in Paper I) Ion density distribution function $\rho(z)/\rho_b$ in an EDL of 1 M 1-1 electrolyte. The surface charge density $\sigma = 0.3725$ C/m$^2$. Several density profiles are shown by different color curves corresponding to each method stated in the legend. Solid and empty circles are MC data [44, 55], respectively, for the density distributions of counter- and co-ions (Paper I).
Since the ionic structure of the EDL crucially depends on the valence of the counter-ions [56, 57], it is worthwhile to explore the ionic density distribution near a charged surface in the case of a 2-1 electrolyte, where the counter-ions are divalent. Towards that end, the ion diameter $d$ is set to 0.84 nm, which is reported in a MC simulation to be a more representative “hydrated diameter” of small ions [57].

Figure 4.4 displays the ionic density profiles calculated from the FMT/MSA and FMT/WCA-$k^2$ methods for a 0.05 M 2-1 electrolyte near a charged surface with $\sigma = 0.24$ C/m$^2$. It is seen that, in this somehow weakly coupled case, the MC results clearly manifest the layering effect in the region around 1.5 $d$ from the surface, but not the charge inversion phenomenon. The FMT/MSA method, however, gives a totally wrong prediction of the structure of the EDL, which does not show the layering effect but the charge inversion phenomenon with the crossover point located roughly at 1.5 $d$ from the surface. Predictions from the HNC-MSA method [58, 59] or equivalently the MSA/MSA method in the nomenclatures of the DFT also exhibit similar features as the results from the FMT/MSA method [57]. In contrast, the FMT/WCA-$k^2$ calculations agree not only qualitatively but also quantitatively better with the MC data. The deviation between the FMT/WCA-$k^2$ and the MC results occurs, in this case, mainly in the description of the valley bottom of the density profiles of the counter-ions where the layering effect plays a part.

When the bulk concentration is increased to 0.2 M, the MC results display both the layering effect and the charge inversion phenomenon, as shown in Fig. 4.5. In this case, the FMT/MSA method is still incapable of predicting the layering effect, but overestimates the charge inversion phenomenon. It seems from both Figs. 4.4 and 4.5 that this method always makes light of the effect of the surface charge density, in cases where the counter-ions are divalent, and it exaggerates the effect of the electrolyte concentration (Paper I). By comparison, the

![FIG. 4.4](image)

**FIG. 4.4** (Color in Paper I) Ion density distribution function $\rho(z)/\rho_b$ in an EDL of 0.05 M, 2-1 electrolyte. The surface charge density $\sigma = 0.24$ C/m$^2$. The hydrated ion diameter is 0.84 nm. The MC results [57] and DFT simulations are symbolized in the same way as in Fig. 4.3 (Paper I).
FMT/WCA-\(k^2\) method gives much better predictions of the charge inversion phenomenon, or the concentration effect, in that its results better reproduce the MC simulations in the region (roughly from 1.5 \(d\) to 3.0 \(d\)) where the density of co-ions is larger than that of counter-ions.

From these comparisons, it is found that the FMT/WCA-\(k^2\) method can well reproduce the MC results for various electrolyte conditions; it succeeds better than other methods such as the FMT/MSA in giving more accurate predictions of ionic structures near a charged surface even when divalent counter-ions are involved. This suggests that it is the WCA improvement of the approximation of the change of the electric residual correlation, by using the correlation-weight function defined in Eq. (4.19), that makes the FMT/WCA-\(k^2\) perform better, since both the FMT/WCA-\(k^2\) and the FMT/MSA methods use the same FMT theory to describe the hard-sphere correlation.

**FIG. 4.5** (Color in Paper I) Ion density distribution function \(\rho(z)/\rho_b\) in an EDL of 0.2 M, 2-1 electrolyte. The surface charge density \(\sigma = 0.24\)C/m\(^2\). The hydrated ion diameter is 0.84 nm. The MC results [57] and DFT simulations are symbolized in the same way as in Fig. 4.3 (Paper I).
The inhomogeneous fluid is of practical importance when a macroscopic solute is present, since the excluded-volume effect and/or the electrostatic effect introduce a solvent-mediated interaction that occurs in general mixtures between solute macro-particles [60]. For instance, an inhomogeneous fluid in a slit is considered as a system of large size colloidal particles in a fluid of micro-particles; at the solid-fluid interface, there is an exclusion of the fluid from the macro-particles in addition to the excluded-volume interaction and/or electrostatic interaction between the micro-particles. Subsequently, this system renders a realization for colloids with lamellar structure immersed in a fluid of much smaller particles and it is used to examine, in particular, the medium-induced colloidal interactions [30, 31, 61, 62].

The question is, then, how to quantify the interaction pressure between surfaces. The contact theorem is simple and has been widely applied to evaluate the pressure at planar surfaces, but it comprises some difficulties in practical use (Paper III). To address those problems, a different equation is formulated to describe the inhomogeneous fluid-mediated interaction pressure in a slit. The resulting expression consists of distinct physical contributions to the pressure, namely, the kinetic contribution, the hard-sphere contribution and the electric contribution. As a consequence, one can apply it to explicitly investigate the influence of the ion-ion correlation effect on the interaction pressure between surfaces. For illustrative purposes, the pressure equation is implemented by using the WCA approach to study the medium-induced interaction pressure in different cases.

