Simulation of Microporous Systems: Confined Fluids in Equilibrium – Diffusion in Zeolites

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Contents

6 Diffusion of Guest Molecules in Zeolites   85

1

Introduction

The molecular theory of the properties of complex surface and interface systems as microporous media or membranes is one of the most important and challenging problems in the contemporary statistical physics of classical interacting many body systems. Despite a considerable progress in the analytical theory of interfacial systems (examples are integral equations, thermodynamic perturbation theory, density functional approaches, ...) in the last decades which provided a principal understanding of basic features not only of the (static) equilibrium behavior but also of the transport properties there are up to now only a few quantitative results available for real systems of practical relevance (e.g. Zeolites or biomembranes). This is due to the extremly complicated intra- and intermolecular interaction conditions in real interfacial systems which strongly hinder the development of analytical approaches.

A breakthrough in the molecular-based description of many body systems - particularly of classical fluids - brought the introduction of molecular simulation methods in the statistical mechanics half a century ago. Two main groups of 'computer experiments' have been established: the Molecular Dynamics methods which trace directly the time development of the system by a numerical solution of the classical equations of motion and the stochastical or Monte Carlo teccniques which generate a chain of random particle configurations simulating the possible microstates of the system permitting the estimation of configurational averages of the observables of interest.

In the last decades due to the dramatic improvement of numerical performance as a result of the development of the modern computer technology simulation methods became a powerful tool for the investigation of more and more complex situations reaching at present from physical chemical and biological to engineering and even economic problems.

Nowadays in sciences and technology simulation techniques have to be considered as a third independent method of research which is on equal terms with experimental and theoretical approaches. On the one hand side these methods allow the simulation of complicated real systems providing basically correct results even under extreme conditions where it is difficult or sometimes impossible to perform real experiments. On the other hand side the simulation of clearly defined model systems provides 'exact' comparison data which are of fundamental importance for the improvement of analytical theories on a molecular level.

This paper deals with the molecular simulation of fluids confined to micropores and porous media comprising both the equilibrium structural and

thermodynamical properties and the transport behavior of the enclosed particles.

The aim of the article is twofold: first, to give a review about recent molecular simulation techniques and the underlying statistical-mechanical concepts and second, to demonstrate the possibilities and limitations of the discussed simulation methods showing recent results for systems and properties selected from the fields of research of the authors.

The theoretical-methodical part starts with a short presentation of the basics of statistical physics introducing the relevant definitions and relations of the field followed by a detailed description of the molecular dynamics and Monte Carlo simulation methods focussing on techniques which are relevant for the simulation of interfacial systems.

The next section of the paper deals with the equilibrium properties of fluids confined to interfaces and micropores of simple geometry. Recent developments in the Monte Carlo simulation of adsorbed fluids are discussed in the context of actual problems in the statistical thermodynamics of fluids on inhomogeneous conditions.

Recent simulation results of the molecular structure and the phase behavior of several classes of fluids reaching from simple to associating systems confined to slit-like pores and thin planar interfaces are reviewed in some detail. Basic problems of the structural organisation of molecularely rough (fluid) interfaces versus the properties of fluid phases confineed to such interfaces are discussed describing both the interface molecules and the fluid particles by a uniform molecular conception which represents the interaction potentials by a hierarchy of contributions starting with the dominating excluded volume effects.

In the following section the transport of particles through porous media is discussed. Especially the simulation results for diffusion processes in Zeolites are reviewed ...

2

Statistical Physics

2.1   Some Notions of the Probability Theory

qquad

2.2   Some Notions of Classical Mechanics

3

Molecular Dynamics (MD) Simulation Techniques

qquad

4

Monte Carlo (MC) Simulation Methods

4.1   General Aspects

In the last section the molecular dynamics simulation techniques have been discussed in some detail. In the following we will deal with the second important approach to molecular simulations the stochastic or Monte Carlo simulation methods. While MD simulations describe the time development of many body systems by numerically solving the equations of motion MC methods estimate the ensemble averages of the relevant observables by means of stochastic processes. Due to the direct observation of the time development MD techniques are able to study both the properties of the system in thermodynamic equilibrium and time-dependent processes as diffusion or heat transfer. MC methods in a classical sense are based on equilibrium statistical mechanics and therefore restricted to equilibrium structural and thermodynamic properties although more general stochastic (random walk) simulation methods permit the treatment of non-equilibrium phenomena too [?]. In general the numerical effort (i.e. the computer time required) is significantly higher for MD simulations than for MC studies. For that reasons simulations of (equilibrium) structure and phase behaviour it is usually more efficient to use MC methods rather then MD.

   Some general problems and technical aspects of molecular simulations are independent from the simulation method used and have to be considered for both MD and MC approaches.

The basic problem of all kinds of molecular simulations consists in the necessity to describe the properties of a macroscopic many particle system by a system of a limited number of particles. Typically a system with about $10^2 3$ particles has to be mapped to en ensemble of a few hundred to thousand particles which can be handled numerically. A general problem represents the application of the statistical mechanics to a small simulation ensemble since the relations of statistical thermodynamics have been derived rigorously only for the limit of infinite numbers of particles (thermodynamic limes). To overcome these finite size problems – quite analogous to the case of MD simulations – periodic boundary conditions are usually applied (for details compare 3) Physically the introduction of periodic boundary conditions means that the original (cubic) simulation box is surrounded by identical copies of that box in all three directions in space forming an infinite extended lattice-like arrangement. In the same way as in MD the application of the minimum image convention (cf. **??**) ensures the correct measurement of the distances between the particles in the original simulation box and their images in the surrounding copies of the original cell. Another point common to all simulation methods is the choice of a suitable initial configuration usually a regular lattice arrangement of the particles. Starting with this configuration in MD the trajectories of all particles are followed (compare last section) and in MC a chain of configurations is generated (see below) where the application of the periodic boundary conditions together with the minimum image convention result in a constant number of particles in the simulation box during the course of the simulation. The system considered here differs from a real fluid by an 'imprinted' periodicy of the length of he simulation cell which leads to the fact that the properties of the system depend on the the size of the basic cell (i.e. on the number of particles in the box). The resulting deviation of a simulated quantity from that of an infinite system is usually denoted by a finite size effect. We will discuss the problem of finite size effects in subsection **??** in some detail.

For the purpose of this article we will review in the following the basics of the most important stochastic simulation techniques of classical many body systems where we focus on methods dealing with structure, thermodynamics and phase behaviour of confined fluids. Starting with the introduction of the most important MC simulation technique for classical fluids the importance sampling in form of the Metropolis algorithm we will deal with some practical aspects of simulation studies. The main part of the section comprise methods for a direct simulation of fluid phase equilibria as Gibbs ensemble and similar

techniques. Discussions of the efficiency of the methods and the possibilities of error estimations are also included.

4.2 Importance Sampling and Metropolis Algorithm

The goal of MC simulations of interacting many body systems consists in the estimation of ensemble averages of physical (thermodynamical) quantities – which were introduced in chapter **??** – by means of stochastic methods. The average of an observable O can be exxpressed in general as an integral of the form

$$\int \int O(\mathbf{r}^N, \mathbf{p}^N) f_0^{(N)}(\mathbf{r}^N \mathbf{p}^N) \mathrm{d}\mathbf{r}^\mathrm{N} \mathrm{d}\mathbf{p}^\mathrm{N}$$

where $f_0^{(N)}(\mathbf{r}^N, \mathbf{p}^N)$ represents the phase density of the statistical ensemble under consideration (compare chapter **??**).

Ensemble averages show the following general features:

1. They are high dimensional integrals depending in general on all impulses and coordinates of the N particles of the system (e.g, $6N$-dimensional integrals in the case of a one-atomic gas)

2. The phase densities vary over many orders of magnitude where often only limited ranges of the phase space provide contributions to the ensemble averages. Foe example in a micro canonical ensemble the phase density is a δ-function of the configurational energy (compare again chapter **??**).

These properties show that conventional integration methods are not suitable for the calculation of ensemble averages. Usual numerical algorithm are to complex for an application to these high dimensional problems. Well-known stochastic methods for the calculation of high dimensional integrals using equal distributed random numbers (simple MC methods) fail too because of the extreme variations of the phase density.

The calculation of phase averages requires the introduction of special techniques using so-called importance sampling based on distributions of specially weighted random numbers which preferrentially sample those parts

of the phase space which provide the largest contributions to the phase integrals.

For the most important statistical ensembles the general ensemble averages can be simplified, particularly, the phase average of a quantity $O(q, p)$ in a canonical ensemble can be written in general as a sum

$$O = O^{id} + O^{ex}$$

where the term O^{id} describes the behaviour of an ideal gas which is given analytically by integration over the impulses of the particles (compare section **??**). The calculation of the ensemble average reduces to the estimation of the average over the excess part O^{ex} the so-called configurational average

$$< O >^{ex} = \frac{\int O(\mathbf{r}^N)) \exp[-\beta U_N(\mathbf{r}^N))] \mathrm{d}\mathbf{r}^N)}{\int \exp[-\beta U_N(\mathbf{r}^N))] \mathrm{d}\mathbf{r}^N)}. \tag{4.1}$$

Although configurational averages in general depend on the (generalized) coordinates of the particles only the mentioned properties of the phase integrals (high dimensionality, and havy varying integrand) apply for these averages too. Therefore the above mentioned special MC integration methods (importance sampling) have to be used for the estimation of configurational averages too.

The introduced relations between the ensemble and the configurational averages are valid not only for canonical conditions but apply also to other important statistical ensembles as the isobar-isotherm and the grand canonical ensemble.

In order to represent the basic ideas of the importance sampling (Metropolis algorithm [**?**]) we restrict ourselves in the following to a canonical ensemble i.e. a system of N particles in a given volume V at a temperature T. The extension of the importance sampling to more general conditions is straightforward.

Using a general notation originally proposed by Binder [**?, ?**] we characterize every particle i ($i = 1, \ldots, N$) of the system by a set of dynamical variables $\{\alpha_i\}$ (spatial vektors $\mathbf{r}_i$, orientations $\mathbf{\Omega}_i$, spin vektors $\mathbf{S}_i$, or the like)

The set $\{\{\alpha_1\}, \{\alpha_2\}, \ldots, \{\alpha_N\}\}$ is called configuration or point in the phase space X genannt.

Denoting in the following the cofigurational part of the Hamilton function (usually the potential energy $\mathcal{H}_N(X)$ the configurational average of a quantity

$O(X)$ is given by

$$< O >= \frac{\int O(X) \exp[-\beta \mathcal{H}_N(X)] \mathrm{d}X}{\int \exp[-\beta \mathcal{H}_N(X)] \mathrm{d}X}. \tag{4.2}$$

If the $\{\alpha_i\}$ can take only discret values the integrals have to be replaced by the corresponding sums where it holds approximately

$$< O >\approx \bar{O} = \frac{\sum\limits_{j=1}^{M} A(X_j) P^{-1}(X_j) \exp[-\beta \mathcal{H}_N(X_j)]}{\sum\limits_{j=1}^{M} P^{-1}(X_j) \exp[-\beta \mathcal{H}_N(X_j)]} \quad , \tag{4.3}$$

where the M phase space points $\{X_j\}$ are chosen randomly corresponding to a given probability distribution $P(X)$ (importance sampling).

In order to realize the importance sampling one generates – according to Metropolis [**?**, **?**, **?**] a chain of configurations in the following way:
Using as a probability distribution for the random choice of the phase space points

$$P(X_j) = P_{eq}(X_j) \propto \exp[-\beta \mathcal{H}_N(X_j)] \quad , \tag{4.4}$$

it follows

$$\bar{O} = \frac{1}{M} \sum\limits_{j=1}^{M} O(X_j) \quad \text{(arithmetic average)}. \tag{4.5}$$

Since P_{eq} is not explicitly known a random walk of points $\{X_j\}$ through the phase space (Markov chain) is constructed which has the property $P(X_j) \rightarrow P_{eq}(X_j)$ for $M \rightarrow \infty$. A sufficient condition for this behaviour is (principle of micro reversibility – detailed balance) that the transition probability $W(X_j \rightarrow X_{j'})$ for $X_j \rightarrow X_{j'}$ meets the condition

$$P_{eq}(X_j) W(X_j \rightarrow X_{j'}) = P_{eq}(X_{j'}) W(X_{j'} \rightarrow X_j). \tag{4.6}$$

It follows

$$\frac{W(X_j \rightarrow X_{j'})}{W(X_{j'} \rightarrow X_j)} = \exp[-\beta \delta \mathcal{H}] \quad \text{with} \quad \delta \mathcal{H} = \mathcal{H}_{\mathcal{N}}(\mathcal{X}_{|'}) - \mathcal{H}_{\mathcal{N}}(\mathcal{X}_{|}) \quad , \tag{4.7}$$

i.e. the ratio *only* depends on the *difference* of the Hamilton functions of the configurations j and j'.

The condition of detailed equilibrium does not completely determine the transition probability $W(X_j \to X_{j'})$.

Therefore according to Metropolis one choses a simple form of W which is compatible with the detailed balance condition, usually:

$$W(X_j \to X_{j'}) = \left\{ \begin{array}{cc} \exp[-\beta\delta\mathcal{H}] & \text{for} \quad \delta\mathcal{H}_N > 0 \\ 1 & \text{otherwise} \end{array} \right. \tag{4.8}$$

The ckaimed convergency of the importance sampling algorithm to the canonical phase average may be proved in a mathematical rigorous way within the theory of stochastic processes. Metropolis et. al [?] give physical arguments for the correct convergency. A detailed discussion of the Metropolis algorithm may be found e.g. in the monographs [?, ?].

The picture 4.1 shows a diagram of the course of simulations according to the Metropolis algorithm.

After discussing the canonical ensemble we proceed now to a system where the number of particles N, the pressure P and the temperatur T are kept fixed. The configurational average of a quantity O in such an isobar-isotherm ensemble is given by (cf. chapter **??**)

$$< O > = \frac{\int\limits_0^\infty \int O(X)\exp\{-\beta[PV + \mathcal{H}_N(X)]\}\mathrm{d}X\mathrm{d}V}{\int\limits_0^\infty \int \exp\{-\beta[PV + \mathcal{H}_N(X)]\}\mathrm{d}X\mathrm{d}V} \quad . \tag{4.9}$$

This average is formally of the same structure as the canonical average if an additional variable V and a modified weight factor are introduced. Considering V formally as a dynamical variable of the system by setting

$$X = \{\{\alpha_1\}, \{\alpha_2\}, ..., \{\alpha_N\}, V\},$$

the relations of the canonical average hold quite analogous for the isobar-isotherm ensemble. Particularly we get

$$W(X_j \to X_{j'}) = \left\{ \begin{array}{cc} \exp\{-\beta[\delta V P + \delta\mathcal{H}_N]\} & \text{for} \quad \delta\mathcal{H}_N > 0 \\ 1 & \text{otherwise} \end{array} \right. \tag{4.10}$$

Generating the chain of configuration (i.e performing transitions from micro state X zu X' we have to consider as an additional basic MC move – besides the particle displacement – an random change of the volume of the system.
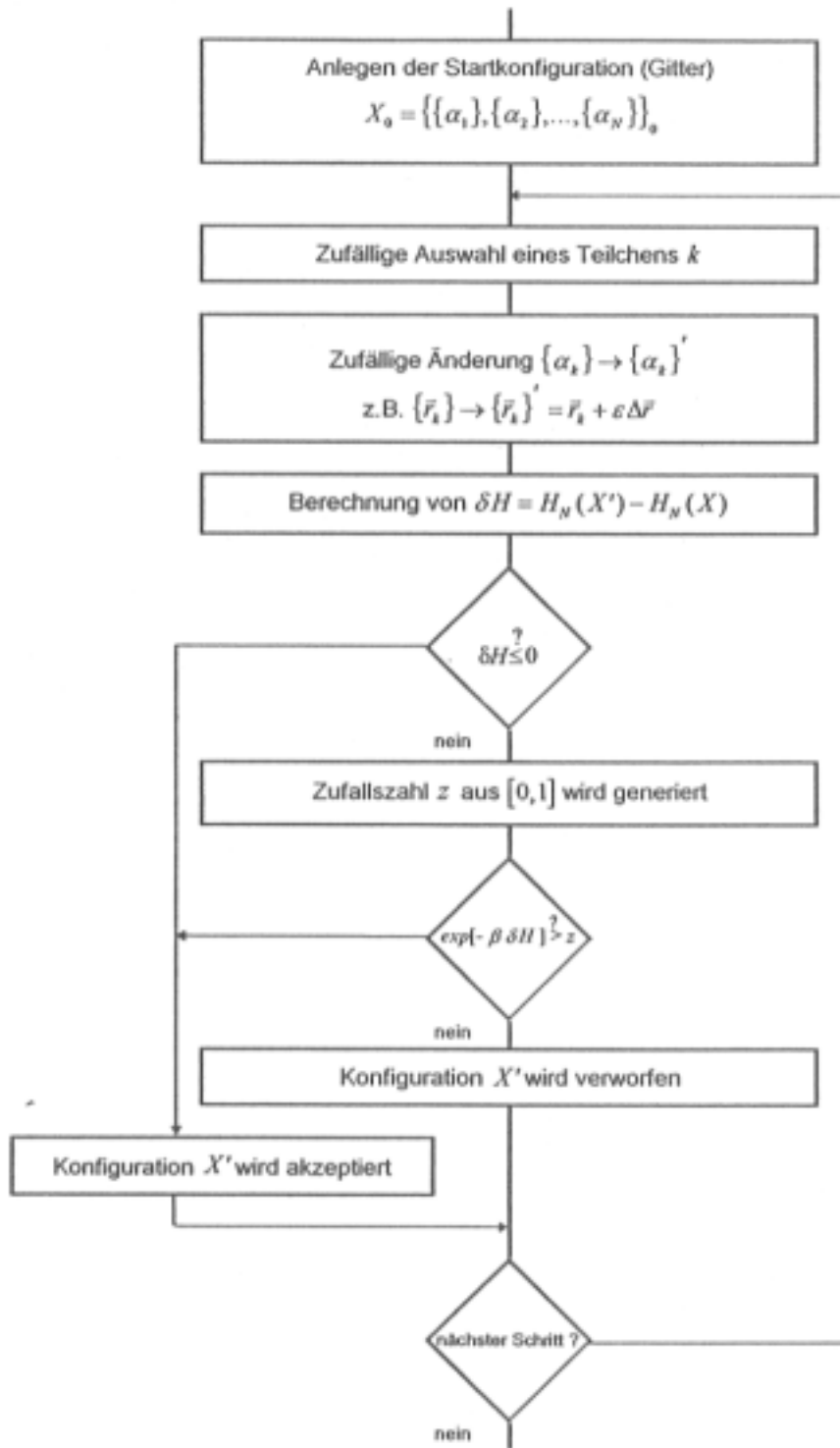
$$V \to V' = V + \lambda\delta V$$

Figure 4.1: Scheme: Metropolis algorithm

where the Metropolis acceptance check has to be performed using the modified Boltzmann factor equ,(4.10) (cf. [?]).

Important for the application of the NPT ensemble is the fact that the volume V itself can be represented directly as a MC average i.e. the equation of state in a volume explicit form

$$< V >_{NPT} = f(P, T, N) \qquad\qquad (4.11)$$

is given as an isotherm-isobaric average where – in contrast to the canonical ensemble – no calculation of distribution functions is necessary. The NPT ensemble represents the natural choice of variables for the simulation of thermodynamic excess quantities of mixtures because these quantities are defined in a volume-explicit form i.e. the pressure is used as the independent variable to measure these quantities.

