This is to certify that the

thesis entitled

A Study of the Simplified Local Density Model

presented by

Hena Pyada

has been accepted towards fulfillment
of the requirements for

Master's degree in Chemical Engr.

Major professor

Date 4/5/94

A STUDY OF THE SIMPLIFIED LOCAL DENSITY MODEL

By

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THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemical Engineering

1994

ABSTRACT

A STUDY OF THE SIMPLIFIED LOCAL DENSITY MODEL

By

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The simplified local density (SLD) model of adsorption [Rangarajan B.,*PhD Thesis*, Michigan State University, 1992] is modified by using the Peng - Robinson equation (PRSLD) to describe fluid structure. The adsorption isotherms predicted by the two SLD models were compared with experimental data for different combinations of fluids and system conditions. For the same solid - fluid interaction parameter ε_{fw}, the PRSLD predicted higher surface excess values. The predicted and experimental isotherms showed qualitative agreement. The quantitative agreement depended on the value of ε_{fw} parameter. For ethylene on graphon the PRSLD predicts isotherms in good agreement with experiment for the same value of ε_{fw} over a wide range of temperatures (263 - 313 K).

In another approach, called the IE approach the SLD density profile is used as an initial guess to solve an integral equation iteratively. The resulting density profile is used to calculate surface excess values. The SLD and IE adsorption isotherms were compared to determine conditions when the SLD is a good approximation. The SLD performs well when there is a strong fluid - solid attraction and when pressure is low ($Pr < 0.6$).

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CHAPTER 1

INTRODUCTION

Adsorption at high pressures is important in supercritical extraction from solids, in pressure swing adsorption of non-ideal gases and for regeneration of adsorbents with high pressure gases in the area of waste treatment, fermentation and food processing industries. There is a need for a simple theory of adsorption which gives good predictions of adsorption behavior for engineering calculations. The theory of adsorption by Langmuir (1918) is simple to use but it predicts only monolayer coverage. Realistic theories must predict multilayer coverage. The BET equation of Brunauer et al., (1938) is a well known multilayer model but it is applicable only to ideal gases and can not be used above the critical temperature of the gas. Another multilayer theory based on the Polanyi equation developed by Dubinin and coworkers (1960) is derived using empirical assumptions.

The engineering models based on principles of chemical physics give promising results. The models of Sullivan (1979), Teletzke (1982) and Tarazona and Evans (1984) which are density functional theories predict multilayer coverage but involve the solution of integral equations, which can be tedious and time consuming.

Somewhere between the empirical theories and the rigorous chemical physical models lie the adsorption theories based on equation of state approach. This approach simplifies the description of the fluid structure by assuming it to obey a particular equation of state, e.g. the van der Waals' (vdW), the Redlich-Kwong (RK) or the Peng-Robinson (PR). The model of Hill-deBoer [deBoer (1953) and Ross and Oliver (1964)] assumes that the adsorbed fluid is a two-dimensional van der Waals' fluid.

Barrer and Robins (1951), developed an equation of state model for multilayer adsorption which assumes that the chemical potential of a fluid molecule at a distance 'z' from the adsorbent surface is made up of the following two terms:

(1) the chemical potential of the usual van der Waals' bulk fluid, appropriate to the temperature T and local density $\rho(z)$ (the local density approximation);

(2) the fluid-solid interaction potential, which is assumed to be the attractive part (z^{-3}) of the integrated 9-3 Lennard-Jones (LJ) potential.

The Simplified Local Density (SLD) model of Rangarajan (1992), is based on the same principles as the model of Barrer and Robins, but uses a better form of the fluid-solid potential (Lennard-Jones partially integrated 10-4 potential) and the attractive van der Waals' parameter varies with distance from adsorption surface.

Actually, the van der Waals' contribution to the local chemical potential does not depend on the local density [Hill (1952,1951)], but on the entire density profile $\rho(z)$. To calculate the actual van der Waals' contribution an integral equation has to be solved. The rigorous solution of the integral equation is very complicated. An iteration scheme for solving the integral equation was developed which uses the density profile obtained from the SLD as a first guess. This approach shall be referred to as the Integral Equation (IE) approach. Though the IE presents a more accurate picture of the forces involved in the adsorption process, it is still an approximation. The objectives of this thesis are:

1. To modify the SLD by using the Peng-Robinson equation of state to calculate the fluid properties, this modified SLD will be referred to as the Peng-Robinson SLD (PRSLD) and the original SLD will be the van der Waals' SLD (vdWSLD).
2. Compare the density profiles and surface excess curves developed by the PRSLD with the vdWSLD.
3. Investigate whether the SLD density profiles are good first approximations for solving the IE.
4. Study and compare the density profiles and adsorption isotherms predicted by the SLD and the IE approaches.