5.1 The contact theorem

As one of the exact sum-rules, the contact theorem [27] is well established to directly relate the pressure to the contact density of the microscopic structure of the inhomogeneous fluid at the interface. For a charged hard-sphere fluid in a charged slit, the general form of the contact theorem is given by

\[ P_{\text{int}} = k_B T \sum_i \rho_i^{(1)} \left( d \right) \frac{\sigma^2}{2\varepsilon_0 \varepsilon_r} \]
In the case of $\sigma = 0$, Eq. (5.1) reduces to the expression of the contact theorem for the interaction pressure of a hard-sphere fluid in a slit with uncharged surfaces.

Provided with the density profile of the fluid under study, the contact theorem is most widely used to evaluate the pressure at planar surfaces [63-65]. In practice, however, it is demanding to obtain the pressure with a satisfactory accuracy since the microscopic density rises precipitately near the surface and consequently this makes the numerical result of the contact density $\rho_i^{(1)}(d/2)$ contain fluctuations. Moreover, the contact theorem itself does not provide a good insight into the underlying physics to interpret the determined pressure.

5.2 A novel formulation

To tackle these problems, i.e., to avoid the use of the contact theorem and to investigate the influence of the ion-ion correlation effect on the interaction pressure, a novel expression for describing the inhomogeneous fluid-mediated interaction pressure in a slit is presented in this section. Since the resulting expression is given as function of the single-particle DCFs, it makes the use of the classic density functional approaches favorable for providing accurate understanding of not only the inhomogeneous architectures near a surface at the molecular level but also the interaction pressures between the surfaces.

5.2.1 Model system

To develop the pressure expression, a general model system of an inhomogeneous electrolyte in a charged slit is used, i.e., the so-called primitive model [49], as described in chapter 4. The equation thus formulated can be easily reduced to the case of a hard-sphere fluid between a pair of parallel planar hard walls as shown in the following.

![Schematic picture of an electrolyte in a charged slit.](FIG 5.1)
Based on the primitive model, as shown in Fig. 5.1, the charged walls are considered to be located at \( z = 0 \) and \( z = h+d \), respectively, where \( h \) is the distance between the center of the contact spheres. The planar surfaces are assumed to be infinitely large, perfectly smooth, so that the charges are smeared out on the surface with a uniform charge density \( \sigma \). The confined electrolyte, which is in equilibrium with the bulk solution, is supposed to consist of both counter-ions and co-ions with either the same or different valences \( z_i \) but identical diameter \( d \). The solvent (e.g. the water) is modeled as a uniform dielectric continuum with its relative dielectric constant the same as that of the charged walls, and hence the image charge effect is not involved.

### 5.2.2 Formulation

To start with, it is noted that the potential of mean force of ionic species \( i \) at a distance \( z \) from the plate, \( w_i(z) \), and the ionic density profile, \( \rho_i^{(1)}(z) \), are related by the Boltzmann relation [66],

\[
-\beta w_i(z) = \ln \frac{\rho_i^{(1)}(z)}{\rho_i^{(1)}(z;0)}
\]

This gives, by means of Eq. (4.17),

\[
-\beta w_i(z) = -\beta z_i e \psi(z) + \Delta \epsilon_i^{\text{HS}}(z) + \Delta \epsilon_i^{\text{EL}}(z)
\]

(5.3)

Since the average force on this ionic species \( i \) is the negative gradient of the potential of mean force,

\[
f_i^{\text{avg}}(z) = -\frac{d w_i(z)}{dz}
\]

(5.4)

the force acting on a slab of fluid confined between the planes \( z = (h+d)/2 \) and \( z = h+d/2 \) by the fluid in \( d/2 \leq z \leq (h+d)/2 \) can be written as [58]

\[
p = -\sum_i \int_{(h+d)/2}^{(h+d)/2} \rho_i^{(1)}(z) \left[ \frac{d w_i(z)}{dz} \right] dz
\]

(5.5)

By using the definition of \( w_i \) in Eq. (5.2), it is obtained from Eq. (5.5) that

\[
p = k_B T \sum_i \rho_i^{(1)}(h+d/2) - k_B T \sum_i \rho_i^{(1)}[(h+d)/2]
\]

(5.6)
Alternatively, applying Eq. (5.3) for \( w_i \) results in the other expression,

\[
p = -z_e \sum_i \int_{(h+d)/2}^{(h+d)/2} \rho_i^{(1)}(z) \frac{d\psi(z)}{dz} dz + k_BT \sum_i \int_{(h+d)/2}^{(h+d)/2} \rho_i^{(1)}(z) \frac{d[\Delta c_i^{HS}(z) + \Delta c_i^{EL}(z)]}{dz} dz \tag{5.7}
\]