Concerning the practical realization of the simulation of structural and thermodynamic quantities of fluids we have to start with the principal ideas given in the last paragraph and we can refer partly to the representation of the basics of MD simulations described in section 3. Particularly, we consider a system consisting of N particles confined to a cubic simulation box where periodic boundary conditions an the minimum image coindition are usually applied (for details compare section 3). The first question which has to be decided concerns the number of particles in the simulatio cell necessary to reproduce the properties of the macroscopic system with sufficient accuracy. The minimum number of particles to be studied depends on the range of the intermolecular forces (correlation length) and the number density and the physical quantities under consideration. In the case of confined (inhomogeneous) fluids additionally the range of the forces between the fluid molecules and the interfaces (walls) have to be taken into account. In practice the number of particles is limited by the computer equipment available.

For normal (nonpolar) fluids (e.g. Lennard-Jones or square-well potentials) the range of the intermolecular interactions amounts to a few particle diameters only. In the case of polar or ionic systems the range of the intermolecular forces is much longer and requires special techniques (e.g. Ewald summation cf. section ??) in order to ensure an adequate consideration of these slowly converging potential contributions in simulation boxes which may be much smaller then the range of these forces. The range of the correlation between two particles 1 and 2 in the fluid is measured by the pair distribution function $g(\mathbf{r}_1, \mathbf{r}_2)$ depending in general on the spatial position of

both particles $\mathbf{r}_1$ and $\mathbf{r}_2$. In the case of a homogeneous and isotropical system the pair distribution function reduces to a function of the distance r of the two particles only the so-called radial distribution function $g(r)$. While $g(r)$ usually describes the pair correlation of simple bulk fluids – which consist of spherical symmetrical molecules and interact via distance dependent pair potentials – the situation in confined fluids is in general much more complicated. Due to the presence of interfaces or pore walls the homogenity and isotropy in space is perturbed and pair correlations have to be described by the use of the full pair dostribution function $g(\mathbf{r}_1, \mathbf{r}_2)$.

In dense fluids without long-ranging (e.g. Coulomb-like) interactions the pair correlation usually decays with oscillations and vanish within four to five molecular diameters [**?**, **?**]. Therefore for these systems the adequate consideration of the intermolecular interaction requires a length of the simulation box which at least counts to about the double of the range of the pair correlations, i.e. in a dense fluid a quantitative estimation of structur and thermodynamics requires the simulation of an ensemble of at least one thousend particles.

As initial configuration of a simulation run usually a regular arrangement of the paricles (e.g.a cubic lattice) is used

The generation of the chain of configurations is schematically shown in the diagram 4.1. The transition from one configuration to the next one takes place by a small random change of one dynamical variable (one degree of freedom) of a andomly chosen particle of the system. In the canonical ensemble that means for simple spherical symmetrical fluids a random displacement of the center of a particle. In the case of molecular fluids addiutionaly a random change of the orientation of a molecule has to be performed whereas for the realization of the orientational move several algorithms are available dependending on the geomety of the molecules [**?**]. Special techniques for non-linear planar and tetrahedral molecules are described in [**?**] and [**?**], respectively.

In the NPT ensemble comprises the chain of configurations besides the (canonical) displacement moves random changes of the volume which have to be accepted according to eq. (4.10). For efficiency reasons one change of the volume is attempted only after a number of displacements which is usually in the order of the number of particles N

The estimation of configurational (ensemble) averages requires that the generated chain of configurations (micro states) represents the thermodynamic equilbrium. The Metropolis algorithm ensures the convergency to the

equilibrium for sufficient long Markov chains (rigorously this holds only if the number of configurations $M \to \infty$). If the simulation is started with a special initial configuration (e.g. regular lattice arrangement) a so-called equilibration run has to be performed where a sufficient large number of configurations has to be generated before the measurement of quantities is performed. The necessary length of the chains for both the equilibration and the averaging of observables can not be specified universally but depends on the interaction potentials and the state conditions similarly as the necessary size of the system.

As in chapter **??** discussed the structur of a fluid is described by the spatial distribution functions where the one particle densities and the pair distribution function are of special interest, since from the knowledge of these functions the thermodynamic properties of the fluid can be estimated. While for bulk fluids the one-particle distributions $\rho^{(1)}$ are usually constant within the entire fluid volume and given by $\rho^{(1)} \equiv \rho = N/V$ in confined fluids the one-particle distribution $\rho^{(1)}(\mathbf{r})$ represent the most important structural quantities. Examples for density distributions (density profiles) of fluids in micropores of simple geometry are given in section **??**.

In the case of simple fluids with spherical symmetrical pair potentials the structure of the fluid is completely described by the radial distribution function $g(r)$ and can be written as

$$g_N^{(2)}(\mathbf{r}^2) = \frac{\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\rho^2} = \frac{\rho_{\Delta r}(r)}{\rho} \tag{4.12}$$

where we have used that g in this case only depends on the distance of two particles $r = |\mathbf{r}_2 - \mathbf{r}_1|$ where in in (4.12) $\rho_{\Delta r}(r) = \rho_N^{(2)}(r)/\rho$ represents the number density of the particles in a spherical shell of the radius r and the width Δr around a particle picked randomly from the system.

Technically the radial distribution function is calculated by counting the number of pairs orf particles with a distance between r and $r + \Delta r$ in the MC configurations. These numbers are registered in so-called histograms and from these by means of eq. (4.12) approximations of $g(r)$ are estimated. For illustration figure 4.2 shows $g(r)$ of a hard spere fluid at different packing fractions η. confined From the radial distribution function $g(r)$ thermodynamical quantities as pressure or internal energy can be estimated directly by means of the relations of statistical mechanics. Some of these relations are given in chapter **??**
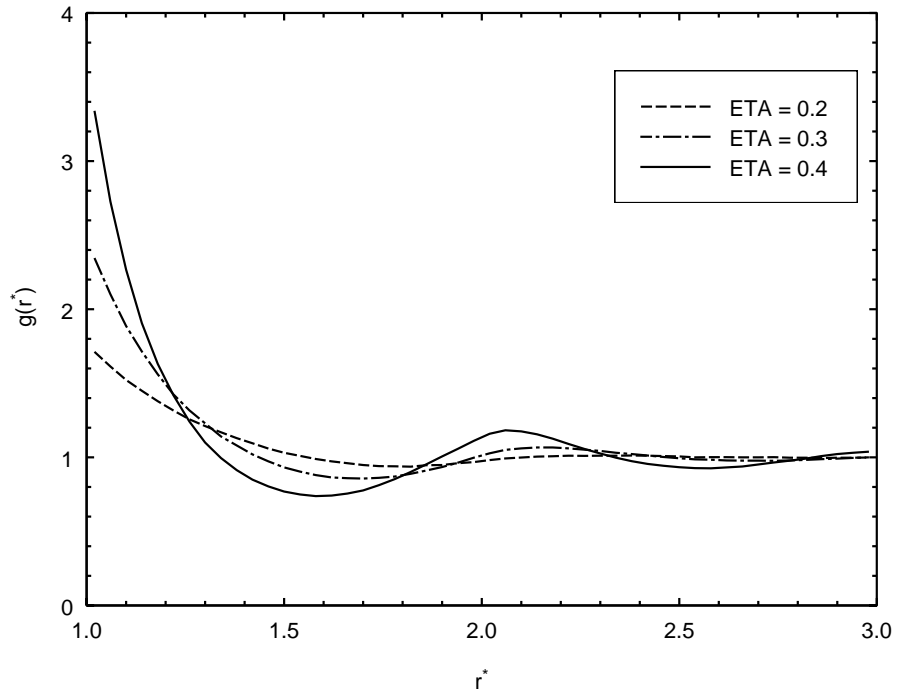
Figure 4.2: Radiale Verteilungsfunktion eines Hartkugelfluids f'ur verschiedene Packungsdichten η. Der Abstand r^* ist auf den Kugeldurchmesser reduziert.

The setting up of histograms is one of the basic techniques to analyze MC configurations. The density profiles of confined fluids are estimated quit similar by counting the number of particles in certain volume ranges registering these numbers in suitable histograms. (cf. section **??**.

4.3   Grand Canonical Ensemble und Chemical Potential

The above discussed simulations in the canonical and the isobar-isotherm ensemble are usually restricted to systems showing a single fluid phase only. To study coexisting fluid phases (fluid phase equilibria) in the bulk and phase coexistence (adsorption, capillary condensation etc.) in confined fluids we have to consider open systems where we – in contrast to NVT and NPT simulations – permit fluctuations of the number of particles.

In the grand canonical ensemble (cf. chapter **??**) we simulate the average number of particles $< N >$ in an open system where the volumen V, the temperature T and the chemical potential μ are kept fixed.

The configurational average in the μVT ensemble has the followintg form:

$$< A >= \frac{1}{Q_\Xi} \sum_{N=0}^{\infty} \frac{\Lambda^{3N}}{N!} \exp[N\beta\mu] \int A(X) \exp\{-\beta\mathcal{H}_N(X)\}\mathrm{d}X \qquad (4.13)$$

where Q_Ξ represents the grand canonical configurational integral given by

$$Q_\Xi = \sum_{N=0}^{\infty} \frac{\Lambda^{3N}}{N!} \exp[N\beta\mu] \int \exp\{-\beta\mathcal{H}_N(X)\}\mathrm{d}X \qquad . \qquad (4.14)$$

In these expressions besides the dynamical variables the number of particles N is variable.

As an additional MC move –besides the random change of the dynamical variables (coordinates) – we have to consider in the grad canonical simulation a random variation of the number of particles N. Since N in contrast to the dynamical variables can take only discret (integer) values at least two changes have to be performed

1. addition of a paricle (at a randomly chosen place) where the transition $X_N \to X_{N+1}$ is accepted with the probability

$$W(N \to N + 1) \propto \exp(-\beta[\mathcal{H}_N - \mathcal{H}_{N+1}]). \qquad (4.15)$$

2. removal of a (randomly chosen) particle where the transition $X_N \to X_{N-1}$ is accepted with the probability

$$W(N \to N - 1) \propto \exp(\beta[\mathcal{H}_N - \mathcal{H}_{N-1}]). \tag{4.16}$$

The average number of particles $\bar{N}$ in equilibrium is obtained by the grand canonical average

$$\bar{N} = \langle N \rangle_{\mu VT}$$

over the chain of generated configurations.

In general the free energy or the chemical potentials, respectively, can not be represented directly by an average over a statistical ensemble i.e. the simulation of these quantities are not possible by means of the usual Metropolis algorithm, Besides the above discussed grand canonical simulations where the chemical potentials are set as parameters in advance the so-called test particle method of Widom [?] offers a way for the direct simulation of chemical potentials. If we remember that the excess of the chemical potential μ^{ex} over that of an ideal gas of the same density and temperature μ^{id} is goven by the change of the free energy by addition of a $(N + 1)$st particle to the system we can write [?]

$$\beta\mu^{ex} = \beta(\mu - \mu^{id}) = -\log \frac{Q_{N+1}}{VQ_N} = -\langle \exp[-\beta(U_{N+1} - U_N)]\rangle_N . \tag{4.17}$$

Q_N is the (canonical) configurational integral for N particles. $< ... >_N$ represents the configurational average in the NVT ensemble.

In practice the test particle method is performed in the following way:

1. generation of M configurations according to the Metropolis algorithmus (in a NVT or a NPT ensemble) or estimation of a corresponding number of time steps in a MD simulation

2. performing a number K of attempts to insert a $(N + 1)$st test particle at a random place in the simulation box

3. in each case calculation of $\exp[-\beta(U_{N+1} - U_N)]$

4. back to step 1.

The accumulation of the average Boltzmann factors of a (virtual) test particle $\langle \exp[-\beta(U_{N+1} - U_N)]\rangle_N$ is performed by frequent iteration of the algorithm. The excess of the chemical potential μ^{ex} is given imediately from the above relations. The optimum number of configurations M to generate between two 'Widom measurements' and the setting of the number of insertion attempts are parameters of the simulation and depend on the interactions in the system under consideration. For simple (bulk and confined) fluids usually $M \approx K \approx N$ is chosen.

Problems appear for high densities and for fluids consisting of non-spherical molecules, since the rate of acceptance for the random insertion of a test particle may become so small that the algorithm breaks down. To study high density fluids and/or systems consisting of highly non-spherical particles modifications of the grand canonical algorithm or of the Widom method are necessary (e,g. simulation methods with gradually particle insertion [?,?,?]). In section ?? these problems will be discussed separately.

4.4 Direct Estimation of Partitition Functuion Derivatives (Virtual Parameter Variation

Gneralizations of Widoms test particle method estimating the chemical potential are techniques using virtual paramerer variations to calculate directly relevant derivatives of the configurational partitition function. [?].

From the standard thermodynamical expressions

$$d\beta A^{ex} = U^{ex}d\beta - \beta P^{ex}dV + \beta\mu^{ex}dN \tag{4.18}$$
$$\beta A^{ex} = -\ln Q_N \tag{4.19}$$

where superscript ex denotes an excess quantity above the ideal-gas value, A is the Helmholtz energy, U the internal energy, and Q_N is the canonical ensemble configurational partition function, it is formally seen that the derivatives of $-\ln Q_N$ with respect to a parameter x selected from the set $\{\beta, V, N\}$ are the respective coefficients of the differentials in eqn. (4.18). .

The TPI method [?] calculates $\beta\mu^{ex}$ by performing trial particle insertions to calculate the derivative $(\partial \beta A^{ex}/\partial N)_{V,T}$. Similarly, although the pressure can be calculated in a standard way from the virial [?], it may also be calculated directly in the simulation by performing trial volume changes

to compute $(\partial \beta A^{ex} / \partial V)_{T,N}$. Thus, some time ago, Eppenga and Frenkel [?] developed a method for calculating the pressure of a hard platelet model system using this approach. Recently, Harismiadis *et. al.* [?] generalized this approach to the calculation of the pressure for general intermolecular potential models, and applied it to the calculation of the pressure in Gibbs ensemble simulations (the Gibbs ensemble will be discussed in detail in the next section.). In the following, we derive a general method for calculating a first derivative of βA^{ex}, which yields the two previously mentioned derivatives as special cases.

Consider a system being simulated in the (N, V, T) ensemble as the *reference system*, denoted by the subscript 0. Then we have

$$\exp(-\beta A_0^{ex}) = Q_0 \tag{4.20}$$

where Q_0 is the partition function for the system with parameter value x_0. Changing x to give a new system labelled by the subscript 1, we have

$$\exp(-\beta A_1^{ex}) = Q_1 \tag{4.21}$$

Dividing these two expressions yields

$$\exp(-\Delta \beta A^{ex}) = < \exp(-\beta \Delta \mathcal{U}) >_0 \tag{4.22}$$

where $< ... >_0$ denotes an average over configurations of the reference system. Setting

$$\Delta \beta A^{ex} = \left(\frac{\partial \beta A^{ex}}{\partial x} \right) \Delta x + O(\Delta x)^2 \tag{4.23}$$

and taking the limit $\Delta x \to 0$ and using equation (4.23) gives

$$\left(\frac{\partial \beta A^{ex}}{\partial x} \right) = - \lim_{\Delta x \to 0} \frac{\ln < \exp(-\beta \Delta \mathcal{U}) >_0}{\Delta x} \tag{4.24}$$

Equation (4.24) is the basis of the Virtual-Parameter-Variation method.

We note that [?], if x and $\partial \beta A / \partial x$ form a conjugate intensive-extensive variable pair, one may perform computer simulations at fixed values of either quantity by means of a Legendre transformation. One example of such a variable pair for the canonical ensemble variables $\{N, V, \beta\}$ with thermodynamic potential βA is $\{N, \beta \mu\}$. Thus, $\beta \mu$ may be measured in a (N, V, β) (canonical ensemble) simulation using the test particle method (which we would denote

as virtual particle variation method), which is a special case of equation
(4.24). Correspondingly, grand canonical ensemble simulations correspond to
fixed $\beta\mu \equiv \partial(\beta A)/\partial N$. Similarly, P may be measured in a canonical ensem-
ble simulation using equation (4.24) (the virtual volume variation method),
and (N, P, T) simulations correspond to fixed $\beta P \equiv -\partial\beta A/\partial V$. A third con-
jugate pair of variables is $\{\beta U, \beta\}$. As for the case considered by Eppenga
and Frenkel [?], equation (4.24) may provide a convenient method to measure
$\beta U \equiv \partial\beta A/\partial\beta$ in a computer simulation for systems of complex geometry.
Finally, simulations at fixed βU may be implemented in an analogous man-
ner. In all these cases, the simulations at specified values of $\beta\mu, P$, or U may
be performed in a canonical ensemble using fluctuating values of V, N, or
β, respectively. The transition probability for consecutive configurations is
given by min $(1, \mathcal{P}_{\Delta x})$, where

$$\mathcal{P}_{\Delta x} = \exp\left(\frac{\partial\beta A^e}{\partial x}\Delta x - \beta\Delta\mathcal{U}\right) \tag{4.25}$$

This is a simple rearrangement of equation (4.24). In a later paragraph
(section **??**) of this article we will show the application of the virtual vol-
ume variation technique to estimate the spreading pressure (thermodynamic
pressure) of fluids confined to slit-like pores.

4.5   Phase Equilibria and Gibbs Ensemble

In the last sections we presented methods as the Widom method or grand
canonical MC which permit the study of the properties of phase equilibria
only at indirect ways via the estimation of the chemical potentials.

Recently Panagiotopoulos [?] proposed a computer experiment – the
Gibbs ensemble approach – which directly simulates the average densities
of the coexisting phases avoiding the expensive (time-consuming) calcula-
tions of the chemical potntials. We will begin with a representation of the
basics of the method in the case of a liquid vapour equilibrium of a simple
fluid before we proceed to the more general case of phase equilibria of inho-
mogeneous (confined) fluids. The basic idea of the Gibbs ensemble method
consists in the representation of a macroscopic system (fluid) with two co-
existing phases (vapour I, liquid II) by means of two microscopic regions
within the corresponding phases which are far from physical contact between
the phases where these regions are modelled by two separate simulation boxes

– with the usual periodic boundary conditions applied –for the gas and liquid phase, respectively.

Obeying the conditions of coexistence of both phases

$$T_I = T_{II} \qquad p_I = p_{II} \qquad \mu_I = \mu_{II} \tag{4.26}$$

the computer experiment is performed by the generation of a chain of configurations which consists of the basic moves (i) particle displacements within the corresponding boxes, (ii) volume fluctuations and (iii) particle transfer between the boxes and converges to the properties of the coexisting phases in equilibrium. The statistical mechanics (cf. chapter **??**) permits the derivation of the phase density of such a Gibbs ensemble from the partition function (for details compare a recent review article of Panagiotoupulos [**?**]) Restricting ourselves to the configurational part we obtain in the simplest case of a vapour liquid equilibrium for the phase density f_G in terms of the number of particles in the gas N_I, the volume of the gas phase, the total number of particles N, the total volume V and the temperature T

$$f_G(N_I, V_I, N, V, T) \propto \exp \left[\ln \frac{N!}{N_I! N_{II}!} \right. $$
$$\left. + N_I \ln V_I + N_{II} \ln V_{II} - \beta U_I(N_I) - \beta U_{II}(N_{II}) \right] \tag{4.27}$$

where additionally hold the conditions

$$N_I + N_{II} = N \qquad \text{und} \qquad V_I + V_{II} = V \quad . \tag{4.28}$$

The structure of the phase density requires the performance of three basic moves during the course of a Gibbs ensemble simulation:

1. displacement of the particles
   In both boxes randomly chosen particles are independently displaced by a (small) random vector. This displacement is accepted with the probability

$$p_d = \min \left\{ 1, \exp(-\beta \Delta U) \right\} \qquad . \tag{4.29}$$

ΔU is the change of the potential energy due to the displacements.