A brief review of different theories of adsorption is presented in Chapter 2. The SLD is discussed and modified using the Peng-Robinson equation in Chapter 3. SLD and IE approaches are discused and compared in Chapter 4. Chapter 5 summarizes the conclusions reached based on these studies.

CHAPTER 2

THEORIES OF ADSORPTION

Adsorption

Sorption is the general term used to define the phenomena in multi-component, multi-phase systems when at least one component has a higher concentration at the interface (between the two different phases) than in any bulk phase. Adsorption is the special case when the sorbed molecules are unable to penetrate into the second bulk phase. Adsorption processes are divided into two areas, physical adsorption and chemisorption. Physical adsorption or physisorption results from intermolecular forces, where as chemisorption results from chemical bonding between fluid (adsorbate) and solid (adsorbent).

Physical adsorption has been the focus of several published studies and reviews. Some of the well known reviews are by Brunauer (1945), Young and Crowell (1962), Ross and Oliver (1964), Defay and Prigogine (1966), Flood (1967) and Nicholson and Parsonage (1982).

Adsorption may be defined by the surface excess $\Gamma^{ex} = n^{ex}/A_s$ = excess moles per unit area,

$$\Gamma^{ex} = \int_{z_0}^{\infty} (\rho(z)-\rho(b))\, dz \qquad 2-1$$

where, $\rho(z)$ is the density of the fluid at a distance z from the wall and $\rho(b)$ is the bulk density of the fluid, z_0 is the plane above the surface of the solid where the gas-solid potential is zero. The surface excess is defined as the number of excess moles per unit area of adsorbent.

To test the accuracy of different adsorption models, reliable experimental data are needed. Among the best data available at high pressure are those collected by Findenegg and co-workers (1983) for gases like krypton, argon, methane, ethylene and propane on graphon.

The following is a summary of some important adsorption models. All the models presented are for adsorption of a pure fluid (mainly gases) adsorbing on a solid adsorbent. Some of the different theories discussed here and a rough guide to the way they are related is shown in Figure 2 - 1.

KINETIC THEORIES:

The Langmuir theory and the BET theory were derived using a kinetic approach. The BET equation is often used for surface area and pore size distribution measurements of adsorbents.

Langmuir Theory:

The Langmuir theory [Langmuir, (1918)] is one of the first theories. It has a two parameter equation

$$\theta = W / W_m = k P / (1+k P) \qquad 2-2$$

where, W is the mass adsorbed, W_m is the amount adsorbed in a monolayer and k is an empirical constant. The Langmuir theory predicts monolayer coverage and adsorption isotherms exhibited by microporous