For a slit system, the expression of \( \psi \) is given by [67]

\[
\psi(z) = \frac{1}{\varepsilon_0 \varepsilon_r} \sum_j \int_{z'}^{(h+d)/2} dz' (z - z') \rho_j^{(1)}(z') z_j e + \psi[(h+d)/2] \tag{5.8}
\]

where \( \psi[(h+d)/2] \) is the potential at the mid-plane between the two surfaces, and it is an undetermined constant. For each specific separation \( h \), \( \psi[(h+d)/2] \) has to be computed by solving the ion density profile in combination with the overall electroneutrality condition of the system,

\[
\sum_i \int_0^{(h+d)/2} dz \rho_i^{(1)}(z) z_i e + \sigma = 0 \tag{5.9}
\]

Thus, the first derivative of the mean electrostatic potential \( \psi \) therein can be given, from Eq. (5.8), as

\[
\frac{d\psi(z)}{dz} = -\frac{1}{\varepsilon_0 \varepsilon_r} \sum_j \int_{z'}^{z} dz' z_j e \rho_j^{(1)}(z') \tag{5.10}
\]

This, together with the electroneutrality condition of Eq. (5.9), allows us to write the first term on the right-hand side of Eq. (5.7) as

\[
z_i e \sum_i \int_{(h+d)/2}^{(h+d)/2} \rho_i^{(1)}(z) \frac{d\psi(z)}{dz} dz = -\frac{\sigma^2}{2\varepsilon_0 \varepsilon_r} \tag{5.11}
\]

and consequently, Eq. (5.7) becomes

\[
p = \frac{\sigma^2}{2\varepsilon_0 \varepsilon_r} + k_BT \sum_i \int_{(h+d)/2}^{(h+d)/2} \rho_i^{(1)}(z) \frac{d[\Delta c_i^{HS}(z) + \Delta c_i^{EL}(z)]}{dz} dz \tag{5.12}
\]
The equivalence of Eqs. (5.6) and (5.12) then yields, after some rearrangement upon the contact theorem as given in Eq. (5.1),

\[
P^{\text{int}} = k_B T \sum_i \rho_i^{(1)} \left[ (h + d) / 2 \right] + k_B T \sum_i \int_{(h + d)/2}^{h+d/2} \rho_i^{(1)}(z) \frac{d}{dz} \left[ \Delta c_i^{\text{HS}}(z) + \Delta c_i^{\text{EL}}(z) \right] dz \tag{5.13}
\]

If the bulk fluid is chosen as the reference state, \( \Delta \) can be discarded to give

\[
P^{\text{int}} = k_B T \sum_i \rho_i^{(1)} \left[ (h + d) / 2 \right] + k_B T \sum_i \int_{(h + d)/2}^{h+d/2} \rho_i^{(1)}(z) \frac{d}{dz} \left[ c_i^{\text{HS}}(z) + c_i^{\text{EL}}(z) \right] dz \tag{5.14}
\]

For a non-charged hard-sphere fluid, one can simply drop \( c_i^{\text{EL}} \) in Eq. (5.14) and the pressure equation for a hard-sphere fluid between a pair of parallel planar hard walls is given as (Paper IV)

\[
P^{\text{int}} = k_B T \sum_i \rho_i^{(1)} \left[ (h + d) / 2 \right] + k_B T \sum_i \int_{(h + d)/2}^{h+d/2} \rho_i^{(1)}(z) \frac{d}{dz} \left[ c_i^{\text{HS}}(z) \right] dz \tag{5.15}
\]

In addition, it should be noted that Eq. (5.14) essentially indicates that \( P^{\text{int}} \) is a sum of three distinct physical contributions, i.e., one can write

\[
P^{\text{int}} = P^{\text{kin}} + P^{\text{HS}} + P^{\text{EL}} \tag{5.16}
\]

with

\[
P^{\text{kin}} = k_B T \sum_i \rho_i^{(1)} \left[ (h + d) / 2 \right] \tag{5.17a}
\]

and

\[
P^{\text{HS}} = k_B T \sum_i \int_{(h + d)/2}^{h+d/2} \rho_i^{(1)}(z) \frac{d}{dz} \left[ c_i^{\text{HS}}(z) \right] dz \tag{5.17b}
\]

and

\[
P^{\text{EL}} = k_B T \sum_i \int_{(h + d)/2}^{h+d/2} \rho_i^{(1)}(z) \frac{d}{dz} \left[ c_i^{\text{EL}}(z) \right] dz \tag{5.17c}
\]
In this manner, the (ideal) kinetic contribution, $P_{\text{kin}}$, depends only on the ionic densities at the mid-plane between the surfaces, and it is the only term considered in the classic Derjauin-Landau-Verwey-Overbeek (DLVO) theory [68, 69] where the ion-ion correlations are neglected. The hard-sphere contribution, $P_{\text{HS}}$, describes the pressure component resulting from the collisions between the hard spheres across the mid-plane, while the electric residual contribution, $P_{\text{EL}}$, is the electrostatic pressure due to the ion-ion electric residual interactions across the mid-plane.