2. Change of the volume
   The volume of the gas phase V_I is changed by the random amount ΔV.
   In order to ensure the constancy of the total volume simultanously the
   volume of the liquid is changed by $-\Delta V$. This change is accepted by
   the probability

$$p_v = \min \left\{ 1, \exp(-\beta \Delta U_I - \beta \Delta U_{II} + N_I \ln \frac{V_I + \Delta V}{V_I} + N_{II} \ln \frac{V_{II} - \Delta V}{V_{II}}) \right\} \quad .(4.30)$$

3. particle transfer
   In order to adjust the different densities of the coexisting phases par-
   ticle transfers between the both simulation boxes are performed. The
   transfer of a particle from region II to a random place in region I is
   accepted with the probability

$$p_{tf} = \min \left\{ 1, \exp(-\beta \Delta U_I - \beta \Delta U_{II} + N_I \ln \frac{(N_I + 1)V_{II}}{N_{II} V_I} \right\} .(4.31)$$

The Gibbs ensemble discussed here posesses a preset temperature, a given
total volume and a constant total number of particles. Considering vapour
liquid equilibria of one-component fluids this canonical Gibbs ensemble rep-
resents the only choice of variables which is consistent with the Gibbs phase
rule, since in the case of two coexisting phases only one intensive indepen-
dent variable (the temperature T) is permitted whereas in the case of many-
component systems the temperature, the pressure and the number of parti-
cles can be set independently which defines a isotherm isobar Gibbs ensemble
The most important difference to the standard (canonical) Gibbs ensemble
consists in a changed volume fluctuation move where now the constraint of
a constant total volume is lifted and independent variations of the volumes
of the both simulation boxes are performed. The technical realization of the
NPT Gibbs ensemble is very similar to the standard Gibbs simulation.
   As initial configurations usually in both boxes regular lattice arrange-
ments are used where the densities in the boxes are chosen as close as pos-
sible to the expected densities of the corresponding coexisting phases. As
mentioned before periodic boundary conditions are applied to both boxes,
In order to fulfil the principle of microscopic reversibility the sequence of the
basic MC moves has to be chosen per random with a preset probability for

each of the three basic steps. The setting of these probabilities determine the efficiency (the convergency properties) of the simulation. In practice these probabilities are chosen in such a way that after each displacement of a particle a number of particle transfers are attempted and after a sequence of about N displacements a trial change of the volume is attempted.

From a technical point of view the recording of so-called control plots is of special importance to monitor the convergency of the simulation run by observing the properties of characteristical quantities as energy, pressure or number of particles in terms of the length of the chain of configurations. Recording the number densities of the coexisting phases (vapour and liquid phases) the adjustment of the phase equilibrium during the course of the Gibbs simulation can be observed directly. In figure 4.3 the typical behaviour of the coexistence densities of both coexisting phases is shown. The data are taken from a Gibbs simulation study ?? of confined square-well fluids.

Another point concerns the dependence of the position of the phase equilibrium on the size of the system. If the number of particles is chosen to small finite size effects may appear which may distort the results. In order to guaranteee reliable results a minimum number of at least about 500 particles per phase (simulation box) have to be considered.

The most important results obtained by simulations in the Gibbs ensemble are critical oroperties and phase diagrams for a number of basic fluid models comprising not only simple fluids as square-well [?] and Lennard Jones fluids [?] but also polar and ionic systems [?]. Using modifications of the Gibbs method (cf. section ??) even molecular fluids with highly elongated molecules (e.g. Kihara fluids ??) and associating fluids are under consideration. The extension of the Gibbs approach to inhomogeneous (confined) fluids will be presented separately in the next paragraph.

A generalization of the Gibbs ensemble to chemical equilibria represents the so-called reaction ensemble recently introduceed by Smith and Triska [?]. In comparison to simulations of non-reacting systems the setting of the chemical equilibrium in the reaction ensemble may be understood as the result of additional constraints in the system. The particle numbers N_i of the species involved have to satisfy the stochiometric condition [?] the system

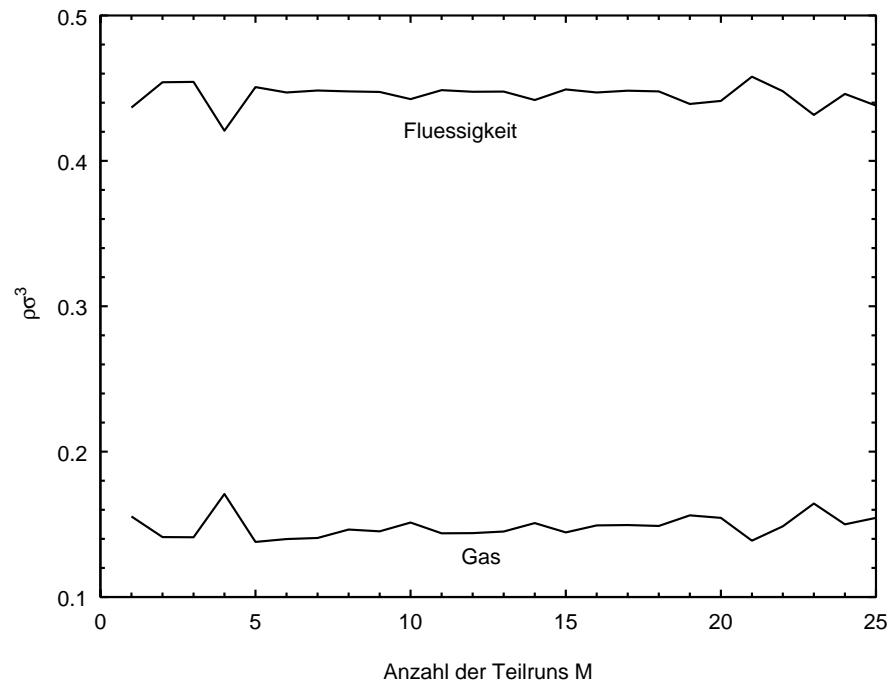$$N_i = N_i^0 + \sum_{j=1}^{R} \nu_{ji}\xi_j; \ i = 1, 2, \ldots, s \tag{4.32}$$

Figure 4.3: Number densities of the coexisting gas and liquid phases versus the length of the MC chain in a subcritical square well fluid

where the index ^{o} denotes a possible initial distribution of the particle numbers. ν_{ji} is the stochiometric coefficient of species i and ξ_j the strength of reaction j. R is the number of (linear independent) stochiometric equations.

The condition of chemical equilibrium is given by

$$\sum_{i=1}^{s} \nu_{ji}\mu_i = 0; \; j = 1, 2, \ldots, R \tag{4.33}$$

where the μ_i are the chemical potentials of species i.

According to the original paper [?] the chain of configurations in the reaction ensemble consists of the following basic moves:

1. particle displacements (NVT moves)

2. reaction steps, consisting of

   (a) random choice of a reaction (in case of several parallel reactions)

   (b) random choice of the direction of the reaction

   (c) random choice of a possible set of reactants and product molecules

   (d) implementation of a reaktion step, which gives the probability between the chosen reactant and product molecules

3. in case of isobar isotherm conditions random volume changes (NPT moves)

The extension of the reaction ensemble to chemical reactions in confined fluids is straight forward and at present under consideration [?,?].

4.6   Gibbs Ensemble for Confined Fluids

The investigation of phase equilibria of bulk fluids by means of the above discussed Gibbs ensemble simulation technique has become in the last years a standard simulation technique for the study of molecular-based models of such equilibria [?].

By way of contrast the simulation method used for the study of fluids in confined regions in equilibrium with a corresponding bulk fluid has typically been the grand canonical ensemble technique (cf. section ??), which allows the study of the properties of a confined fluid in equilibrium with a bulk fluid of specified chemical potential and temperature. Since the grand canonical

method is typically only useful in the study of single-phase systems in each region, recently the Gibbs methodologie has been extended to more general confined fluid phase equilibria.

Originally the adaption of the Gibbs ensemble to inhomogeneous conditions ls due to Panagiotopoulos too [?] which allows in principle the study of adsorption equilibria between bulk fluids and fluids confined in pores and of capillary condensation phenomena (phase equilibria) of fluids confined in pores. Here we present a recently developed [?] more general version to simulate inhomogeneous phase equilibria involving two coexisting fluid phases either in the bulk or in the confined region (pore).

We consider a fluid distributed over a bulk region (I) and a pore (II) with preset temperature T, total volume $V = V_I + V_{II}$, and total number of particles $N = N_I + N_{II}$,i.e. the bulk and pore region together form a canonical ensemble. The thermodynamic equilibrium between both regions requires:

$$T_I = T_{II} \qquad\qquad \mu_I = \mu_{II} \tag{4.34}$$

As discussed in detail by Panagiotopoulos [?], pressure is not a relevant variable for the description of bulk-pore equilibrium. This means that both the total volume of the two bulk boxes and the volume of the pore box must be kept fixed during the course of the simulation. Two simulation boxes represent the bulk (I) and the pore (II) in regions 'far from the physical contact area' between both regions. If there are coexisting phases within a region these are described by two boxes representing coexisting vapor and liquid phases, either in the bulk (I^v, I^l) or in the pore (II^v, II^l).

In a close analogy to the standard Gibbs ensemble we have to consider a chain of configurations consists of three types of moves (i) random displacements of particles within their boxes and (ii) random transfers of particles between the bulk box (I) and the pore box (II) and (iii) MC moves within and between sub-boxes (if necessary)
converging to the equilibrium distribution of the particles:

1. Particle displacement:
   random displacements of the particles (independently in their boxes) accepted with the probability:

   $$p_d = \min\left\{1, \exp(-\beta\Delta U)\right\} \tag{4.35}$$

   where ΔU is the change of the configurational energy.

2. Particle transfer:
   The transfer of a randomly chosen particle from region II to a random location in region I accepted with probability:

$$p_{tf} = \min\left\{1, \exp(-\beta(\Delta U_I + \Delta U_{II}) - \ln\frac{(N_I + 1)V_{II}}{N_{II}V_I}\right\} \qquad (4.36)$$

3. Moves in sub-boxes (if necessary):
   If vapour and liquid phases coexist either in (I) or (II)

   (a) Volume changes of subboxes of one region:
       Increase of V_l by randomly chosen ΔV (and decrease of V_v by ΔV) accepted with the probability

$$p_v = \min\left\{1, \exp(-\beta(\Delta U_l + \Delta U_v) + N_l \ln\frac{V_l + \Delta V}{V_l} + N_v \ln\frac{V_v - \Delta V}{V_v}\right\}(4.37)$$

   (b) Particle transfer between subboxes of one region: The probability of acceptance is analogous to move 2.

In the original paper of Panagiotopoulos [?] Lennard-Jones fluids in cylindrical pores have been studied where the adsorption of the fluid in the pore and the pore-pore gas-liquid equilibrium (capillary condensation) have been simulated. In section ?? more recent results [?] of a three-box simulation of the phase equilibria of square-well fluids in planar slits will be presented where particularly the three-state coexistence densities and the corresponding chemical potentials have been calculated.

4.7 Efficiency Problems

4.7.1 Particle Insertion at High Densities

As discussed above MC methods for the simulation of chemical potentials grand canonical simulations and phase and reaction equilibria comprise as basic moves the (virtual or real) insertion of test particles or the transfer or exchange of molecules between the simulation boxes.

Widoms test particle method calculates the chemical potential by the change of the free energy if an additional particle is inserted in the system at a random location. In the μ, V, T ensemble the attempt to insert or delete

a particle is – which is accepted by a probability depending of the change of configurational energy – determines the setting of the equilibrium number density. A similar role play in Gibbs and reaction ensemble simulations the probabilities of particle transfer or exchange, respectively.

In general the efficiency of the mentioned simulation techniques depends essentially on the probability to find a cavity in the system which is able to accomodate an additional particle. This probability decreases rapidly with increasing number density of the fluid phase and may become for usual liquid densities (e.g. at the triple point) so small that we get a so small acception rate for the particle insertion/transfer steps that the convergency of the corresponding Markov chain may break down in the high density range.

During the last years a number of approaches have been proposed in order to overcome the mentionet efficiency problems. These techniques comprise modifications of the particle insertion move, the introduction of extended ensembles and the use of modified importance sampling methods with non-Boltzmann probability distributions which completely avoid the insertion of particles. In the following we will diuscuss some of these methods in more detail. Although these methods showed an improved efficiency for a number of important fluid models (e.g. high density Lennard-Jones fluids [?] or Kihara fluids with highly elongated molecules [?]) a general valid methodical and universal applicable concept to overcome the basic problem of decreasing insertion probability with increasing density and complexity of the fluid does not exist up to now. Similarly, for confined fluids the low particle insertion probability in complex interface systems considerably hinders the application of advanced techniques for a direct simulation of phase equilibria.

4.7.2   Gradual Particle Insertion

To overcome the mentioned efficiency problems recently a mew simulation technique has been proposed [?, ?, ?] which modifies the classical Widom method in such a way that in place of an additional fluid molecule at the present a point particle is inserted into the system whose size and interaction energy varies over (artificial) intermediate states between zero and the full size (interaction) of an original fluid molecule.

Statistical-mechanical that means the introduction of an ensemble of particles consisting of a number of (canonical) subensembles with a different size (state) of the test particle (the so-called scaled particle). The Markov chain to be generated comprises for this system two basic moves:

- translations (rotations) of the partiucles within their subensembles

- transitions between the subensembles by variation of the extend of coupling of the scalede particle

The possible transitions can be represented graphically in the following way:

$$\underset{1}{[N]} \longleftrightarrow \underset{w_1}{[N + \sigma_1]} \longleftrightarrow \underset{w_2}{[N + \sigma_2]} \longleftrightarrow ... \longleftrightarrow \underset{w_k}{[N + \sigma_k \equiv N + 1]} \quad (4.38)$$

[...] denotes the corresponding subensembles. w_i are the statistical weights of these ensembles. $[N] \longrightarrow [N + \sigma_1]$ means the generation of a particle of diameter σ_1 at a random place in the fluid. The inverse transition $[N + \sigma_1] \longleftarrow [N]$ describes the deletion of the scaled particle.

The transition from one subensemble in the chain (4.38) to the next one (either to the right or to the left) is accepted with the probability

$$P(\text{old} \longrightarrow \text{new}) = \min\{1, \frac{p_{new \rightarrow old}}{p_{old \rightarrow new}} \frac{w_{new} \exp(-\beta U_{new})}{w_{old} \exp(-\beta U_{old})}\} \quad (4.39)$$

where $p_{new \rightarrow old}$ and $p_{old \rightarrow new}$ denote (preset) a priori probabilities of the corresponding transitions. Starting with the definition of the excess part of the chemical potential by means of statistical-mechanical relations the excess μ^{ex} over an ideal gas of the same state conditions it can be written [?]

$$\beta \mu^{ex} = \ln[w_k \frac{\text{Prob}[N]}{\text{Prob}[N + 1]}], \quad (4.40)$$

where $\text{Prob}[N]$ means the probability of observing the state $[N]$ in the chain of subensembles (4.38)

The most important physical difference between Widoms test particle method and the gradual particle insertion technique consists in the fact that in the original Widom method the insertion of the testparticle only is performed virtually for the only purpose of the estimation of the average Boltzmann factor (4.17) since in the gradual insertion method the test particle (scaled particle is considered during the course of the simulation as a real existing (partly) coupled $(N + 1)$-st fluid paticle.

The consideration of the test particle as a real particle of the system permits at least in principle the impementation of the gradual particle insertion technique to other simulation methods which require particle insertion or transfer. The extension to grand canonical simulations is straight forward

and has been applied to both fluids with spherical [?] and non-spherical [**?**]
particles. molecular fluids. The combination of the gradual particle inser-
tion with Gibbs ensemble simulations is also under consideration [**?**,**?**] leads
us to the subject of extended ensembles and will be discussed in the next
paragraph.

There are several other methods intending to improve the effiency of
the particle insertion step in molecular simulations. We mention the so-
called scaled-particle MC method of Smith und Labik [?] which is similar to
the gradual particle insertion and has been applied even to the simulation
of the chemical potential of fluids confined to slit-like pores [**?**]. Another
proposed technique is the so-called excluded volume mapping [?] which traces
the behaviour of cavities in the system which are able to accommodate a fluid
pare4ticle.

A recent review [?] comparing all available techniques to improve particle
insertion in simulations of the chemical potential comes to the conclusion that
the above discussed gradual particle insertion method is up to now the most
efficient approach to simulate chemical potentials. Therefore the application
of this method to confined fluids in complex interface systems is expected to
bring some progress in this complicated field of simulations.

4.7.3   Extended Ensembles

Extended ensemble are created by the addition of (unphysical) states to
an existing ensemble. As an example we present here the so-called extended
Gibbs ensemble which combines the standard Gibbs ensemble with the above
discussed gradual particle insertion method. As describet above the gradual
particle insertion estimation of chemical potentials may be considered as a
simulation of a collection of canonical subensemble which differ by the extent
of coupling (the 'size') of a scaled test particle. The chain of configurations
consists of the combination of the Markov chains of the subensenbles where
transitions between the subensembles may take place by the probabilities
given by equation (4.39)

In a close analogy we introduce here a set of modified Gibbs ensembles
where each of them contains a scaled (fluctuating particles and the subensem-
bles differ by the coupling of the interaction of the fluctuating particle to the
other fluid molecules.

A Markov chain is generated which permits transitions between the mod-
ified Gibbs ensembles. The goal is the construction of a way within the

set of subensembles (i.e. between configurations with partial coupled scaled particles) which increases the probability of the particle transfer from one simulation box to the other in comparison with the standard Gibbs ensemble.

In order to construct such a chain of configurations in place of the usual particle transfer step the following transitions are considered

1. Change of the extend of coupling of the fluctuating particle remaining in the same box (corresponds in the gradual particle insertion to a transition in the chain of subensembles (4.38))

2. Insertion of the fluctuating particle in the other simulation box (possibly by a simultanous change of the extend of coupling)

For the described set of Gibbs ensembles with fluctuating particles (the extended Gibbs ensemble) the partitioh function can be written quite analogous to the standard Gibbs ensemble [?, ?]. From the form of this partition function the acceptance probabilities for the above mentioned transitions for the changes of coupling of the scaled paricle and the insertion probabilities of the scaled paricles can be derived. While for transition 1. relation (4.39) holds quite analogous to the gradual particle method we find for transfer step 2. the probability to transfer successfully a scaled particle with an extent of coupling i from box a in box b with an extent of coupling j to be equal to:

$$P_{a,b}^{(i,j)} = \min\{1, \frac{w_b^j p_{b,a}^{j,i}}{w_a^i p_{a,b}^{i,j}} \frac{V_b N_a}{V_a(N_b + 1)} \frac{\exp[-\beta\psi_b^j N_b]}{\exp[-\beta\psi_a^i(N_a - 1)]}. \tag{4.41}$$

In equation (4.41) the w_x^k are the statistical weights of the corresponding subensembles. ψ_a^i represents the change of the potential energie if a fluctuating particle with an extent of coupling i is removed from box a and ψ_b^j the corresponding change of energy if the fluctuating particle is inserted in box b with the extent of coupling j. Details of the method has to be taken from the original papers.

For both simple fluids (mixtures of square well fluids [?]) and fluids with non-spherical particles (Kihara fluids with highly elongated molecules [?]) a significant increase of the efficiency of particle insertion has been proved.

Closely related to the extended Gibbs ensemble is the combination of the Gibbs simulation with Valeaus concept [?] of a MC approach with thermodynamic scaling [?]. This method permits the simultaneous estimation of the

coexistence densities for a number of similar systems (i.e. systems with similar intermolecular potentials) at a number of different temperatures during a single simulation run.

The basic idea of the method is the use of MC sampling with non-Boltzmann distributions (similar to the umbrella sampling technique [**?**, **?**]) which generates a chain of configurations representing simultanously the micro states of a larger number of similar systems. The configuration averages of interesting quantities (particularely the densities of coexisting phases) for a number of neighbouring state points (or a set of similar pair potentials) can then be estimated by an analysis of the generated uniform Markov chains.

Crucial for the efficiency of the method is the suitable choice of the distribution of random numbers used for the construction of the Markov chain. Although there is no general technique for an optimal choice of this sampling distribution numerical procedures have been developed which pernit a step by step improvement of the sampling functions by an iterative approach leading to an increase of the efficiency.