Following this, it should be stressed that although Eq. (5.14) is derived on the basis of the contact theorem [27], the pressure evaluated at the mid-plane is expected to be determined with greater accuracy than the pressure at the surface in the contact theorem. The reason for this is that the pressure components $P_{\text{HS}}$ and $P_{\text{EL}}$ in Eq. (5.17) make use of the calculations of the single-particle DCF as well as the density profile in the entire range of half the system, and therefore they contain fewer numerical fluctuations than considering only the contact density in the contact theorem.

Furthermore, it is to be noted that $P_{\text{kin}}$, $P_{\text{HS}}$ and $P_{\text{EL}}$ are functions of the direct results that are readily available from the density functional approaches, i.e., the single-particle DCF and the density distribution of the fluid under study. This makes both the WCA-N and FMT/WCA-$k^2$ methods, proposed in the previous chapter, easily applicable for investigating the pressure behavior of an inhomogeneous fluid in a slit.

### 5.3 Application

Before the pressure equation can be used with great confidence, it is firstly applied in a test to predict the hard-sphere fluid-mediated interaction pressure, which is a sum of a kinetic pressure contribution and a hard-sphere pressure contribution (Paper IV). When the electrostatic pressure is included, the pressure equation is used to investigate the excluded-volume effect and the electrostatic effect of the ion-ion correlations on the interaction pressure between charged surfaces immersed in an electrolyte, and consequently to explain the counter-intuitive attraction between identically charged colloids in the presence of multivalent counter-ions [70-72]. Based on the MC validation of the above calculations with the DFTs, the pressure equation is applied by using the FMT/WCA-$k^2$ method to study the swelling pressure of Na-bentonite for different salt conditions.

#### 5.3.1 Hard-sphere fluid between a pair of parallel planar hard walls

For the purpose of comparison and also to demonstrate the versatility of the WCA approach, the pressure equation, i.e., Eq. (5.15), is implemented with the WCA-N method and a newly proposed WCA-DA method to study the behavior of hard-sphere fluid-mediated interaction pressure between a pair of parallel planar hard walls. To start with, the WCA-DA method is briefly discussed in the following.
In the WCA-DA method, the approximation scheme given in Eq. (4.3) is still employed to evaluate \( c^{(2)} \), but two density-weight functions are selected to define the weighted density. One is

\[
w_{m,1}(r) = c^{(2)(PY)}(r; \rho_b)
\]  

which represents a unique specification of \( w_{m,n} \) from Denton and Ashcroft [12], with the PY equation of the pair DCF being evaluated at a bulk density \( \rho_b \).

The other is

\[
w_{m,2}(z', z) = \delta(|z' - z|)
\]

Consequently, the two density-weight factors \( \lambda_{m,n} \) are related by, via Eq. (3.21),

\[
\lambda_{m,2} = 1 - \lambda_{m,1}
\]

and they can be properly determined with the same constraint as given in Eq. (4.9).

To define the correlation-weight functions by considering the symmetry property of \( c^{(2)}(r, s) \), one can, e.g., adopt a single \( f_m \) function as suggested in Eq. (4.6) with the correlation-weight factor \( a_m = 1 \).

With this, a new DFT method has been formulated within the framework of the WCA approach and it is named as the WCA-DA method to emphasize the use of a density-weight function from Denton and Ashcroft. Having discussed the WCA-DA method, Eq. (5.15) is applied to predict the hard-sphere fluid-mediated interaction pressure upon the WCA-N and WCA-DA calculations of the hard-sphere density profile equation, i.e., Eq. (4.2). The results from the FMT approach [19, 20] and the MC simulations [73] are also included. The physical parameters used in the DFT calculations are set to be identical to those of the MC simulations.

Fig. 5.2 shows the pressure \( P^{\text{int}} \), as well as its pressure components \( P^{\text{kin}} \) and \( P^{H_S} \), for a hard-sphere fluid in a slit at a bulk reduced density \( \rho_d d^3 = 0.7 \). In this figure, the pressures calculated from each DFT method are expressed in a dimensionless form \( \beta P_d d^3 \) and plotted as function of a dimensionless surface separation \( H/d \), while the MC data are given by the solid circles.

It can be observed in Fig. 5.2 that the MC data suggests an oscillatory behavior of the interaction pressures over the entire range of the separation distances until \( H = 4d \). \( P^{\text{int}} \) begins
to decrease sharply when the surfaces start to separate until $H \sim 1.5d$ and then increases to a local pressure maximum at a separation distance of about $2d$. Consequently, an interaction pressure “dip” is formed at around $H = 1.5d$. Such a characteristic feature of the hard-sphere fluid-mediated interaction pressure can, nevertheless, be clearly analyzed in terms of its pressure components, when the WCA and FMT calculations of $P_{\text{kin}}$ and $P_{\text{HS}}$ are presented separately. The results show that the hard-sphere pressure contribution experiences a “peak” value and dominates over the kinetic pressure contribution at about the same location as the interaction pressure maximum.

The comparisons, in Fig. 5.2, demonstrate that the WCA-DA method agrees reasonably well with the MC simulations in the whole range of the pressures studied. It is, however, also found that the WCA-N method is slightly inferior to the WCA-DA method and/or the FMT approach to match the MC results of the local pressure extrema at $H < 3.5d$. The reason for this is clearly manifested by the pressure components analysis as shown in Fig. 5.2: the magnitudes of the kinetic pressure “peak” and the hard-sphere pressure “peak” at $H \sim 3.2d$ and $H \sim 2d$, respectively, as well as the hard-sphere pressure “dip” at $H \sim 3.2d$, are incorrectly produced by the WCA-N method as compared to those obtained by the WCA-DA and FMT methods. This suggests that it is the WCA-DA approximation scheme, i.e., the definitions of $w_{m,n}$ and $f_m$ through Eqs. (5.18), (5.19) and (4.6), that makes the WCA-DA method perform better than the WCA-N method, when the density of the hard-sphere fluid is high and the excluded-volume interaction between the hard spheres therefore becomes very strong.

5.3.2 Electrolyte in a charged slit
Based on the model system shown in Fig. 5.1, Eq. (5.16) is applied by using the FMT/WCA-\(k^2\) method (and the FMT/MSA method) to predict the electrolyte-mediated interaction pressure in a charged slit. In order to compare with the MC simulations [74, 75], a net pressure \(P_{\text{net}}\) between the charged surfaces immersed in an electrolyte is presented in the following figures, where the van der Waals force is not accounted for,

\[
P_{\text{net}} = P_{\text{int}} - P_{b}
\]  

(5.21)

where \(P_{b}\) also can be determined from Eq. (5.16) in the case of \(h \rightarrow \infty\).

Towards that end, the ionic density profile equation, i.e., Eq. (4.17), is solved by using the standard Picard iteration method. At each step, the electroneutrality condition as given in Eq. (5.9) is applied to determine the mid-plane potential in Eq. (5.8). This iteration continues until the relative error of the calculated densities is below 0.1 %. The parameters used for the calculations are set to be identical to those in the MC simulations: the temperature \(T = 298.15\) K, the relative dielectric constant of the solvent \(\varepsilon_r = 78.54\), the ion diameter \(d = 0.425\) nm, and the surface charged density \(\sigma = -0.267\) C/m\(^2\).

It is well known that for symmetric, monovalent electrolytes, the modified Gouy-Chapmann theory predicts only a monotonic behavior of the net pressure, in conflict with the MC results, as shown in Fig 5.3a, where the confined electrolyte is in equilibrium with a 1:1 bulk solution at a concentration of 1.0 M. It is observed that the MC results exhibit a narrow “shoulder” at a separation of around 4.2 Å, roughly the same order of magnitude as the ionic diameter. When the separation goes beyond ~ 15 Å, however, the pressure between the charged surfaces becomes nearly identical to the pressure in the bulk solution, as a result of a very weak overlapping of the electric double layers.

By comparison, the FMT/WCA-\(k^2\) method can well reproduce the MC pressures at all separations, as seen in Fig 5.3, while the commonly used FMT/MSA method is accurate only when the separation becomes large. In particular, in the range of \(h < \sim 10\) Å, the FMT/MSA method always underestimates the net pressure.

In Fig. 5.3b, the FMT/WCA internal pressure \(P_{\text{int}}\) and its components \(P_{\text{kin}}, P_{\text{HS}}\) and \(P_{\text{EL}}\), as well as the MGC internal pressure \(P_{\text{MG}}\), are presented to explore the behaviors of the net pressure in a 1:1 electrolyte. It is evident that the hard-sphere pressure is always repulsive. When the separation is less than \(1d\), it decreases with decreasing separation due to the fact that less space between the plates would make the ions move and collide with greater difficulty in the z-direction. When the separation is larger than \(1d\), however, it decreases with increasing separation because fewer collisions between the ions would result as more space becomes available. As a consequence, the hard-sphere pressure shows a peak at a separation of \(1d\), which takes the main responsibility for the “shoulder” shape of the internal pressure when \(P_{\text{HS}}\) prevails over \(P_{\text{kin}}\) and \(P_{\text{EL}}\) in the region around \(1d\).

The electric residual pressure \(P_{\text{EL}}\), on the other hand, is always attractive and it increases with
increasing separation. In contrast, the kinetic pressure $P_{\text{kin}}$ is of repulsive, colligative origin and it decreases monotonically with increasing separation as a result of large available space and weak attraction between the plates and the counter-ions. It increases rapidly as the plates approach each other to a very small separation, where the hard-sphere pressure diminishes and the electric residual pressure remains at a low value. The sum of the kinetic pressure and the hard-sphere pressure is, however, always larger than the electric residual pressure, leading the internal pressure between the plates to being always positive at all separations.

However, it has been reported that when divalent counter-ions are involved in the electrolyte, the interaction between identically charged surfaces would exhibit a more complex pressure behavior and it may turn to be attractive at some separations [70-72]. To examine this, a 2:1 electrolyte case is studied and the results are shown below.