In the original paper [?] the application of the Gibbs method with thermodynamic scaling to the group of the $(n, 12)$-Lennard-Jones fluids is described where within a single simulation run the phase equilibrium densities for a number of neighbouring temperatures for several pair potentials have been estimated simultanously.

A wide application of the described method however depends on the progress in developing general criteria to an optimal choice of the sampling function.

4.7.4   Special Sampling Methods

Since in the last sections improvements of the efficiency of the insertion of particles have been discuss we will review in the following recent sampling techniques which concern state conditions where conventional methods of the simulation of phase equilibria fail. This refers on the one hand to the properties near the critical point and on the other hand the range of low (strongly subcritical) temperatures where liquid phases of high density may appear. Although these methods are not used in a large scale so far we have to mention these approaches because of their methical importance for future developments. A detailed description of these methods however is beyond of scope of this article and we have to refer to the original literature.

For an investigation of the critical and the weakly subcritical two phase

regions in fluid phase equilibria in the last years a number of methods origialy developed in solid state theory have been extended to fluid systems. particularely, finit size scaling techniques [**?**] have been combined with so-called histogram reweighting MC methods FeSw88,FeSw89,Swe93 and in recent time succesfully applied to phase equilibria of simple fluids.

Starting point for these methods is the introduction of a coupled probability density $p_L(\rho, U)$, which represents the probability to find a configuration with a given density ρ and a configurational energy U. In order to determine the function $p_L(\rho, U)$ a series of grand canonical simulations is performed, where always after a distinct number of configurations (ρ, U) histograms are recorded. Following Ferrenberg and Swendsen [**?**, **?**] the wanted probability density can be represented in a uniform way by a weigted average of the distributions $p_L^{(i)}(\rho, U)$ $(i = 1, ..., R)$ of hte R performed simulation runs where the weight of a special contribution essentially depends on the frequency of occurence K_m in run m. From the general representation of $p_L(\rho, U)$ the corresponding distributions for the state conditions of interest can be estimated from the knowledge of the frequencies K_m by means of specific histogram reweighting methods. An approximate determination of the position of the critical point is possible by an analysis of the density histograms. While above the critical temperature a density distribution around a single equilibrium value is found we observe in the subcritical region a bimodale distribution where the maxima represent the coexistence densities of the liquid and the gas phase, respectively [**?**, **?**].

In order to determine the critical parameters accurately finite size scaling techniques are used [**?**, **?**]. To apply these methods which have been originally developed to Ising-like lattice models the concept of field mixing has been introduced recently [**?**, **?**]. The essence of this method consists in the study (simulation) of a series of systems of different sizes (number of particles) where from the properties of the series of finite systems with increasing numbers of paricles can be concluded to the properties of the infinite system by the use of theoretically foundet general scaling relations.

For example the following relation holds between the critical temperature $T_c^*(L)$ of a system with a finite bos length L and that of the infinite system

$$T_c^*(\infty) - T_c^*(L) \propto L^{-(\theta+1)/\nu} \tag{4.42}$$

where the numerical values of the parameters θ and ν have to be taken from the original papers. If $T_c^*(L)$ is plotted versus $L^{-(\theta+1)/\nu}$ equation (4.42) predicts a linear relation. For simple systems (two- and three- dimensional

Lennard-Jones fluids this relation could be proved explicitely [**?**, **?**, **?**]) By extrapolation of thiss relation to the infinite system the critical temperatute can be calculated. This procedure represents up to now the most precise metod to estimate the critical data and can be applied quite analogously to the critical density and the critical pressure.

The described methods for the estimation of the coexistence densities are restricted to state conditions near the critical point only. For lower sub-critical temperatures the barrier of the free energy between the coexisting fluid phases becomes so large that long existing metastable states may appear what results in bad statistical properties of the Markov chain which drastically slows down the convergency of the configurational averages.

An alternative offers the above discussed Gibbs simulation which reaches the phase equilibrium by means of an unphysical particle transfer between the coexisting phases (bypassing the real interface) but – as described above – the applicability of Gibbs techniques are restricted by the drastically decreasing insertion probabilities with increasing density of the coexisting phases.

Another way out provide the so-called multi canobical simulations introduced recently [**?**]. The basic idea of this simulation method consists in a procedure to avoid the problems resulting from the high barrier in the free energy to replace the usual Boltzmann distribution by an a priori weighted distribution which is flat enough to permit transitions between the coexisting phases. Explicitly an effective Hamilton is introduced.

$$\mathcal{H}'_N(X, \rho) = \mathcal{H}_N(X, \rho) + g(\rho) \tag{4.43}$$

which defines a pseudo-Boltzmann distribution taking in case of the density the following form

$$P'(\rho) = \frac{1}{Q'} \prod_{i=1}^{N=L^d} \int \exp\{-[\mathcal{H}'_N(X, \rho) + \mu L^d \rho + g(\rho)]\}dX_i, \tag{4.44}$$

where Q' is the multi canonical partition function, and L the length of the simulation box and d the dimension of the system. Choosing $g(\rho) \approx \ln P(\rho)$ where $P(\rho)$ represents the wanted Boltzmann distribution of the density one recognices that $P'(\rho) \approx$ const. holds for all ρ. Thus an efficient accumulation of the weighted $P'(\rho)$ diagrams is possible. The wanted Boltzmann weigted density distribution $P(\rho)$ is than given by

$$P(\rho) = P'(\rho) \exp[-g(\rho)]. \tag{4.45}$$

In practice the multi canonical simulation is performed as an iterative procedure. One starts with a state point near T_c where the coexistence densities can be determined by a conventional grand canonical simulation (using recent histogram-reweighting methods if necessary). From this starting poin one gets succesively to lower and lower subcritical temperatures where an increasing improvement of the efficiency against the conventional μVT simulation is reached [?].

Practical results are available for Lennard-Jones fluids where in comparison with Gibbs simulations a significant reduction of the scatter of the results could be reached [?]. To what extent these improvements can be extended to more complex systems –especially with long ranging interactions – has to be proved by future studies.

With respect to confined fluids advanced sampling methods are of growing importance. Particularely, qualitative properties related to the change of dimesionality in thin adsorbed fluid films (transition from 3d to 2d systems) are studied by finite size scaling and similar techniques. The critical properties of thin fluid films are also under consideration using the equivalence of lattice gas models with the Ising ferromagnet [?].

4.8 Convergency and Errors

The esitimation of errors is in molecular simulations – quite similar as in real experiments – from a special importance. The accuracy of MC simulations is determined mainly from two factors, firstly the convergency properties of the Markov chains and secondly the errors caused by the finitness (smallness) of the simulated systems.

In general the convergency of the generated chain of microstates to the configurational averages is ensured by the use of techniques derived by probability theory arguments as the Metropolisd Algorithm.

However, less known is about the details of the convergency behaviour of the markov chains. The application of the standard methods of the numerical mathematics are hindered by the fact that neighbouring micro states in the chain of configurations are highly correlatet since they differ usually only by one degree of freedom (e.g. the position of a random chosen particle). On these conditions the usual standard deviations to the configurational averages represent as a measure of the statistical errors only a rough approximation. The real fluctuation of the averages are usually underestimated.

In general the characterization of the statistical properties of highly correlated data is an unsolved problem so far. In practice two methods have to be proved for the error estimation of simulation data: the calculation of correlation coefficients and the block average method. The first one belongs to the standard techniques of error estimation which we will not discuss here in detail. The second one the method of blck averages has a more specific importance for simulation studies and therefore will be presented here shortly. This renormalization technique was proposed by Wilson [?] and worked out in detail by Flyvbjerg and Petersen [?].

Starting point is a set of correlated data $x_1, x_2, ..., x_n$ with an average m whose statistical error (variance $\sigma^2(m)$ has to be estimated. The algorthm divides the original data in blocks of two values each

$$x'_i = \frac{1}{2}(x_{2i-1} + x_{2i}) \qquad \text{with} \qquad n' = n/2. \tag{4.46}$$

It can be shown [?] that average and variance are invariant against this transformation, i.e. it holds

$$m' = m \qquad \text{und} \qquad \sigma^2(m') = \sigma^2(m). \tag{4.47}$$

The transformation (4.46) is now repeated many times whereby the data set $\{x_k\}$ is always divided in half and for each iteration step the variance remains conserved. Now the series

$$\frac{c_0}{n-1}, \quad \frac{c'_0}{n'-1}, \quad \frac{c''_0}{n''-1}, \quad ... \tag{4.48}$$

is considered with

$$c_0 = \frac{1}{n}\sum_{k=1}^{n}(x_k - m)^2. \tag{4.49}$$

In general it holds for all iteration steps

$$\sigma^2(m) \geq \left\langle \frac{c_0}{n-1} \right\rangle. \tag{4.50}$$

As an approximation for $\left\langle \frac{c_0}{n-1} \right\rangle$ the expression $\frac{c_0}{n-1}$ is used.

Drawing $\frac{c_0^k}{n^k-1}$ versus the number of iterations k this value increases monotonously until the distance between the blocked data becomes smaller then the correlation length of the process whereby $\frac{c_0^k}{n^k-1}$ gets independent from k, i.e. the

function reaches a plateau which does not change if the iteration is continued, although it shows large fluctuations for small n values.

This behaviour can be understood formally as a fix point of the linear transformation (4.46) (cf. [?]). The value of the plateau of $\frac{c_0^k}{n^k-1}$ is the wanted approximation for the variance of the original data. If the fix point is not reached until the end of the iterations (i.e. $\frac{c_0^k}{n^k-1}$ does not become constant) the obtained value is an lower limit for the variance $\sigma^2(m)$.

Compared to other methods – particularely the calculation of correlation coefficients – the block average technique is conceptual simple and it provides simultaneous information about the reliability of the error estimation

Besides the above discussed statistical fluctuations of the MC averages we have to take into account as a source of systematic errors the finite size (smalness) of a simulated system in comparison with a real macroscopic system. As discussed in section **??** simulation studies of classical many body systems are performed typically with numbers of particles between a few hundred to a few thousend – in special cases up to a few tenthousend (hundredthousend) – depending on the problems under consideration and the computer equipment available.

If we consider such small systems as closed – i.e. enclosed in a container – we fined compared to macroscopic systems (infinite extended) fluid two important differences.

1. In systems consisting of only a few particles the wall-particle interactions influence the properties of the fluid. it holds the statistical mechanics (thermodynamics) of small systems where the thermodynamic limit $(N \to \infty)$ does not exist. The transition to macroscopic systems is usually performed by the application of periodic boundary conditions, which results in the existence of a thermodynamic limit ensuring the validity of the usual relations of the statistical mechanics. Considering confined systems we have to take into account the wall fluid interactions as an intrinsic property of inhomogeneous fluids. In these cases the application of periodic boundar y conditions is typically restricted to special directions in space depending on the symmetry of the confinement (cf. sectionXXX

2. finite size effects in a narrower sense are caused by the artificial periodicity of the fluid structure due to the application of periodic boundary

conditions.

In general the finite simulated system represents the properties of the macroscopic system only if the range of the spatial fluctuations are small in comparison with the basic length of the simulation box. This condition is usually fulfilled for systems consisting of a few hundred (thousend) particles for state points sufficiently far from the critical point. In the critical region large spatial fluctuations of the structure may take place which require special simulation techniques (see below). The main problem consists in the fact that in general an a-priori estimation of the correlation length is not possible since these depends on the detais (particularly, the range) of the intermolecular potentials. For that reason the estimation of the size of finite size effects of the MC averages requires simulations of the same system with a different number of particles.

Approaching the critical point the fluctuations increase strongly and they diverge for $T \to T_c$ where in the neighbourhood of T_c hold general scaling laws which can be derived by means of the theory of finite size scaling and can be used for the calculation of the critical properties (cf. the paragraph about sepcial sampling methods).

In small systems on subcritical state conditions where two (several) fluid phases coexist size-dependent nucleations of domains of the differnt phases are observed which hinder the accumulation of representative statistical data. To get reliable results a minimum size of the system (usually a few hundred (thousand) particles per phase) are required.

Another range of states where problems in simulations may arise is the high density transition region from the fluid to the solid state. Here metastable states with a long life time may exist which may be difficult to identify. As an example we mention simulations of exp-6 fluids in the high density region [**?**, **?**] where it the specific problems of simulations on extreme state conditions are discussed in detail.

In general the carful estimation of potential sources of errors is one of the most important criteria to evaluate the reliability of simulation data [?]. Especially this is necessary if unknown simulation programs are applied (e.g. commercial programs, which often are used as 'black box') The application of such software requires in any case an intense study of the implemented simulation algorithms in order to be able to judge the possibilities and limitations of the methods [**?**].

5

Equilibrium Properties of Confined Fluids

In this chapter we will discuss the possibilities and limitations of molecular simulations in describing of basic structural and thermodynamic properties of fluides adsorbed at interfaces and/or confined to micropores including the study of equilibria of coexisting fluid phases distributed over bulk and confined regions. While in the section **??** the simulation techniques (paricularely, stochastic or MC methods) suitable for the study of systems in thermodynamic equilibrium have been presented in some detail we will here demonstrate the capacity of simulation studies of confined fluids by means of selected examples and we will point on the relation between molecular simulation and statistical-mechanical theory. We restrict our treatment mostly on the properties of fluids confined to single micropores. Only some remarks concerning porous materials will be given. A complete review of the simulation of microporous media is beyond the scope of this paper although in section **??** the simulation of transport phenomena in zeolites will be considered in some detail.

5.1 Basic Molecular Models of Interfaces and Micropores

In order to understand the on a molecular level structure and thermodynamics of interacting many particle systems – especially classical fluids – on restricting geometrical conditions idealized models of interfaces and micro-
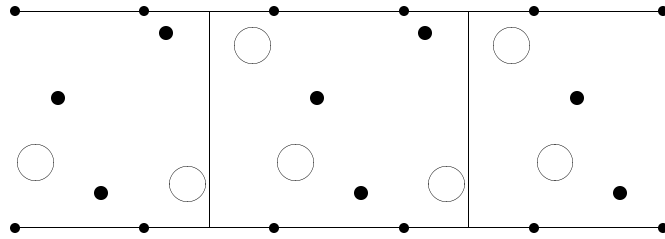
Figure 5.1: Modell of a slit-like pore

pores are of special importance. Such models are on the one hand simple enough to permit a statistical-mechanical treatment and on the other hand they are able to model the typical properties of a confinement which lead to geometrically determined features of the behaviour of the confined fluid.

The range of the influence of interfaces on the structure of bulk fluids (in particular inhomogenities in the number densities) depends essentially on the specific interactions of the class of fluids under consideration and for dense fluids typically amounts to several times the average distance between the centers of the particles

In order to simulate such interface or surface effects on a molecular level one usually considers fluids enclosed in basic cells of simple geometry with dimensions in the order of the expected range of these effects [?].

The most common models to study the behaviour of confined fluids are slit-like or cylindrical micropores where the wide of the slit or the diameter of the pore, respectively reach from a few to the order of hundred nanometers.

In this paper most of the simulation studies we discuss deal with fluids enclosed in slit-like pores (more general are confined in planar interface layers). Therefore we present these models in the following in some edetail.

Figure 5.1 shows a scheme of a fluid confined to a slit-like pore. A cartesian coordinate system is introduced where a slit pore is modeled by two

parallel areas (planar walls) in the (x, y) plane which have a distance L in the z direction.In this – in the (x, y) plane infinitely extended assumed slit – a fluid is enclosed whose intermolecular forces are described by a potential U_{ff}. The interactions between the walls and the confined fluid particles are given by a potential function U_{fw}, possible forces between the atoms at the surface (interface) are represented by the function U_{ww}. The total potential energy of the fluid-pore system is given by the sum

$$U_p = U_{ff} + U_{fw} + U_{ww}. \tag{5.1}$$

If we restrict our consideration of the intermolecular forces to site-site models with N interaction sites (atoms) per fluid molecule – as it is done in most of simulation studies of confined fluids – the potential energy U_{ff} can be written in general in agreement with (??) as

$$U_{ff} = \sum_{i<j}^{N} \sum_{\alpha i, \beta j} u(r_{\alpha i, \beta j}) \tag{5.2}$$

where $u(r_{\alpha i, \beta j})$ is the site-site potential between site α of particle i and site β of particle j which only depends from the (scalare) distance of the involvrd sites.

The interaction of a fluid particle with the wall u_{fw} in the simplest case depends only from the z-coordinates of the centers of the fluid particles inside the pore, i.e. it holds $u_{fw} \to u_w(z)$. In the case of hard walls we have therefore for (hard-core) fluids consisting of molecules with a diameter σ σ

$$u_w(z) = \begin{cases} \infty & \text{f'ur} \quad \mid z \mid > (L - \sigma)/2 \\ 0 & \text{f'ur} \quad \mid z \mid < (L - \sigma)/2, \end{cases} \tag{5.3}$$

where the walls of the pore are assumed to be at $z = \pm L/2$.

Molecularely rough interfaces can be modeled by discrete molecules additionally distributed over the smooth interfaces which interact via a pair potential u_{sf} with the fluid molecules. The total fluid-wall interaction is than given by

$$U_{fw} = \sum_{i=1}^{N} u_w(z_i) + \sum_{i=1}^{N} \sum_{j=1}^{K} u_{sf}(r_{i,j}). \tag{5.4}$$

In (5.4) i means on of the N fluid molekules and j is one of the K interface molecules.

If the interface molecules are assumed to be movable along the walls where they interact pairwise via a pair potential u_{ww} the influence of the structure of the interface by the nature and the amount of the enclosed fluid can be investigated.

In order to illustrate the modeling of the molecular roughness of interfaces (micropres) as they are observed at so-called 'fluid' interfaces [?] for example at the amphiphilic interfaces of phospholipid bilayers we consider two basic models one of them with fixed and the other with freely movable surface molecules:

Model A.

At the walls of a slit-like pores the centers of a given number of spherical interaction site molecules ('surface' molecules – in the simplest case hard spheres) are regularly (lattice-like) or randomly (stochastically)distributed and kept fixed on their positions. The properties of a fluid confined to this pore is studied in terms of the size (ineraction energy) and the distribution of the surface molecules.

Model B.
In this model there are again a given number of interaction site molecules (spheres) located at the walls (interfaces) of a slit-like pore. But in contrast to model A these surface particles are assumed to be freely movable along the walls which results in a distributon of surface molecules permanently changing depending on both the interaction between the interface molecules themselves and the interaction with the molecules of the confined fluid, The fixing of the wall molecules is reached by an attractive force in the wall region (wide $\Delta L + \sigma$) which is modeled in the simplest case by a potential well of suitable depth and wide. Variants of the models consider diverse types of pair potentials u_{sf} and u_{ww} which may be hard-core-like or of Lennard-Jones type. If associating forces are involved the modeling of 'hydrophobe' and 'hydrophile' interfaces is possible in a simple way (compare section **??**).