In Fig. 5.4a, the net pressures between the charged plates are plotted as a function of surface separations for the case of a 2.0 M 2:1 electrolyte. It is seen that the MC results [74, 75] display an extremely sophisticated pattern: the pressure curve is strongly oscillatory to give not only two attractive minima but also a repulsive maximum, while the “shoulder” shape observed in the 1:1 electrolyte is absent.

As can be found in Fig. 5.4a, the FMT/WCA method reproduces the important features of the MC simulations. Albeit the predictions deviate slightly from the MC results at narrow separations between 2 Å and 5 Å, the nice agreements in the regions around the repulsive peak at ~ 8.0 Å and the secondary attractive minimum at ~ 12 Å are remarkable. By contrast, the FMT/MSA method overestimates both the primary attractive minimum at roughly 3 Å and
the repulsive maximum around 8 Å. It even diverges somehow from the MC results at large separations when the electric double layer interactions are not intensive.

In order to explore the oscillatory pattern of the net pressures and also to understand the origin of the attraction shown in Fig. 5.4a, the individual components of the internal pressure are presented from the FMT/WCA calculations in Fig. 5.4b. Clearly, as a result of the interplay among those pressure contributions, three distinct regions are identified on the plot of the internal pressure $P_{\text{int}}$. In the first region of $h < 1d$, $P_{\text{int}}$ first goes down to a minimum and then up. In the second region of $h$ between 1d and 2d, $P_{\text{int}}$ continues to rise until a maximum and then turns down. In the third region of $h > 2d$, a secondary minimum is observed. Since these features are in conformity with those shown in Fig. 5.4a and no negative values of $P_{\text{int}}$ are found, the attractive net pressures can only result from a relatively high bulk pressure $P_{\text{bulk}}$, which is on the order of magnitude of the internal pressure at the end point where $h = 15$ Å.

5.3.3 The swelling pressure of Na-bentonite

Having successfully predicted the electrolyte-mediated interaction pressure in a charged slit, as compared to the MC simulations, in this section the pressure expression is implemented by using the FMT/WCA-$k^2$ method to study the swelling pressure of Na-bentonite for different salt conditions, including comparisons with experimental data.

Natural Na-bentonite of the Wyoming type (MX-80), consisting mainly of montmorillonite, swells when it comes into contact with water. This swelling property together with its low permeability makes Na-bentonite an ideal candidate for buffer and backfill material in the
deep geological repository of nuclear waste in, e.g., the Swedish KBS-3 disposal concept for spent nuclear fuels [76]. The swelling pressure as well as the volumetric strain varies at different ionic strength. In dilute electrolyte solutions, the bentonite particles may even form a stable sol and be carried away through the rock fractures by the seeping water; this causes a buffer loss [30]. Therefore, a theoretical approach that can predict the swelling pressure of colloidal particles is needed, to not only understand the swelling behavior of Na-bentonite but also assess the performance of the KBS-3 repository design [76].

As the swelling constituent of Na-bentonite, the montmorillonite has a thin plate-like shape with a central octahedral layer, consisting of mostly aluminium, sandwiched between two tetrahedral layers of mostly silicon oxide. The exchange of Si(IV) with, e.g., Al in the tetrahedral layer and Al by, e.g., Mg in the octahedral layer causes negative surplus charges, which are neutralized by the sodium cations residing on the outer surface of the montmorillonite sheet [31]. These compensating cations dissolve in water when the clay is wetted. They can be exchanged with other ions by ion exchange, when the clay is exposed to saline solutions. This impacts the swelling behavior of Na-bentonite.

To describe the interaction between montmorillonite sheets, the model system shown in Fig. 5.1 is applied. The swelling pressure $p_s$ between charged surfaces immersed in a solution is calculated, in this study, via

$$p_s = p_{\text{int}} - p_b + p_{\text{vdW}}$$

(5.22)

where $p_{\text{int}}$ and $p_b$ are determined through Eq. (5.16) by using the FMT/WCA-$k^2$ method. $p_{\text{vdW}}$ accounts for the van der Waals attraction between the surfaces, which can be obtained through the conventional Hamaker-De Boer theory for parallel slabs [40].

In order to compare the predictions from the FMT/WCA-$k^2$ method, a Donnan equilibrium-based DLVO model method (Paper V) with, however, point charge representations of the ions, is used to determine the swelling pressure of Na-bentonite. As a result, the ion-ion correlation effect is not considered. However, in addition to the electrostatic repulsion and van der Waals attraction of the DLVO type, the hydration effect is included in the model method since it has been argued to be critical at small surface separations (below 1-2 nm) [77]. Based on this, the swelling pressure between charged walls can be generally written as

$$p_s = p_{\text{osm}} + p_{\text{hydr}} + p_{\text{vdW}}$$

(5.23)

where $p_{\text{osm}}$ represents an osmotic pressure arising from the ion concentration difference between the confined electrolyte and the bulk solution, while $p_{\text{hydr}}$ describes the hydration repulsion between the surfaces. In Eq. (5.23), the exponential law [40] is applied to calculate $p_{\text{hydr}}$. The evaluation of $p_{\text{osm}}$ is based on the expression of Karnland et al [78], which is derived from a general thermodynamic model by the use of a Donnan equilibrium calculation.
In a set of experiments, the purified and fully Na-exchanged MX-80 was placed in a sample holder exposed to the test solution in a swelling pressure apparatus [78]. For each concentration of the test electrolyte, the swelling pressure \( P_s \) was given in terms of the dry density \( \rho_d \) of the bentonite or, equivalently, the distance \( H \) between montmorillonite sheets\(^\ddagger\). With these experimental results, the capability of the FMT/WCA-\( k^2 \) method will be examined, through Eq. (5.22), to predict the swelling pressure of Na-bentonite provided with the ion diameter \( d = 0.425 \) nm, temperature \( T = 298.15 \) K and the surface charge density \( \sigma = -0.1106 \) C/m\(^2\) [78]. Results from the Donnan equilibrium-based DLVO model method, i.e., Eq. (5.23), are also presented, aiming to compare them with the FMT/WCA predictions.

In Fig. 5.5, results from the DLVO model method, with and without accounting for \( p^{\text{hydr}} \) in Eq. (5.23), are presented to explore the hydration effect on the swelling pressure of Na-bentonite in distilled water. These results are compared with the experimental data [78] at different bentonite dry densities. It is seen that the calculations from the Donnan equilibrium-based DLVO model method agree well with the measured swelling pressures for the dry densities up to 2000 kg/m\(^3\). By contrast, when \( p^{\text{hydr}} \) is excluded, the model predictions deviate considerably for the swelling pressures at high dry densities or small surface separations. It is also found that, in Fig. 5.5, the magnitude of the hydration repulsion \( p^{\text{hydr}} \) starts to exceed the osmotic pressure \( p^{\text{osm}} \) and the van der Waals attraction \( p^{\text{hydr}} \) at about \( \rho_d > 1500 \) kg/m\(^3\) or \( H < 1 \) nm. Such an additional strongly repulsive short-range force is also confirmed in earlier studies [40, 79], and therefore the hydration effect should be well represented in models where ions are considered to be point charges only (Paper V).

\[ H = \frac{2V_w}{V_m a_m} \]

\(^\ddagger\)The distance \( H \) between montmorillonite sheets is related to \( \rho_d \) implicitly by \( H = \frac{2V_w}{V_m a_m} \), where \( V_w \) is the total water volume, \( V_m \) is the total volume of the montmorillonite which is a function of \( \rho_d \), and \( a_m \) gives the specific area of the montmorillonite.
In this study, however, the main interest is to predict the swelling pressures of Na-bentonite by the FMT/WCA-$k^2$ method for different salt conditions. In Fig. 5.6, the FMT/WCA-$k^2$ results are presented at certain dry densities, for which the measured swelling pressures of Na-bentonite are available, respectively, in the case of a 0.1, 0.3 and 1.0 M NaCl solution. The experimental results demonstrate that the Na-bentonite swells much more strongly as the dry density increases at each concentration and the swelling pressure of Na-bentonite is systematically reduced at all clay dry densities when the concentration of the bulk electrolyte increases. It is to be noted that the predictions of the FMT/WCA-$k^2$ method agree reasonably well with the experimental data in all the cases shown in Fig. 5.6, being consistent with the results of the Donnan equilibrium-based DLVO model method even at higher dry densities where the hydration effect turns to be very important. This suggests that the hydration repulsion is mainly attributed to the excluded volume effect of particularly hydrated counterions in the vicinity of the interface [57, 79]. Since such an effect of ion particle interactions has already been considered in the FMT/WCA-$k^2$ pressure simulation, as discussed before, in terms of the single-particle DCFs, it is concluded that the hydration effect between charged surfaces can be well accounted for if the ions are treated with a finite size and, consequently, the ion-ion correlations are taken into account.

**Figure 5.6** (Color in Paper V) Swelling pressures vs. bentonite dry densities at different salt conditions. Triangles: experimental data; curves: Donnan equilibrium-based DLVO model method; dots: FMT/WCA-$k^2$ approach (Paper V).
Among the existing density functional approaches, the weighted correlation approach (WCA) proposed in this work can be regarded as a rigorous theory for studying the structural and thermodynamic properties of inhomogeneous fluids at an interface. The principle of the WCA approach relies on an exact expression, in terms of a weighted pair direct correlation function, for evaluating the change of the single-particle direct correlation function. Based on this formulation, the WCA approach generalizes those DFT strategies commonly used to describe the free energy functional or the single-particle direct correlation function of an inhomogeneous fluid in a consistent manner, and therefore it is able to highlight the assumptions and limitations in different density functional approaches. More importantly, since the WCA approach opens a generic way for evaluating the single-particle direct correlation function, which accounts for the system non-ideality arising from various intermolecular interactions/correlations, it should be possible to apply the current WCA approach to a certain level of complexity, depending on the system of interest. For example, recent implementations of the WCA approach, in the studies of electric double layer capacitance in a slit and adsorption of ions on a polyampholyte surface, have been reported [80, 81].