Figures 5.2 and 5.3 represent the discussed basic models of molecularely rough interfaces. The most important differnce between both models consists in the fact that model A describes a fixed rigid interface structure while in model B the mobility of the wall molecules permits a representation of the structural self-organization of the interface in the interplay with the confined fluid (cf. section **??** which is crucial for the modeling of flexible ('fluid') inter-
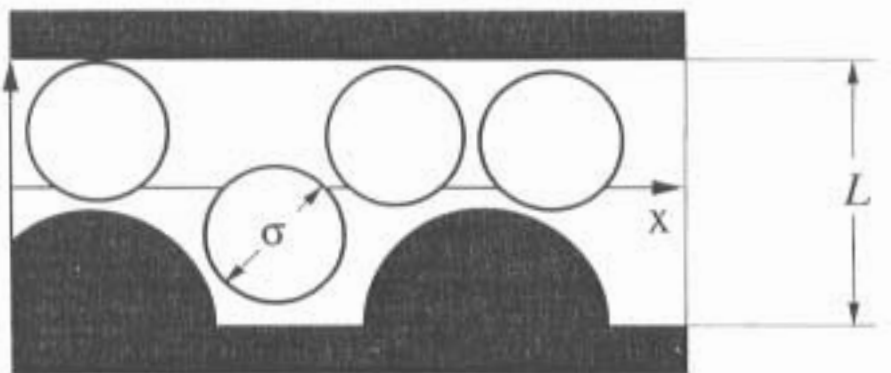
Figure 5.2: Basic models of molecularly rough interfaces (Model A)
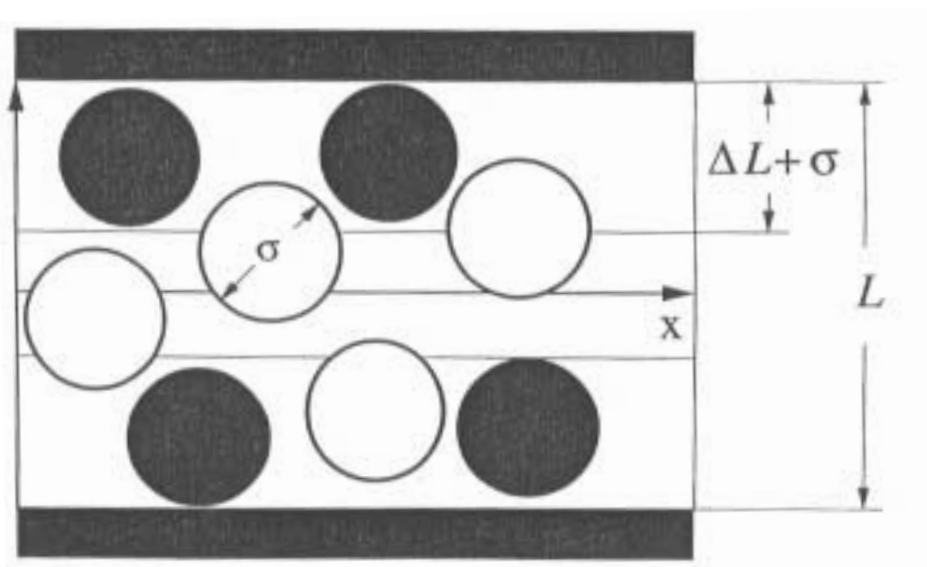

Figure 5.3: Basic models of molecularly rough interfaces (Model B)

faces appearing in biological relevant interface structures e.g. biomembranes.

In general MC simulationss of fluids confined to the above discussed molecular interface structures allow the study of equilibrium properties of the fluids (density distribution, order of the molecules, pressure at the wall etc.) in terms of the structure (roughness) of the interface including feed-back effects from the fluid properties to the interface structure. Some illustrative examples for simulation studies of of confined fluids in molecularly rough slit-like pores will be discussed in the following sections.

Penetrable interfaces are obtained if the (hard) wall is replaced by a finite potential barrier i.e. if in (5.4) for all z is set $U_w(z) \leq C$ with $C < \infty$ and for the discrete the surface forming particles a suitable pairpotential is assumed [?].

As simulation cell for a fluid in a slit-like pore of wide L as prisma is used with a quadratic basic area and an edge length l_{xy} in the (x, y)-plane and a height of L in the z-direction. This simulation box which is filled with the fluid under consideration is periodically repeated in two edimensions (in x- and y-direction) whereby an infinitely extended system is emulated.

Quite analogously fluids confined in cylindrical pores can be studied. Assuming the pore is extended in z-direction and has a radius R a cylinder of radius R and of heigth l_z is used as the simulation cell which is periodically continued in the z-direction. According to the symmetry of this cell usually cylinder coordinates are used. coordinates are used

Due to the periodic continuation for fluids confined in micropores of simple geometry (e.g. slit-like, cylindrical or cubic pores) the transition to infinite extended systems possible. Therefore a thermodynamic limit ($N \to \infty$) can be defined which ensures the validity of the laws of statistical mechanis.

In contrast to the above systems fluids in closed cavities (e.g. in spherical micropores) have to be considered as real finite systems where the relations of the thermodynamics of small systems have to be applied [?].

Concerning the representation of microporous media we have to distinguish between systems with a regular lattice-like arrangements of cavities and channels as zeolites and materials with a random distribution of micropores. While in the first case the structure can be represented by regular geometrical models in the second case the modelling of these random media is a serious problem.

Since extensions of lattice-like models which describe the random pore arrangements by disturbed regular matrix models are not able to reproduce adequatelely the disordered nature of these materials a computer based

stochastic geometrical modelling of fluids enclosed in microporous media has been developed (Madden and Glandt [?]). The approach considers a binary mixture where one component represent the constituents (hard particles) forming the microporous matrix and the other component consists of the fluid molecules. By simulation of this mixture random arrangements of the constituent fluid systems are generated. Stopping the simulation and keeping the constituents fixed the properties of the fluid confined in these random arrangements of constituents representing a disorderd porous medium can be studied. Some results of these studies will be reported below.

5.2 Statistical Thermodynamics of Inhomogeneous Fluids

Fluids confined to micropores or adsorbed on interfaces have to be considered as fluids on inhomogeneous conditions. The microscopic (statistical-mechanical) description of such systems is characterized by a number density (one-particle density $\rho^{(1)}$ which – in contrast to (homogeneous) bulk fluids – is not isotropic [?, ?],but it depends on the position within the system, i.e. it holds $\rho^{(1)} = \rho^{(1)}(x, y, z)$. This density represents the local particle density in the volume element $\Delta V(\mathbf{r})$ with the coordinate vector $\mathbf{r}(x, y, z)$. To simpify matter the one-particle density $\rho^{(1)}(x, y, z)$ is denoted in the following by $\rho(x, y, z)$ only.

In the special case of a fluid consisting of N spherical particles, which is enclosed in a micropore an average particle density ρ can be defined as the average $\rho(x, y, z)$ over the volume of the pore V_{pore}

$$\rho \equiv < \rho(x, y, z) >_{V_{pore}} = N/V_{pore} \tag{5.5}$$

In the case of fluids confined to geomerically simple confinements this general dependence reduces to simpler relations according to the symmetry of the arrangement. In the case of a planar interface – which may be located in the the (x, y)-plane – the density depends on the z-direction orthogonal to the interface. in this case $\rho^{(1)}(z)$ is called density profile. Similarly in planar slits ρ only depends on the distance perpendicular to one wall. In cylindrical pores with smooth walls the density depends on the distance from the axis of the cylinder only. That means in planar slits with smooth walls – which will be discussed in more detail below – the structure of the confined fluid is

described completely by the density profile $\rho(z)$. In this case the estimation of the pressure acting on the wall P_{w} is given by integrating over the density profile. Particularely simple is the situation for hard sphere fluids at a hard wall where the so-called contact theorem [?,?] gives a direct relation between P_{w} and the value of the density profile $\rho(z)$ at the wall. Is the wall located at $z = Z_w$ we obtain explicitly

$$P_{\mathrm{w}}/kT = \rho(Z_{\mathrm{w}} - \sigma/2) = \rho_{\mathrm{c}}. \tag{5.6}$$

The contact theorem (5.6) cann be generalized to fluids consisting of non-spherical hard bodies [?,?].

In general in an inhomogeneous fluid a scalar (mechanical) pressure which is uniform in the whole system does not exist [?] but such a pressure has to be replaced formally by a tensor which depends on the direction in space in a complicated way and can be calculated explicitly only in special cases [?,?].

Besides the mechanical pressure discussed above in recent times the definition of a suitable pressures is proposed for a themodynamical characterization of equilibria between confined (e.g. microporous) fluid and bulk fluid phases [?,?]. Considering the equilibrium between two inhomogeneous phases a so-called thermodynamic pressure can be defined formally as a suitable average of the mechanical pressure in a spatial direction depending on the symmetry of the model where the equality of this pressure in both phases – besides the equality of the chemical potentials – determines the position of the equilibrium.

In the case of a fluid confined to a planar slit-like pore the suitable thermodynamic pressure is given by the so-called spreading pressure Π which is defined as the average of the mechanical pressure parallel to the walls of the pore. According to Forsman and Woodward [?, ?] Π can be simulated by an iterative estimation of the condition of phase equilibrium in a so-called isostress ensemble (cf. sectionXXX).

In general the excess of the thermodynamic pressure P^{ex} compared to an ideal gas is given as the partial derivative of the excess of the free energy A^{ex} with respect to the volume V of the fluid.

$$\left(\frac{\partial \beta A^{\mathrm{ex}}}{\partial V}\right)_{\beta, N} = -\beta P^{\mathrm{ex}}. \tag{5.7}$$

Definition (5.7) is the starting point for the diurect simulation of the thermodynamic pressure by means of virtual volume changes (cf. sectionXXX).

Some results will be given below for hard sphere and square-well fluids in slit-like pores.

In general the statistical mechanical treatment of fluids on inhomogeneous conditions requires the investigation of an interacting many body system in an additional extern potential. For this integro differential equations for the estimation of the one-particle density have been derived. For the solution of these equations usually additional approximations are necessare which depend on both the fluid class under consideration and the behaviour of the external – the inhomogenity causing – potential. Because of the complexity of this problem we restrict our study to the behaviour of a fluid near a wall. More general information can be found in the original literature e.g. in [?, ?]. Formally we can reduce our problem to the study of a homogeneous two component mixture where one component represents the fluid and the other the wall. The 'wall' component is considered as infinite diluted with a size of the particles going to infinity [?, ?]. For this mixture where the components are denoted by 1 and 2 and the corresponding mole fractions by x_1 and x_2 respectively (for $x_2 \to 0$) the coupled Ornstein-Zernike (OZ) relations can be written down

$$h_{11}(1,2) = c_{11}(1,2) + \rho \int h_{11}(1,3)c_{11}(2,3)\mathrm{d}3 \tag{5.8}$$

$$h_{12}(1,2) = c_{12}(1,2) + \rho \int h_{12}(1,3)c_{12}(2,3)\mathrm{d}3 \tag{5.9}$$

$$h_{21}(1,2) = c_{21}(1,2) + \rho \int h_{21}(1,3)c_{21}(2,3)\mathrm{d}3 \tag{5.10}$$

$$h_{22}(1,2) = c_{22}(1,2) + \rho \int h_{22}(1,3)c_{22}(2,3)d3. \tag{5.11}$$

Equation (5.8) represents the OZ-relation for the pure fluid (component 1), (5.11) has no physical meaning because of the infinite dilution of component 2 and the coupling between wall and fluid is equivalently described by (5.9) or (5.10). Suitable for the numerical treatment is (5.10). Assuming that the particles of component 2 ('wall particles') can get infinite large than the wall-particle interaction depends only on the distance z from the interface. This leads to the identities

$$\rho_B = \rho = \lim_{z \to \infty} \rho^{(1)}(z), \qquad \rho h(1,2) = \rho^{(1)}(z) - \rho_B \qquad \text{and} \qquad c(z) = c_{12}(r) \tag{5.12}$$

Than equation (5.10) gets the following form:

$$\rho^{(1)}(z) = c(z) + \rho_B \int c_B(|\mathbf{r} - \mathbf{r}'|)[\rho^{(1)}(z') - \rho_B]\mathrm{d}\mathbf{r}', \qquad (5.13)$$

where $c_B(r)$ means the direct correlation function of the free bulk fluid. In order to obtain a numerical solution for the density profile $\rho^{(1)}(z)$ it is necessary – quite analogous to a homogeneous fluid – to introduce besides the OZ-equation (5.13) a suitable closure. As in the case of bulk fluids both the Percus Yevick and the hyper netted chain approximation are used [?, ?, ?]. Fluids confined to micropores of simple symmetry (mostly cylindrical or slit-like pores) were studied by means of integral equations too [?, ?]. Comparisons of the results of diverse integral equation methods with computer simulations are given e.g. in [?].

During the last years the range of applications of Integral equations has been extended to inhomogeneous fluids confined to microporous media. The physical situation is thereby described – in generalization of the above wall-fluid problem as a binary mixture between a rigid matrix of interaction sites which characterize the porous medium and a fluid distributed in this pore system [?]. Besides computer simulations of such structures (cf. the last paragraph) recently exact statistical-mechanical relations for the thermodynamic properties of the confined fluids could be derived and [?, ?] have been applied to the estimation of phase equilibria of simple fluids in matrices consisting of hard spheres [?].

Finally we mention a technique for the estimation of the one-particle density –which found increasing attention during the last years – the so-called density functional theory. This approach starts – quite analogous to the well-known thermodynamic perturbation theories [?] – with an explicite separation of long and short ranging parts of the intermolecular potential.

The basic idea of the density functional formalism consists in the attempt to find an ansatz (functional of the one-particle density) which has as an lower limit the exact value of the grand potential Ω in a corresponding grand canonical ensemble which can be estimated by means of a variation method. If we consider an ensemble of systems with a phase density $f(\mathbf{r}^N, \mathbf{p}^N, N)$, of which the average number density at the location $\mathbf{r}$ may be denoted by $n(\mathbf{r})$ than f reduces in equilibrium to the phase density f_0 of the grand canonical ensemble and it holds for the average particle density $n(\mathbf{r}) = \rho^{(1)}(\mathbf{r})$.

For the mentioned system in an external field $\Phi(r)$ – which represents the confinement – one constructs a functional $\Omega_\Phi[n]$ of the functions $n(\mathbf{r})$

(density functional) which in equilibrium turns into the grand potential Ω.

$$\Omega_\Phi[n] = \Omega_\Phi[\rho^{(1)}] = -k_B T \ln \Xi = \Omega(\mu, V, T). \tag{5.14}$$

where Ξ represents the grand canonical partition function [?]. for a suitable ansatz $\Omega_\Phi[n]$ which comprises a linear combination in the Hamilton functions H_N and the probability densities f_N (for particle numbers $N = 1 \cdots \infty$) Ω represents the minimum of the functional Ω_Φ where the functional derivative of $\Omega_\Pi[n]$ with respect to $n(\mathbf{r})$ disapears on the condition $n = \rho^{(1)}$. This relation together with equation (5.14) forms the basis for the estimation of $\rho^{(1)}(\mathbf{r})$ by variation of the density functional.

Technical details have to be taken from the original literature (cf. e.g. [?, ?]). A review of the original density functional methods is found in the monograph [?]. More recent methodical developments are given in [?, ?]. Applications of density functional methods to simple fluids in micropores of simple geometry are presented in [?] in comparison with the results of computer simulations. Recent variants of integral equations and density functional techniques for hard sphere fluids in slit-like pores are discussed and compared in [?]. Extensions of the formalism to polyatomic and chain molecules were proposed recently too [?].

Evaluating the results of the density functional theories we have to take into account that on the one hand side these formalisms permit a good description of (pseudo)experimental results for many applications but on the other hand they usually include some heuristic elements which reduce the univerality of the methods and restrict the ability of predictions in comparison with

As a final conclusion of our discussion of the statistical mechanics of inhomogeneous fluids we have to state that the analytical microscopic theory of – despite a significant progress during the last two decades – is restricted usually to simple model systems. Particularely, practical interesting systems as real microporous media and biological active interfaces (biomembranes) are in many cases beyond the scope of rigorous theories. The theoretical description of such complex systems is usually restricted to simulation techniques which we have been presented in section **??**. The importance of molecular simulations is thereby two-fold: (i) they provide (correct) pseudo-experimental results for model systems which represent fundamental data for the development of molecular theories and (ii) simulations allow the study of complex systems of practical interest even on conditions not available in real experiments.

5.3   Selected Results for Slit-like Pores

As discussed in the last sections slit-like pores (or more general planar interface structures) represent one of the basic models of interest to study confined fluids not only from an academic point of view but also in experimental relevant real interface situations. According to the general goal of this article to point to the typical procedures and the capacity of molecular simulations we present in the following selected examples comprising both structural and thermodynamic quantities and phase equilibria of fluids confined to slit-like pores. In these examples simple fluids are represented by molecules interacting pairwise additiv via a square-well potential

$$u_{SW}(r_{12}) = \infty, \ r_{12} < \sigma \tag{5.15}$$

$$= \ -\epsilon, \ \sigma < r_{12} < \lambda\sigma \tag{5.16}$$

$$= \ 0, \ r_{12} > \lambda\sigma \tag{5.17}$$

where r_{12} is the distance between particles 1 and 2, σ is the hard-core diameter, ϵ is an energy parameter, and $\lambda =$ is the square-well width parameter ($\lambda = 1.5$ in all cases). The hard-sphere fluid is a special case of the square-well fluid with $\lambda = 0$, To represent associating fluids the so-called primitive models due to Nezbeda, Smith and Kolafa are used [?, ?, ?] which describe water-like fluids by hard-core molecules with additional off-center interaction sites modelling explicitly hydrogen bonds by short ranging attractive forces.

In the last paragraph we give a short discussion of an associating fluid enclosed in a more general planar interface structure showing self-organization of the surface-fluid arrangement.

Although – as mentioned above – a complete review of the equilibrium properties of confined fluids goes beyond the scope of this article we will besides the presented examples refer to some other important developments in the field too. What concerns phase equilibria of confined fluids a number of comprehensive review papers are available. [?, ?, ?]

5.3.1   Structure:Density Profiles and Spatial Distribution Functions

Usually the structural properties of confined fluids are studied in single phase simulations in the canonical, isobaric-isothermal or grand canonical ensemble,

We will show in the following the typical properties of the one-particle density in slit-like pores for several classes of liquids reaching from simple fluids as hard spheres and square-well fluids to associating water-like systems modelled by the above mentioned promitive models.The aim is rather to show the general features of the density profiles than to present detailed results for special systems.

Shown are simulation results of the density profiles of the mentioned fluids in hard planar slits of different width which reach from 2.5σ to 8.0σ where σ represents the diameter of the hard core of the molecules. The data are taken from the paper [**?**]. Typical results for narrow slits ($L = 2.5\sigma$) are shown in figure 5.4. Density profiles for more wide slits where L is much larger as the correlation length of the intermolecular potential of the confined fluids i.e. this case represents the behaviour of the one-particle densities near a single (hard) wall.

Hard sphere and square-well fluids show oscillations of the one-particle densities with a period in the order of the diameter of the particles which is typically for sinple fluids not only for the here shown hard-core fluids [**?**, **?**] but also for Lennard-Jones systems [**?**, **?**, **?**] The very similar form of the density profiles of confined hard- and soft-core fluids is quite analogous to the well-known properties of the pair distribution function in bulk fluids [**?**] where the structure of simple fluids is essentially given by a suitable defined hard-core of the molecules representing the mutual exclusion volume of a pair of particles.

For the Primitive Model of associating (waterlike) fluids we obtain a completely other picture, particularely in the case of larger slit widths. We find only a (relatively weak) maximum at the walls which is caused by the hard wall-particle interaction. In the inner part of the slit there do not exist density oscilations comparable with the simple fluids ones but there are only small stochastical fluctuations of the particle density. This my be explained by the fact that in the center of the slit due to the hydrogen bonds clusters and extended networks are formed similar to the bulk water structure. This explanation is supported by the fact that the thermodynamic state behaviour of the fluid confined to narrow slits of a width of only a few particle diameters can be described by equations of state of bulk fluids surprisingly good [**?**, **?**] in contrast to simple hard-core fluids which show marked oscillations over the entire slit up to a slit width of about six particle diameters what results in significant deviations of the state behaviour in comparison to the bulk.

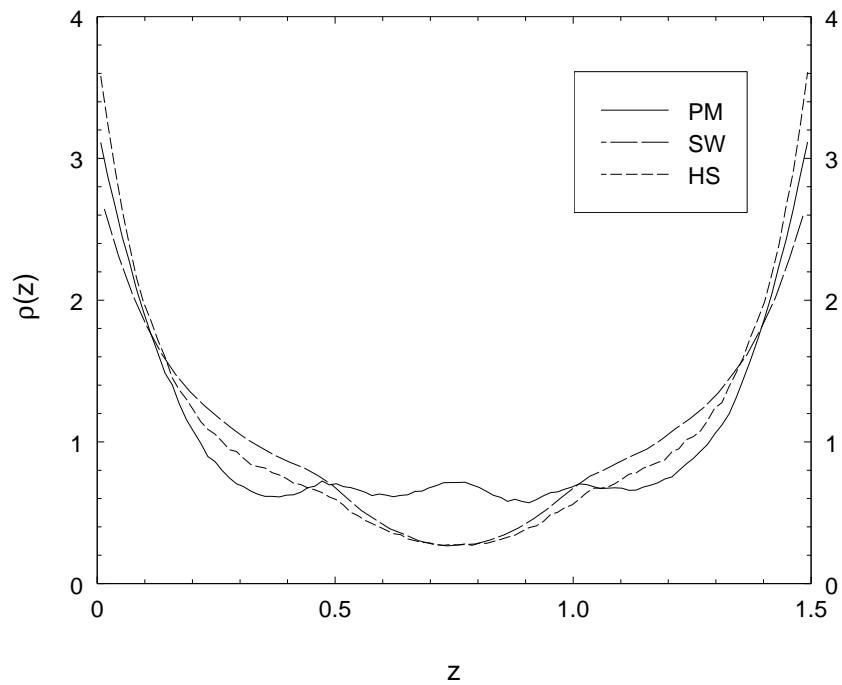The behavior of the Primitive Model of water confined to wide slit-like

Figure 5.4: Density profiles of hard spheres (HS), square-well fluids (SW) and associating Fluids (PM) in narrow slit-like pores ($L = 2.5\sigma$)
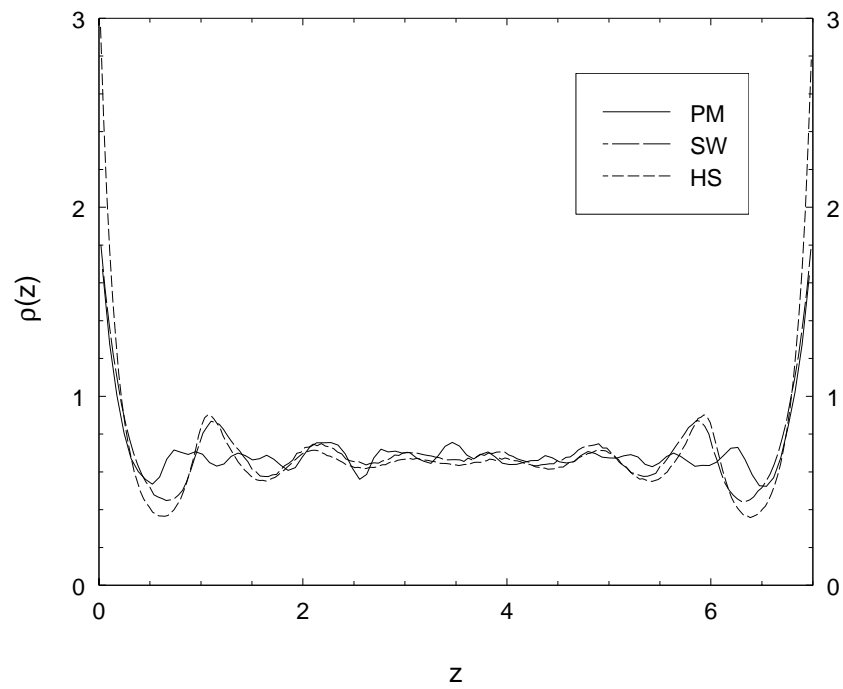
Figure 5.5: Density profiles of hard spheres (HS), square-well fluids (SW) and associating Fluids (PM) in wide slit-like pores ($L = 8\sigma$)i.e. at a single free interface

pores shown in figure 5.5 is found to be aqualitatively in agreement with the behaviour of a similar model at a single hard wall [?].

The formation of associating structures can be studied by consideration of the density profiles of fluids with increasing strength of the hydrogen bonds. It is found (figure 5.6)that – quite analogously to the behaviour in the bulk [?] – in micropores exists a 'critical' strength of association above that the form of the density profile suddenly changes from that of a simple fluid with the typical density oscillations to an profil showing the characteristical associating features discussed above.

In order to gain deeper insight into the molecular structure of associating fluids – besides the above discussed one-particle density – the formation of molecular clusters i.e. the occurence of association itself has been studied in detail for the mentioned water models [?, ?, ?]. Of special interest was the distribution of the particles over clusters of different size in terms of the strength of the associating forces (hydrogen bonds) where especially the formation of the so-called percolating clusters [?,?] (i.e. associating networks which penetrate the entire simulation box) has been observed. One Aspect of general interest concerns the influence of the restricting geometry (interface) on the structure of the associating network of the confined fluid. This effect will be illustrated comparing the distributions of cluster sizes in bulk and confined fluids at the same thermodynamical conditions. [?] In figures 5.7 and 5.8 typical cases are shown where the strength of association was chosen slightly above the critical association force and this force increased slightly going from figure 5.7 to figure 5.8

While in bulk fluids (circles) in both cases most of the particles belong to large clusters (i.e. to the associating network) one clearly recognices considering the confined fluid (squares) the symmetry breaking effect of the restricted geometry. In contrast to the bulk there are in case of a relatively weak bonding force (figure 5.7, $\beta = 2.0$) the molecules distributed among clusters of small and medium size. which are not able to form a macroscopic network. If the hydrogen bonding is strengthened only slightly from $\beta = 2.0$ to $\beta = 2.5$ (figure 5.8) the number of particles located in larger clusters is significantly increased what points to the transition of the structure of the confined fluid from a simple fluid character to the extendened networks in associating liquids. That means: the restricted geometry hinders the formation of associating structures in case of relatively weak bonding forces where we observe in the bulk already extended networks. Increasing the associating interaction – analogous to the bulk – a spontaneous transition to the network
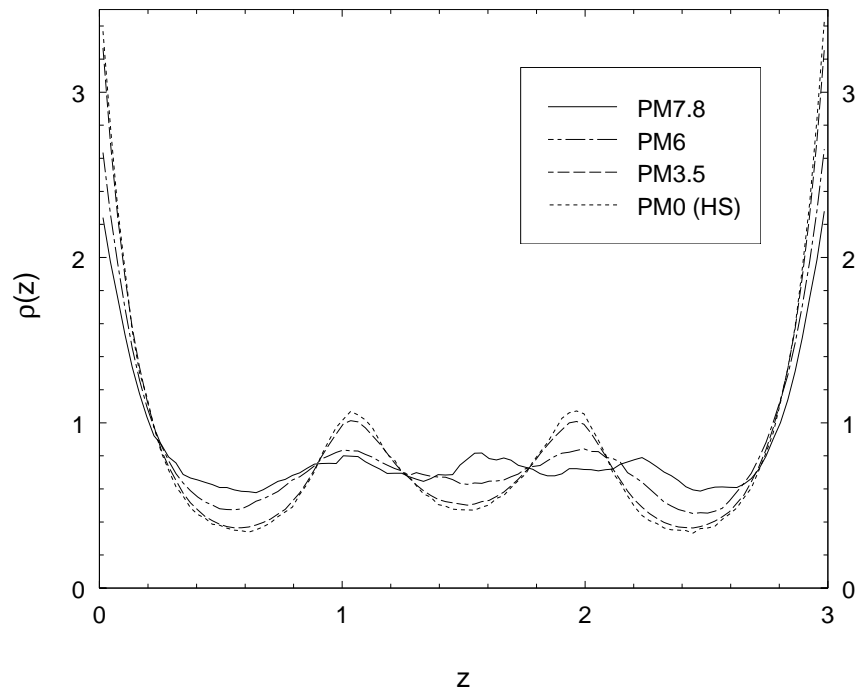
Figure 5.6: Density profile of associating fluids in slit-like pores ($L = 4\sigma$) versus the strength of the associating forces (the numbers describe the strength of association, 0 means no association : hard spheres)
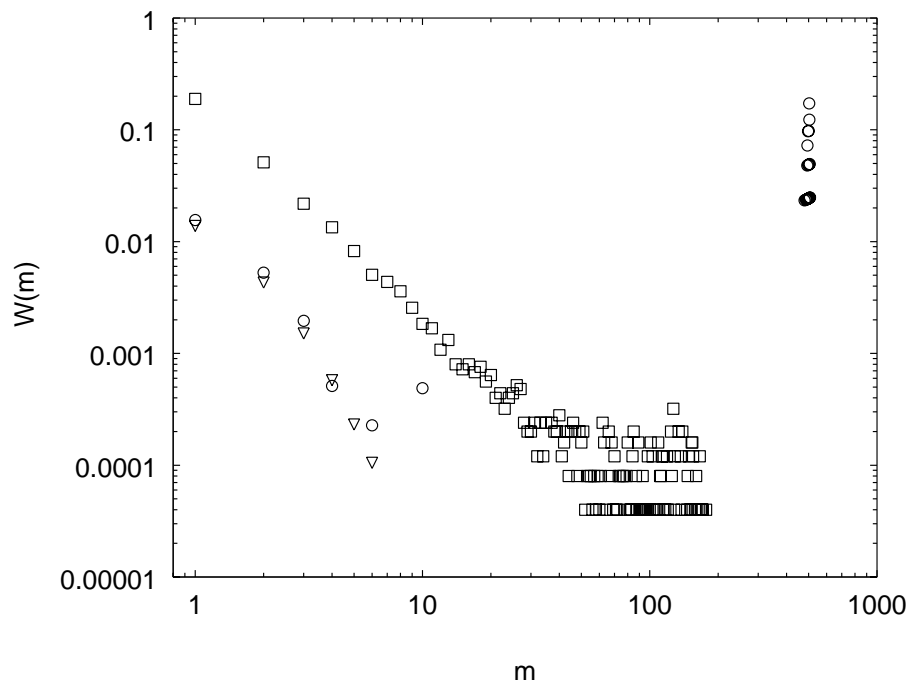
Figure 5.7: Distribution of cluster sizes of assoziating fluids in the bulk and in a slit-like pore ($L = 2.5\sigma$) for a strength of association of $\beta = 2$ (explanation of symbols in the text).
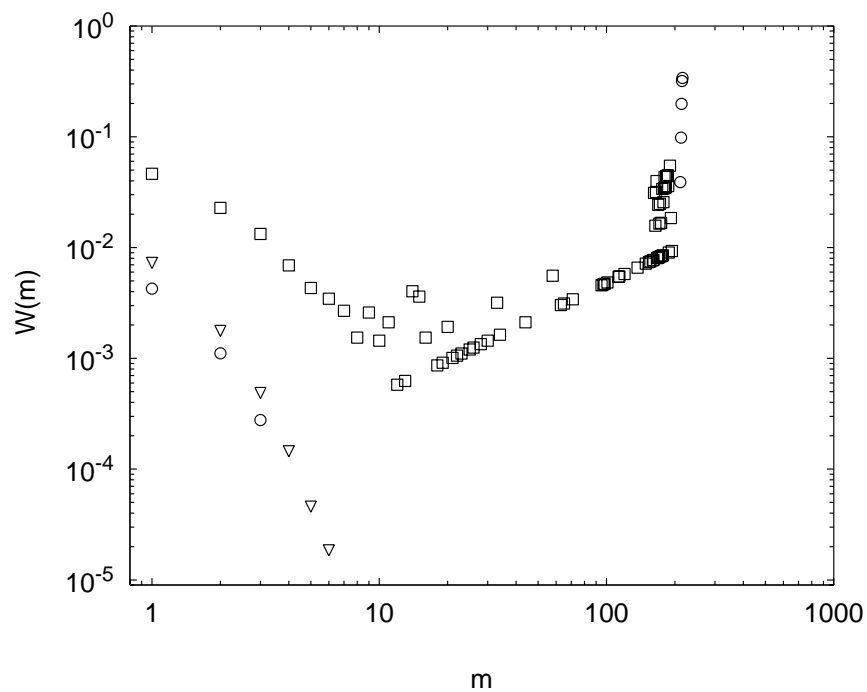
Figure 5.8: Distribution of cluster sizes of assoziating fluids in the bulk and in a slit-like pore ($L = 2.5\sigma$) for a strength of association of $\beta = 2.5$ (explanation of symbols in the text).

structure takes place, i,e, the 'critical' strength of association is shifted to higher values by the influence of the interface.

In very narrow slits where three-dimensional tetrahedral networks can not be formed for geometrical reasons we find in case of strong hydrogen bonds linear chains or quasi-two-dimensional nets [?].

For a more detailed consideration of fluids confined to planar slits – besides the one-particle densities – pair distribution functions maybe considered. The problem is here – as discussed earlier – that the confined fluid structure is not spatially isotropic what means that the distribution of particles around a given molecule depends on the position of that particle in the slit i.e. pair distribution functions of inhomogeneous fluids depend – besides the relative possition of a pair of particles – in general on additional variables (e.g. the distance from the walls). Computer studies have been done for the (two-dimensional) radial distributions of particles in planes parallel to the walls [?, ?].

5.3.2   Pressures and chemical potentials

As mentioned before (cf. section ??) in confined fluids an (uniform) mechanical pressure does not exist in general but it has to be replaced by a tensor depending on the position and direction in space. We will in the following restrict to the case of slit-like pores, where we will consider two important problems, the pressure at the wall and the spreading pressure which is the averaged mechanical pressure parallel to the walls and has the meaning of a thermodynamic pressure in phase equilibria comprising bulk and confined fluids.

The estimation of the pressure at the wall of the slit is straighforward for fluids consisting of hard-core molecules via the contact theorem where in case of smooth interfaces the value of the particle density at the wall (the contact density) is proportional to the pressure at the wall (equation(refcont-t)). In case of molecularly rough (hard) interfaces the pressure has to be calculated by the analysis of the distribution of the of the (different) local slit width averaging over the corresponeding contact values.

Figure 5.9 shows the simulation results [?] of the distribution of the (average) contact values of the particle density of a hard sphere fluid in a slit with one smooth and one molecularly rough interface (according to model A in section ??) in comparison with a pore with two smooth (hard) walls. The influence of the roughness on the contact density and therefore on the
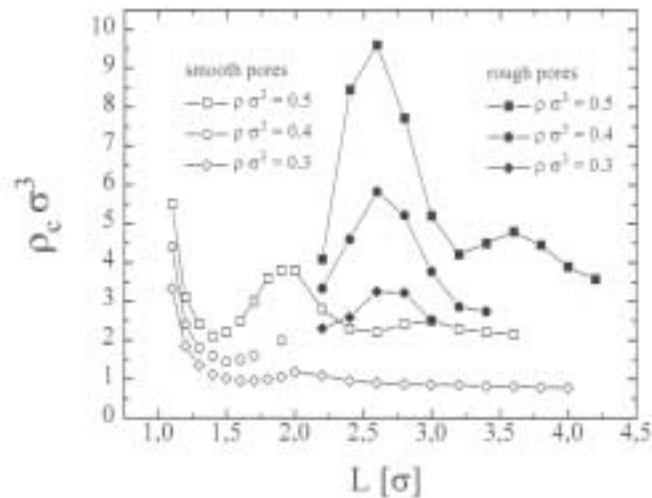
Figure 5.9: Average of the contact density of a hard sphere fluid in a slit-like pore versus the slit width with one smooth and one molecularly rough (according to model A) wall in comparison with the contact density in a slit-like pore with two smooth walls

pressure at the wall can be directly read from the figure.

The most interesting feature of the results is that the value of the pressure is oscillating versus the slit width rather than monotonously decaying as one may expect. Although the exact form of this function depends on the roughness of the interfaces the general behaviour is not changed going from smooth to molecularly rough walls.

Looking on Lennard-Jones fluids in narrow slits a very similar behaviour of the pressure at the walls versus the width of the slit is found [?]. In general the problem of the behaviour of the pressure in terms of the distance of the walls is an actual problem in experimental studies of planar interface structures e.g. biologically active phospholipid bilayers [?]. The more general problem of the pressure of the walls in confined fluids consisting of non-spherical particles is discussed e.g. in [?, ?]

Another important quantity for the characterization of confined fluids is the chemical potential μ. As discussed before, particularely the equilibrium condition of coexisting phases is governed by the equality of the corresponding phases. Therefore a large number of simulation studies of chemical potentials using both the grand canonical ensemble and Widoms test particle

method have been performed for confined fluid models [?]. To illustrate the general behaviour of the chemical potential we will again show some results for fluids confined to slit-like pores. Results for $\beta\mu$ as a function of density
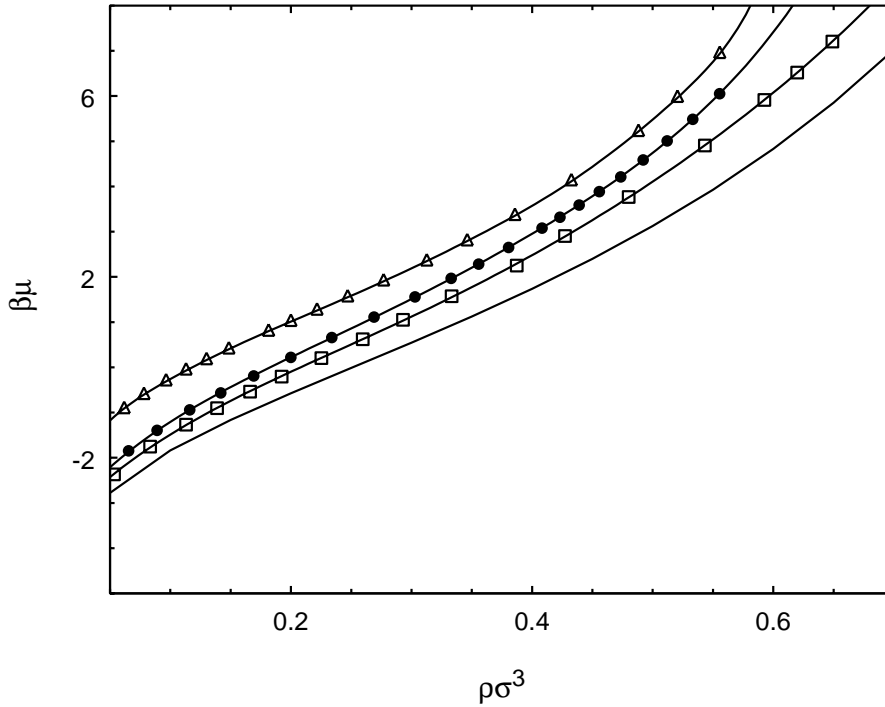

Figure 5.10: Total chemical potential of the hard-sphere fluid in a hard planar slit as a function of density for several slit widths, calculated using the TPI method. The curves are smoothed numerical fits to the computer simulation data. Also shown (lower curve, for comparison only) are the hard-sphere bulk-fluid results, obtained from the analytical Carnahan-Starling-Kolafa equation of state [?]. The triangles denote results at the slit width $L = 1.25\sigma$; circles at $L = 2.5\sigma$; and squares at $L = 4\sigma$.

for the HS fluid confined to hard planar slits of various widths are shown in figure 5.10 (we also show the bulk-fluid HS results for comparison). The total chemical potential is calculated according to

$$\beta\mu = \ln(\rho_s\sigma^3) + \beta\mu^{ex} \qquad (5.18)$$

where $\beta\mu^{ex}$ is the excess chemical potential per particle with respect to an

ideal gas at the density ρ_s given by

$$\rho_s = \frac{N}{LA} \tag{5.19}$$

where A denotes an area parallel to the slit walls. The smoothed curve is a numerical fit to the simulation data. Figure 5.11 shows $\beta\mu$ for the
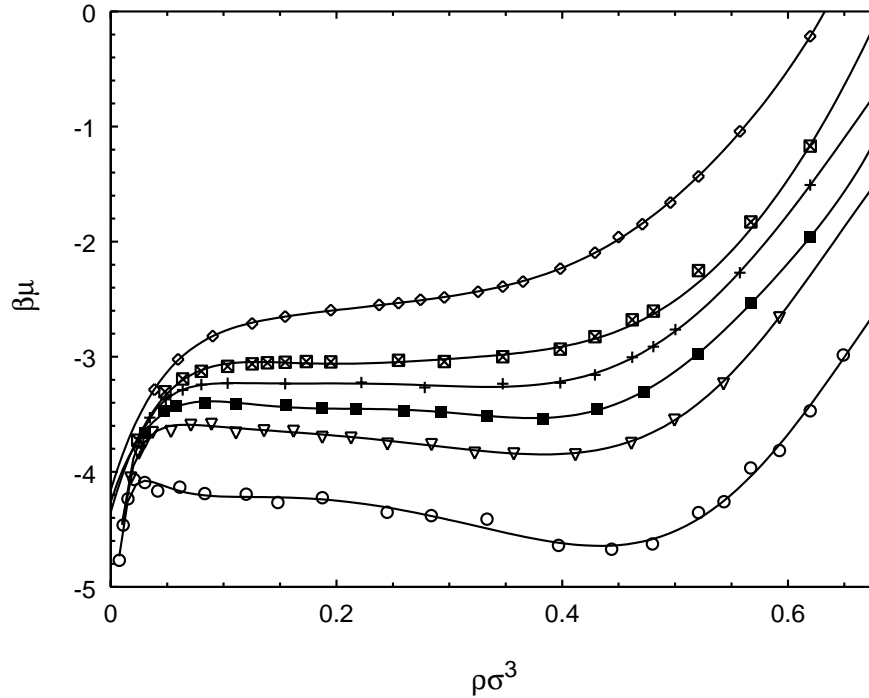

Figure 5.11: Total chemical potential of the square-well fluid with $\lambda = 1.5\sigma$ in a hard planar slit of width $L = 4\sigma$ as a function of density at several reduced temperatures, $T^* = kT/\epsilon$, calculated using the TPI method. The curves are smoothed numerical fits to the computer simulation data. Open circles denote results at $T^* = 0.8$, inverted triangles at $T^* = 0.9$, filled squares at $T^* = 0.95$, crosses at $T^* = 1.0$, crosses in squares at $T^* = 1.05$, and diamonds at $T^* = 1.2$.

square-well slit fluid as a function of density in a hard planar slit of width $L = 4\sigma$, at several temperatures. The smoothed curves are numerical fits to the simulation data, and the van der Waals loops indicate subcritical temperatures.