In this study, the WCA approach is applied to study the hard-sphere and ionic structures of an inhomogeneous fluid at an interface. Calculations in a range of surface separations and bulk densities (Paper II) show that the WCA approach is capable of reproducing the Monte Carlo hard-sphere density profile between two hard walls. When the WCA approach is combined with the fundamental measure theory, it is found that the FMT/WCA-k^2 method is successful in predicting the fine features (e.g., the layering effect and charge inversion phenomenon) of the structural property of an ionic fluid near a highly charged surface (Paper I).

On the other hand, a novel expression is developed to describe the medium-induced interaction pressure and it is applied in studying the interaction between plate-like smectite particles. This expression is a sum of distinct physical components that involves different contributions to the single-particle direct correlation function, and therefore can be conveniently used in any density functional approach. Based on this formulation, the FMT/WCA-k^2 method is demonstrated to predict well the interaction pressure between charged surfaces and the swelling pressure of Na-bentonite for various salt strengths. It is found in the simulations that a non-intuitive attraction occurs between identically charged surfaces when divalent counter-ions are present in the electrolyte. However, such a theoretical finding cannot explain some observations [76]. For instance, the attractive forces predicted by the DFT calculation would simply indicate a collapse of calcium smectite sheets, while a
swelling behavior has been experimentally observed in the calcium system even if the swelling pressure decreases more rapidly with larger separation distances between the sheets compared to that of the sodium system. It is anticipated that this contradiction may be attributed to the use of the commonly applied primitive model of the electrolyte: the microions are treated as charged hard spheres with equal diameter. More problematically, the solvent (e.g., water) is considered as a structureless dielectric continuum and the heterogeneity of the charge distribution on the macro-particle surface is overlooked. Thus, it is recommended to continue to perform the WCA study (with either the FMT/WCA-$k^2$ method or a pure WCA method) in a non-primitive model where the effects of ionic size, solvent structure, surface charge heterogeneity etc. on the electrolyte-mediated interaction pressure can be explored.
LIST OF SYMBOLS AND ABBREVIATIONS

\( \varepsilon_0 \)  
Permittivity of the vacuum

\( \varepsilon_r \)  
Relative dielectric constant of the medium

\( \sigma \)  
Homogeneous surface charge density

\( i \)  
Ion species

\( \psi \)  
Mean electrostatic potential

\( z_i \)  
Valence of the ion species \( i \)

\( e \)  
Elementary charge

\( \kappa \)  
Debye parameter

\( A \)  
Thermal de Broglie wavelength

\( k_B \)  
Boltzmann constant

\( T \)  
Absolute temperature

\( R \)  
Gas constant

\( F \)  
Intrinsic (Helmholtz) free energy

\( F^{\text{id}} \)  
Ideal part of the intrinsic free energy

\( F^{\text{ex}} \)  
Excess part of the intrinsic free energy

\( u \)  
External potential

\( \Omega \)  
Grand potential

\( \mu \)  
Chemical potential

\( \rho^{(1)}(\mathbf{r}) \)  
Single-particle density at position \( \mathbf{r} \)

\( \bar{\rho}_m(\mathbf{r}') \)  
Weighted density evaluated at \( \mathbf{r}' \)

\( \rho_b \)  
Bulk density

\( p^{\text{int}} \)  
Internal pressure between the surfaces

\( P_b \)  
Pressure of the bulk fluid

\( p^{\text{net}} \)  
Net pressure between the surfaces immersed in a solution

\( p_s \)  
Swelling pressure

\( p^{\text{vdW}} \)  
van der Waals attraction between the surfaces

\( p^{\text{osm}} \)  
Osmotic pressure

\( p^{\text{hydr}} \)  
Hydration repulsion between the surfaces

\( c^{(1)} \)  
Single-particle direct correlation function.

\( c^{(2)} \)  
Pair direct correlation function
\( \tau^{(2)} \)  
Weighted pair direct correlation function

\( f_m \)  
Correlation-weight function

\( \alpha_m \)  
Correlation-weight factor

\( w_{m,n} \)  
Density-weight function

\( \lambda_{m,n} \)  
Density-weight factor

\( H \)  
Separation between the surfaces

\( h \)  
Distance between the center of the contact spheres.

\( z \)  
Distance from the surface

\( d \)  
Diameter of the hard spheres

\( w_i(z) \)  
Potential of mean force of ionic species \( i \) at a distance \( z \)

\( \delta(x) \)  
Dirac delta function

\( \Theta(x) \)  
Heaviside step function

DCF  
Direct correlation function

WDA  
Weighted density approximations

FMT  
Fundamental measure theory

WCA  
Weighted correlation approach

DFT  
Density functional theory

MC  
Monte Carlo

MGC  
Modified Gouy-Chapmann

PB  
Poisson-Boltzmann

DLVO  
Derjauin-Landau-Verwey-Overbeek

MSA  
Mean spherical approximation

PY  
Percus-Yevick

EDL  
Electric double layer

PM  
Primitive model

CO  
Direct Coulomb contribution

HS  
Hard-sphere contribution

EL  
Electric residual contribution

kin  
Kinetic contribution
REFERENCES