The importance of the simulation results for the chemical potential data will be discussed in the following in the context of the estimation of the spreading pressure and in the next section in the context of the determination of the phase diagram of fluids in slit pores.

The next problem we will discuss is the estimation of the spreading pressure Π in a slit where we will demonstrate two routes (i) an indirect method starting with the simulation results of the chemical potentials and estimating Π by a Gibbs-Duhem integration and (ii)) the direct simulation of this quantity by the virtual parameter variation method (virtual volume change) introduced in section ??).

For a slit hard sphere and square-well fluid the spreading pressure can be calculated from the $\mu(\rho)$ simulation data – presented in figures 5.10 and 5.11, respectively – indirectly by integration of the Gibbs-Duhem equation in the following form:

$$
\begin{aligned}
\beta\Pi &= \beta\Pi^{ideal} + \beta\Pi^e \\
&= \rho + \rho\beta\mu^e - \int_0^\rho \beta\mu^e d\rho
\end{aligned}
\tag{5.20}
$$

The virtual volume variation method for the slit fluid consists in the calculation of

$$
\beta\Pi^{ex} \equiv -(\partial\beta A^{ex}/\partial V)_{N,\beta}
\tag{5.21}
$$

in agreement with equation (5.7) where Π^{ex} denotes the excess of the spreading pressure over an ideal gas on the same state conditions. The simulations were carried out as follows: A conventional (N, V, T) simulation was performed in the slit of width L employing the usual periodic boundary conditions in the x and y directions (for the geometry of the simulation box compare sectionXXX), accompanied by trial volume change steps conducted at appropriate intervals in the Markov chain of configurations. Each such step consisted of the following parts:

1. a random decrease of the simulation box volume $\Delta V = A\Delta\ell$, performed by a change of the length of the simulation box from l to $l - \Delta\ell$, where $\Delta\ell = \alpha\Delta\ell_{max}$, and α is a random number uniformly distributed on $[0, 1]$.

2. calculation of the resulting change in the Boltzmann factor, $\exp(-\beta\Delta\mathcal{U})$, where $\Delta\mathcal{U}$ is the change in the configurational energy $\mathcal{U}$ due to the volume change ΔV.

3. recording of the values of $\exp(-\beta\Delta\mathcal{U})$ in equal-sized bins of a volume histogram corresponding to ΔV in step 1.

At the end of the simulation run, the average values of $\exp(-\beta\Delta\mathcal{U})$ were analyzed as a function of ΔV, and extrapolated to $\Delta V = 0$ by performing a linear regression of $\exp(-\beta\Delta\mathcal{U})$ on ΔV near $\Delta V = 0$. The spreading pressure is then given by

$$\left(\frac{\partial \beta A^{ex}}{\partial V}\right) = -\lim_{\Delta V \to 0}\frac{\ln < \exp(-\beta\Delta\mathcal{U}) >_0}{\Delta V} \tag{5.22}$$

in agreement with the general expression equation (4.24) given in section **??**

The results for the spreading pressure of hard sphere fluids at several slit widths are shown in Figure 5.12. The curves were obtained by numerically integrating the smoothed chemical potential results of Figure 5.10. The agreement of the spreading pressure estimated by both routes is excellent. Figure 5.12 shows the spreading pressure calculated by the virtual volume change method and by integration of the Gibbs-Duhem equation, (5.20), for systems of Fig. 5.11.

As in the case of the hard sphere fluid, the agreement of Π obtained by the Gibbs-Duhem integration with the Π obtained by direct simulation is again excellent, even in the two-phase region.

The presented simulation data [?] are the first quantitative results for the spreading pressure of a confined fluid model so far. The special importance of these results consists in the interpretation of the spreading pressure as the thermodynamic pressure governing the corresponding fluid phase equilibria in the confinement (compare next section). The meaning of Π as a thermodynamic pressure is explicitly confirmed by the numerical consistency of the direct simulated spreading pressure with the pressure obtained by a thermodynamic integration of the Gibbs-Duhem equation.

5.3.3 Phase Equilibria

General Aspects

Before we present selected results of fluid phase equilibria (capillary condensation) in slit-like pores we will discuss here some thermodynamic aspects concerning the classification of the possible types of phase transitions which may appear in confined fluids especially fluids confined to micropores of simple geometry.
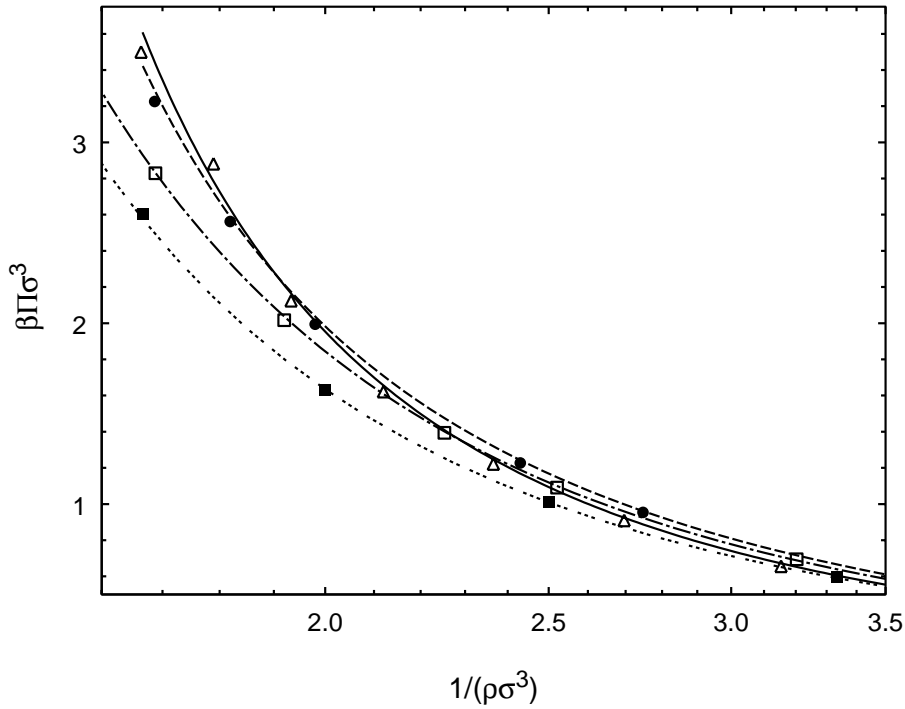
Figure 5.12: Spreading pressure of the hard-sphere fluid in a hard planar slit as a function of reduced volume for the slit widths shown in Fig. 4. The curves are the results of the Gibbs-Duhem equation, (5.20), using the smoothed chemical potential data of Fig. 4. The symbols denote the VVV results; for notation, see the caption to Fig. 5.10. The bulk fluid results are shown for comparison purposes; the dashed line is the result of the Carnahan-Starling-Kolafa equation of state [?] and the filled squares are the virtual volume variation results.

Pore-Bulk Equilibria and Capillary Condensation in Slit-like Pores

The simplest case of coexisting phases in a slit-bulk system is the distribution of a single phase (supercritical) fluid between a bulk and a pore region e.g. the phase equilibrium of an inhomogeneous hard sphere fluid distributed over a bulk and a slit region

f"ur Hartkugelfluide sowohl Vergleichsdaten f"ur die Bulkregion aus analytischen Zustandsgleichungen [?] vorliegen als auch Resultate gro"skanonischer Simulationen f"ur Fluide im Schlitz [?]. Ein Vergleich mit Ergebnissen von fr"uheren Gibbs-Simulationen war nicht m"oglich, da – wie schon erw"ahnt
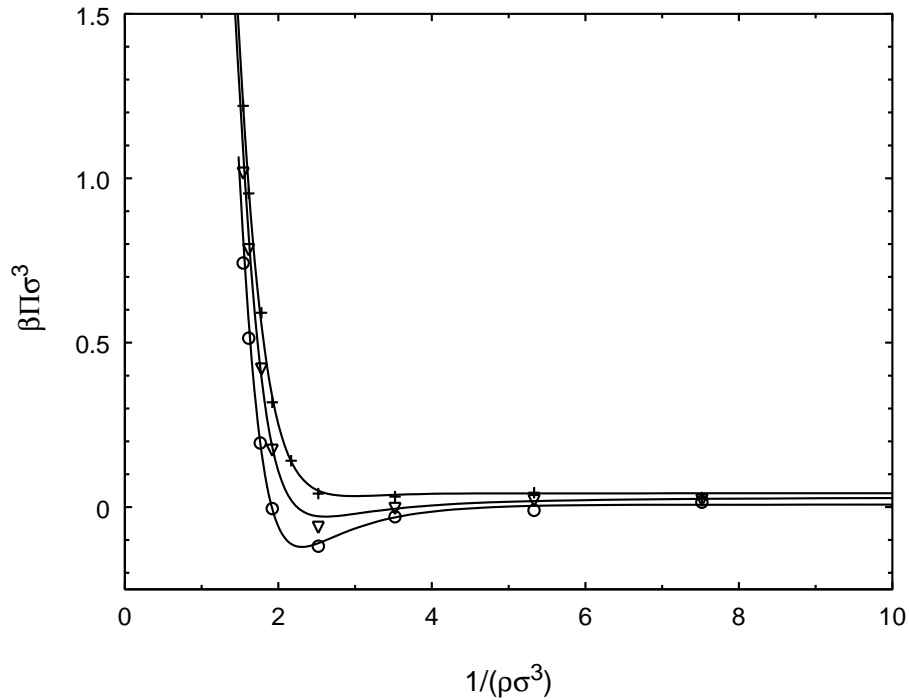
Figure 5.13: Spreading pressure of a square-well fluid with $\lambda = 1.5\sigma$ in a hard planar slit of width $L = 4\sigma$ as a function of reduced volume at the temperatures of Fig. 6. Symbols are the VVV results, and the curves are obtained from the Gibbs-Duhem equation, (5.20), using the smoothed chemical potential data of Fig. 5.11. See Fig. 5.11 for explanation of the symbols.

– au"ser in der Originalarbeit von Panagiotopoulos "uber zylindrische Poren die Gibbs-Technik bisher praktisch nicht f"ur inhomogene Syteme eingesetzt wurde. Die Simulationen der inhomogenen Hartkugelfluide zeigten gute "Ubereinstimmung der ermittelten Koexistenzdichten mit den genannten Literaturdaten. In separaten Widom-Simulationen f"ur die Bulk- und die Schlitzphase wurde die "Ubereinstimmung der Chemischen Potentiale in beiden Gebieten best"atigt.

"Ahnliche Simulationen wurden f"ur "uberkritische *square-well*-Fluide durchgef"uhrt. Obwohl hier keine Vergleichsdaten zur Verf"ugung standen, konnte die Konsistenz der Resultate auch in diesem Falle durch Best"atigung der Gleichheit der Chemischen Potentiale festgestellt werden. Einzelheiten dieser Simulationen sind der Arbeit [?] zu entnehmen.

Im Zentrum der Untersuchungen stand das Studium der oben genannten gekoppelten Mehrphasengleichgewichte in unterkritischen *square-well*-Systemen. Ausgangspunkt f'ur unsere Betrachtungen war der leicht unterkritische Zustandsbereich von freien *square-well*-Fluiden, f'ur dessen Phasengleichgewicht genaue Simulationsdaten vorliegen. Unsere Simulationen f'uhrten wir bei den von Vega et al. [**?**] untersuchten Temperaturen aus, wobei wir an die fl'ussige und die Gasphase im freien Fluid zus"atzlich einen mit Fluid gef'ullten planaren Schlitz ankoppelten. Mittels einer Drei-Box-Simulation ermittelten wir die Koexistenzdichten der drei beteiligten Phasen. Dabei konnten wir die Gleichgewichtswerte f'ur die Bulk-Phasen aus der Arbeit [?] mit guter Genauigkeit best"atigen und fanden im Schlitz eine mit dem Bulk im Gleichgewicht stehende verd"unnte Gasphase. Das gefundene ρT Diagramm des inhomogenen Dreiphasensystems ist in Abb 5.14 aufgezeichnet.

Durch unabh"angig durchgef'uhrte NVT-Widom-Simulationen in allen drei Phasen konnte die Gleichheit der Chemischen Potentiale gezeigt werden. Die gefundenen Werte der Chemischen Potentiale f'ur die Koexistenzdichten in den drei beteiligten Phasen im untersuchten Temperaturbereich ($T^* = 1.05$ bis $T^* = 1.20$; $T^* = k_B T/\epsilon$) sind in Abb. 5.15 dargestellt (vgl. hierzu auch die Originalarbeit [?]).

5.3.4   water-like phases at molecularly rough interfaces (selforganization)

Die Simulationen von assoziativen Fluiden an rauhen Grenzfl"achen gehen ebenfalls von den Modellen A und B aus, wobei neben den reinen Hartkugelkr"aften zwischen den Grenzfl"achen- und Fluidmolek"ulen spezifische kurzreichende attraktive Wechselwirkungen ber"ucksichtigt werden, die analog der H-Br"uckenbindungen als azentrische *square-well*-Potentiale modelliert werden.

Diese Studien, die grundlegende Informationen zur Hydratation an molekular strukturierten Grenzschichten liefern, werden in enger Abstimmung mit experimentellen Hydratationsuntersuchungen durchgef'uhrt und sind noch nicht abgeschlossen. Es liegen aber bereits interessante Ergebnisse vor, die z.Z. in einer Publikation (Preprint [?]) zusammengestellt werden. Die wichtigsten Erkenntnisse werden im folgenden zusammen mit weiteren noch unver"offentlichen Resultaten diskutiert. Im Detail werden zwei Varianten des Modelles B f'ur molekular rauhe Schlitzpoen untersucht:
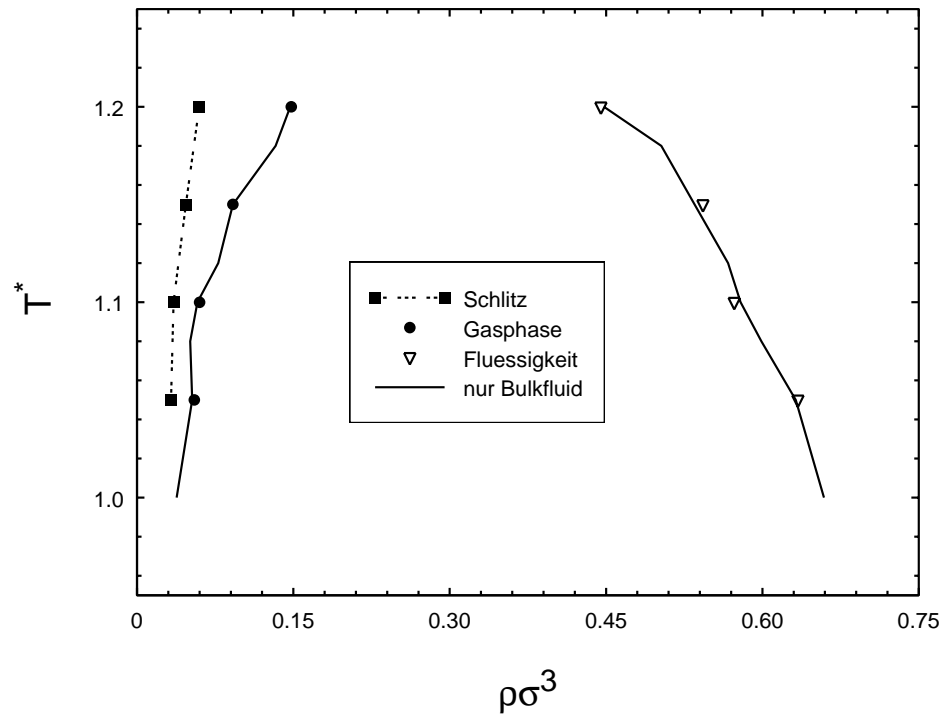
Figure 5.14: Koexistenzdichten im unterkritischen Temperaturbereich in einem Dreiphasen-Gleichgewicht zwischen freiem Fluid und einem Fluid in einer Schlitzpore
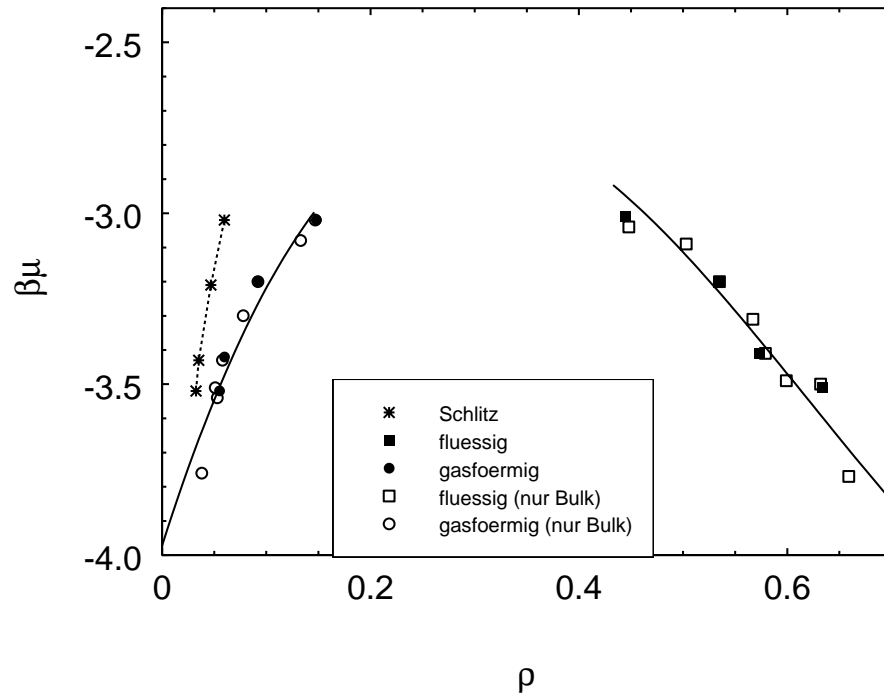
Figure 5.15: Chemische Potentiale als Funktion der Dichte in einem Dreiphasen-Gleichgewicht zwischen freiem Fluid und einem Fluid in einer Schlitzpore
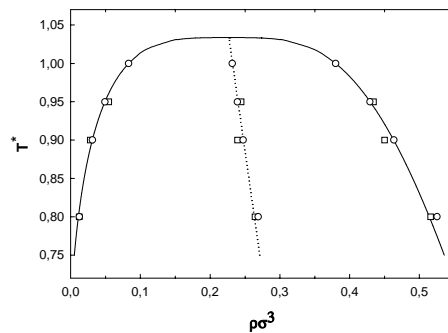
Figure 5.16: Temperature-density vapor-liquid coexistence curve (solid line) for the square-well fluid with $\lambda = 1.5$ in a hard planar slit of width $L = 4\sigma$. The rectilinear diameter line given by $(\rho_\ell + \rho_v)/2$ is also shown (dotted line). The curves are the result of a numerical fit to equation (**??**); circles are the phase equilibrium data from Table I, and squares are the Gibbs Ensemble simulation results from Table I.

- ein 'hydrophobes' Modell, bei dem die Wechselwirkungen zwischen den Grenzfl"achenmolek"ule untereinander und zwischen Fluid- und Grenzfl"achenteilchen auschlie"slich *hard-core*-Kr"afte sind

  sowie

- ein 'hydrophiles' Modell, das neben den genannten *excluded volume*-Wechselwirkungen zus"atzlich assoziative Kr"afte zwischen den Grenzfl"achenteilchen untereinander und zwischen Fluid und Grenzfl"ache zul"a"st.

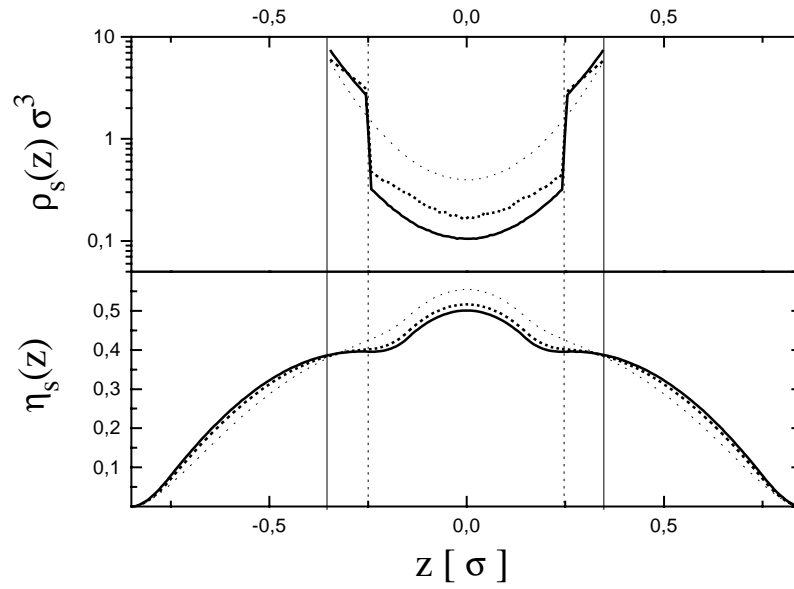In Abbildung 5.17 wird im oberen Teil zun"achst die Verteilung der Dichte

Figure 5.17: Dichte- und Raumerf"ullungsprofile der Oberfl"achenmolek"ule in molekular rauhen Schlitzporen ($L = 1.7\ \sigma$; 'hydrophob'; volle Linie, 'hydrophil': gestrichelt, harte Kugeln: punktiert)

der Oberfl"achenmolek"ule $\rho_s(z)$ f"ur beide Modelle in einem sehr engen Schlitz ($L = 1.7\sigma$) dargestellt, wenn sich kein Fluid in der Pore befindet. Die Dichteverteilungen f"ur 'hydrophobe'und 'hydrophile' Poren werden mit der Dichte eines einfachen Hartkugelfluides verglichen. Im unteren Teil des Bildes sind die zu den gezeigten Dichteprofilen geh"origen lateralen Raumerf"ullungsprofile $\eta_s(z)$ aufgezeichnet. Beim Vergleich der Dichteprofile mit dem des einfachen Hartkugelfluides erkennt man deutlich die Ausbildung von Schichten von Oberfl"achenmolek"ulen an den W"anden, die auf die Wirkung der (anziehenden) Potentialmulden an den Porenw"anden zur"uckzuf"uhren ist. Interessant ist, da"s die diskutierten Oberfl"achenschichten bei Betrachtung der Raumerf"ullung nicht gefunden werden, sondern im Gegenteil die Packungsdichte im Zentrum des Schlitzes am h"ochsten ist, was die Tatsache widerspiegelt, da"s die beiden Oberfl"achen sich in engem Kontakt befinden und deren Struktur stark korreliert ist, wobei die Unterschiede zu einem Fluid aus harten Kugeln gering sind.

Wir betrachten nun die Verteilung der Teilchendichte in beiden Modellen f"ur den Fall, da"s neben den Oberfl"achenmolek"ulen sich ein assoziierendes Fluid (modelliert durch PM Wasser) im Schlitz befindet. Abbildung 5.18 zeigt die Einteilchendichten $\rho_i(z)$ f"ur Schlitzbreiten von $L = 2.31\sigma$, 3.02σ and 3.82σ. Der Index i steht dabei f"ur Oberfl"achenmolek"ule (durchgezogene Kurven) und Fluidteilchen (punktierte Kurven), wobei jeweils die linken Bilder die 'hydrophoben' und jeweils die rechten die 'hydrophilen' Porenmodelle bedeuten. Die Abbildung zeigt signifikante Unterschiede zwischen den Dichteprofilen beider Modelle. W"ahrend die Fluide in den 'hydrophoben' Poren ein Verhalten von $\rho(z)$ zeigen, das mit denen von Hartkugelfluiden vergleichbar ist (siehe [?]), sind in 'hydrophilen' Poren die *hard-core*-artigen Oszillationen der Dichteprofile infolge der zus"atzlichen assoziatven Oberfl"achenkr"afte deutlich abgeschw"acht. Trotz der genannten Unterschiede zwischen beiden Modellen werden zwei grunds"atzliche Effekte der Selbstorganisation in beiden F"allen beobachtet. Es zeigt sich zum einen mit steigender Schlitzbreite eine Reorganisation der Oberfl"achen aufgrund der abnehmenden Korrelationen zwischen den W"anden und zum anderen wird in den Porenzentren der breiteren Schlitze eine weitgehend homogene Mischung von Oberfl"achen- und Fluidteilchen sichtbar. Beide Selbstorganisationseffekte werden unter bestimmten Bedingungen in realen Biomembranen gefunden [?, ?].

Um einen tieferen Einblick in die molekulare Struktur des Fluid-Porensystemes zu gewinnen, wurde – ganz analog der Untersuchungen an strukturlosen
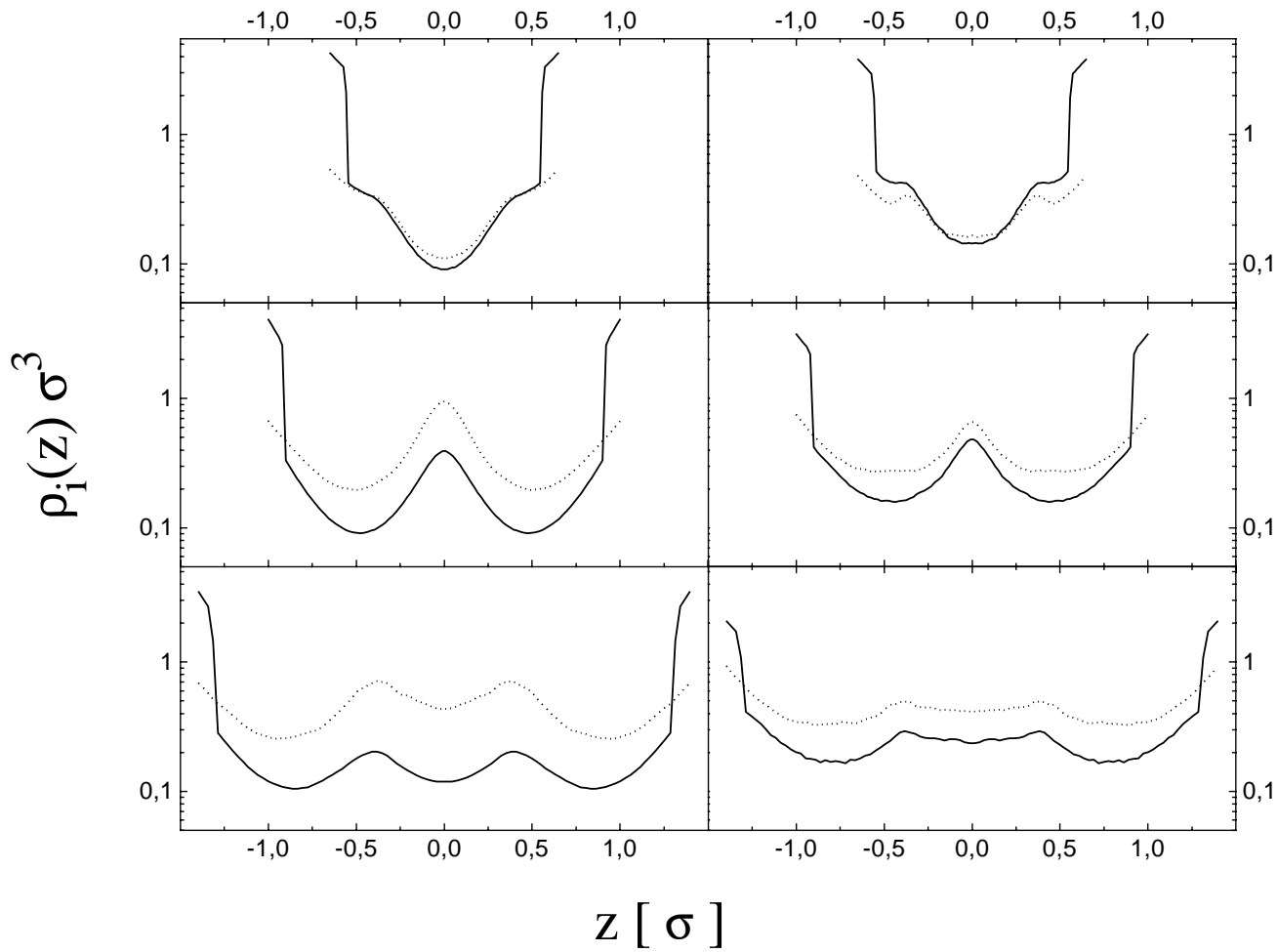
Figure 5.18: Dichteprofile der Oberfl"achen- und Fluidmolek"ule in Schlitz-
poren verschiedener Breite (Oberfl"achenmolek"ule: volle Kurven; Flu-
idteilchen: punktiert; linke Bilder: 'hydrophobe' Poren; rechte Bilder: 'hy-
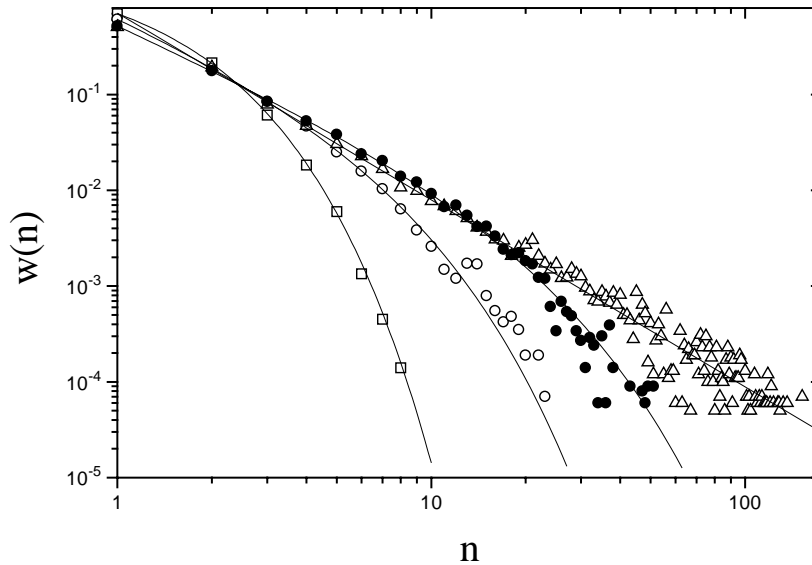drophile' Poren)

Figure 5.19: Verteilungen der Gr"o"sen der Molek"ulcluster in 'hydrophoben' und 'hydrophilen' Schlitzporen (Erkl"arung der Symbole, siehe Text)

Oberfl"achen – f"ur beide Modelle die Verteilung der Gr"o"sen $w(N)$ der durch Wasserstoffbr"ucken verbundenen Molek"ulcluster studiert. Die Ergebnisse sind in Abbildung 5.19 dargestellt. F"ur 'hydrophobe' Poren existieren nur Cluster aus Fluidmolek"ulen (d.h. Wassercluster (gef"ullte Kreise)). Im Falle 'hydrophiler Poren sind dagegen drei Typen von Clustern m"oglich, neben den reinen Wasserclustern (Kreise) sind Cluster, die ausschlie"slich aus Oberfl"achenmolek"ulen bestehen (Quadrate) und gemischte Fluid-Oberfl"achen-Cluster (Dreiecke) vorhanden. Die Analyse zeigt, da"s f"ur beide Porentypen gro"se Cluster (Netzwerke) existieren, die die gesamte Pore "uberspannen. Im 'hydrophilen' Falle sind gro"se Cluster allerdings im wesentlichen in den aus Oberfl"achen- und Fluidmolek"ulen zusammengesetzten Aggregaten zu finden, w"ahrend die reinen Fluidcluster sogar kleiner sind als im 'hydrophoben' System.

Details der Strukturbildung k"onnen der Analyse von S"attigungsprofilen $S_i(z)$ entnommen werden, die die Dichteverteilung von Molek"ulen beschreiben, die jeweils mit i H-Br"ucken mit anderen Teilchen verbunden sind. i kann
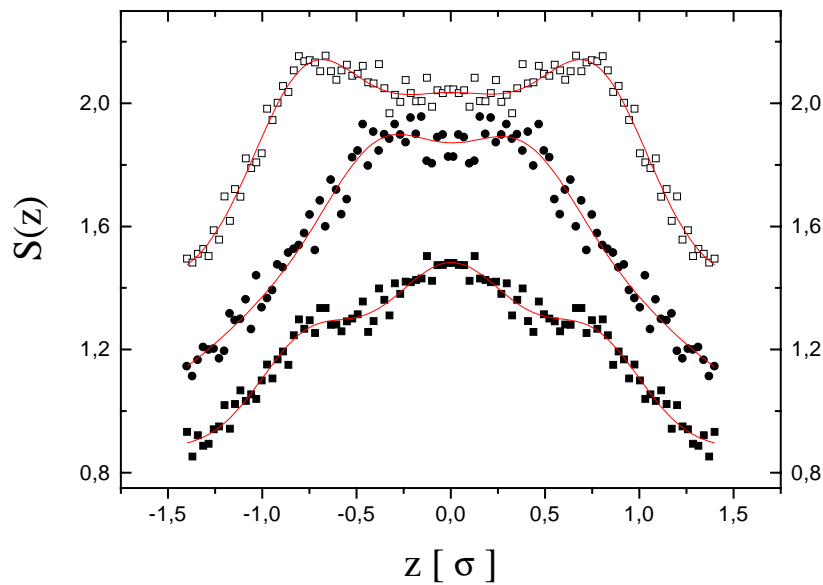
Figure 5.20: Profile der S"atttigung der H-Br"uckenbindungen in Schlitz-
poren (Kreise: 'hydrophob'; Quadrate: hydrophil, gef"ullt nur Fluid-Fluid-
Bindungen, offen zus"atzlich Fluid-Oberfl"achen-Bindungen)

dabei die Werte von 0 (freies Teilchen bis 4 (voll ges"attigter Bindungszus-
tand) annehmen.

   Abbildung 5.20 zeigt typische Resultate f"ur einen Schlitz der Breite
$L = 3.02\sigma$. Der wesentliche Unterschied zwischen 'hydrophoben' und 'hy-
drophilen' Poren besteht darin, da"s im ersten Falle eine gleichm"a"sige im
wesentlichen lineare Abnahme der S"attigung vom Zentrum zu den Gren-
zfl"achen der Pore beobachtet wird, w"ahrend im zweiten Modell deutliche
Maxima der S"attigung gefunden werden, bevor ein starker Abfall zu den
W"anden hin erfolgt. Die Analyse der S"attigungsprofile dient insbesondere
der Festlegung effektiver Schlitzbreiten, die einen Vergleich der Fluidstruk-
tur in glatten und molekular rauhen Poren erm"oglichen sollen. (Einzelheiten
dazu sind in der Originalarbeit [?] enthalten.)

   Zusammenfassend kann die molekulare Struktur des Fluid-Poren-Systems
anhand der Schlitzbreite klassifiziert werden.

- F"ur sehr schmale Schlitze ist die Struktur beider Porenoberfl"achen stark korreliert. Das in der Pore befindliche Fluid kann keine eigene zusammenh"angende Struktur ausbilden, sondern liegt in Form einzelner Molek"ule vor und beeinflu"st mit steigender Konzentration die Ausbildung der Grenzfl"achenstrukturen.

- Erreicht die Schichtdicke etwa $L = 3\sigma$, so kann sich im Zentrum des Schlitzes eine bulk-artige Wasserstruktur herausbilden. die aber noch stark von den Oberfl"achen beeinflu"st ist und wie im Falle von glatten W"anden mit zunehmender Schlitzbreite einen "Ubergang von kleinen Molek"ulclustern zu Netzwerkstrukturen zeigt.

- Im Falle deutlich breiterer Schlitze wird die Herausbildung separater Wandschichten und eines ausgedehnten Bulkfluides im Inneren der Pore beobachtet. Diese Gebiete sind weitgehend entkoppelt und k"onnen bis zu einem gewissen Grade als separate Phasen aufgefa"st werden. Unter bestimmten Bedingungen k"onnen an den W"anden festk"orperartige Schichten auftreten, w"ahrend im Inneren der Pore ein fluider Zustand vorliegt. Eine analoge Situation wird auch experimentell in Lipid-Wasser-Systemen gefunden.

Weitergehende Informationen "uber die Struktur des Fluid-Grenzfl"achen-Systems k"onnen aus der Orientierung der Molek"ule in der N"ahe der Grenzfl"achen erhalten werden. Die Simulation der Ordnungsparameter der Orientierung ist mit sehr hohem numerischen Aufwand verbunden und steht zur Zeit im Brennpunkt der Forschung.

Obwohl weitere Untersuchungen erforderlich sind, um eine endg"ultige Einsch"atzung der Leistungsf"ahigkeit der aufgebauten Modelle zur Behandlung von Hydratationsph"anomenen in molekular strukturierten Porensystemen (Modellmembranen) geben zu k"onnen, kann gesagt werden, da"s die entwickelte konzeptionell einfache und einheitliche Methodik zur Beschreibung der wesentlichen Wechselwirkungen in Wasser-Poren-Systemen in der Lage ist, wesentliche experimentell gefundene Strukturcharakteristika zu reproduzieren und ein solide theoretische Basis zur molekularstatistischen Behandlung der Thermodynamik und des Phasenverhaltens derartiger Systeme bildet, die "uber die M"oglichkeiten "ublicher Gittermodelle [?, ?, ?] hinausgehen.

6

Diffusion of Guest Molecules in Zeolites

6.0.5 Structured Propagators and van Hove Functions in describing the diffusion behaviour of guest-molecules in zeolites

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Notation