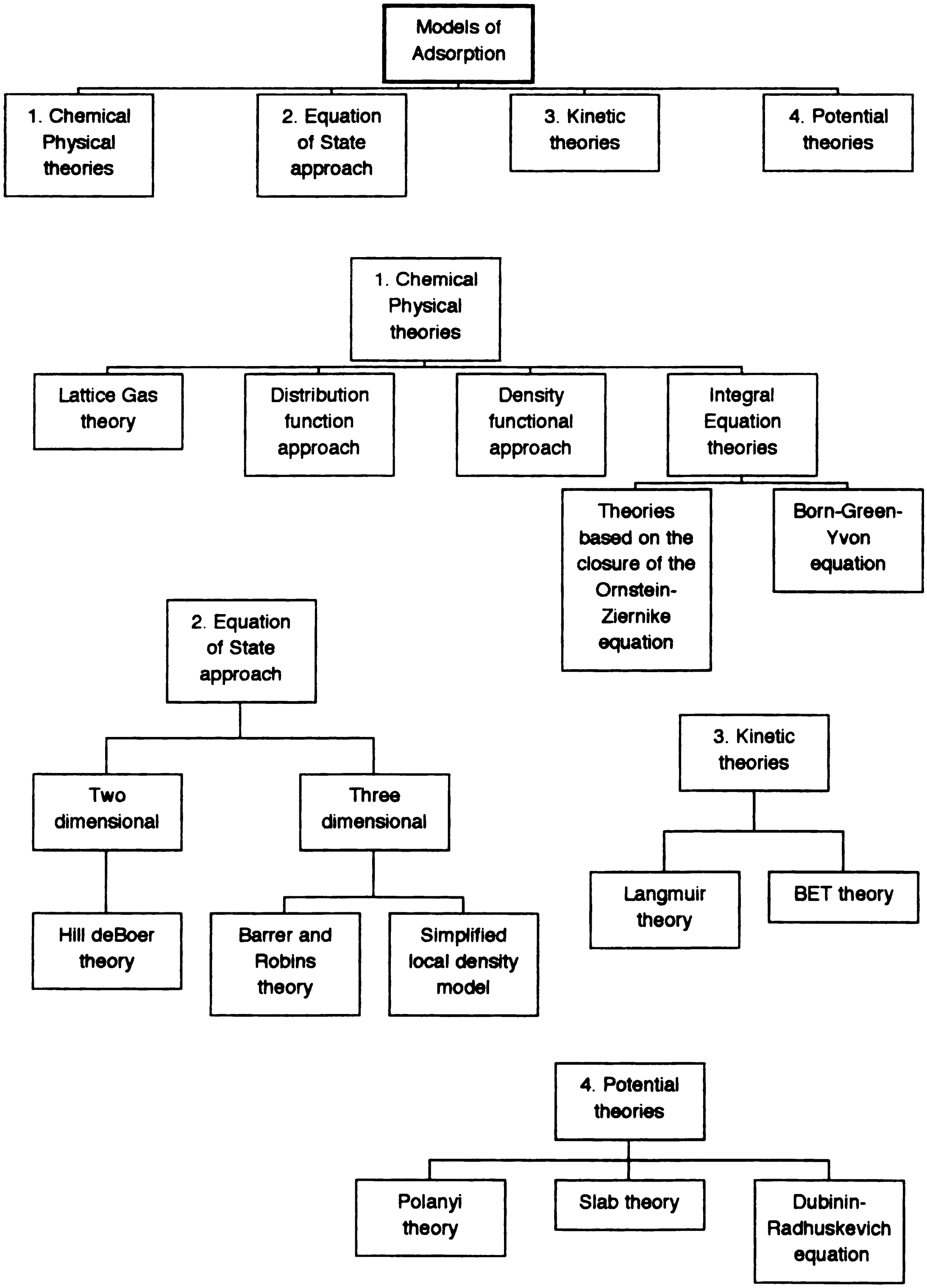

Figure 2 - 1 : A brief classification of adsorption models.

adsorbents and thus is more valid for chemisorption applications. It assumes that molecules are adsorbed at specific sites on the surface and vibrate around these sites. Adsorbed molecules do not move laterally, i.e. adsorption is localized.

BET Theory:

This theory was proposed by Brunauer, Emmett and Teller (Brunauer et al., 1938) and it extends the Langmuir isotherm to multi-layers.

$$W/W_m = N/N_m = C(P/P_o) / [(1-P/P_o)(1-P/P_o+C(P/P_o)] \qquad 2-3$$

where, P_o is the vapor pressure of a pure fluid, N is the number of moles adsorbed and C is a constant related to the fraction of surface that is uncovered.

The theory assumes that molecules adsorb in stacks or layers and that the upper most molecules in the adsorbed stacks are in equilibrium with the vapor. The first adsorbed layer is treated separately and all the layers above the first layer are condensed and treated as a liquid. Other assumptions are that the surface is homogeneous, there are no lateral interactions between adsorbed molecules i.e. localized adsorption and the fluid is an ideal gas. The BET equation is quite successful in the range $0.05 < P/P_o < 0.35$ and sub-critical temperatures of the fluid.

POTENTIAL THEORIES:

The potential theories assume that a potential field exists on the surface of the solid which attracts the fluid particle. The oldest of these is the Polanyi theory which states that the cumulative volume of the adsorbed space is a function of the potential energy of the surface. This function is called the characteristic curve. Dubinin postulated different forms of the characteristic curve for different types of adsorbents. The Slab theory or the Frenkel-Halsey-Hill theory (FHH) gives an approximation of the form of the adsorption potential. This form is valid at large thicknesses of the adsorbed layer.

Polanyi Theory:

The Polanyi equation (Polanyi, 1914) can be written as follows :

$$\ln (P/P_0) = \varepsilon_i/kT \qquad 2\text{-}4$$

where, ε_i is the potential energy of an equipotential surface enclosing a volume V_i which is being filled at a relative pressure (P/P_0) and k is the Boltzmann constant. The cumulative volume of the adsorbed space is a function of ε_i. This function is characteristic of the particular gas-solid system and hence is referred to as the characteristic curve. The characteristic curve is independent of temperature since the adsorption potential expresses the work of temperature independent dispersion forces. If the characteristic curve is determined at one temperature it is possible to predict adsorption isotherms at other temperatures for the same gas-solid system. One of the drawbacks of this theory is that ε_i is a free energy and not a potential energy and therefore it is a function of temperature.

Dubinin-Radhuskevich Equation

The approach of Dubinin and his co-workers (1960), is empirical and based on the Polanyi equation. They postulated the functional form of the characteristic curve using semi-empirical functions for two types of adsorbents. For microporous adsorbents like activated carbon the following form, often called the Dubinin-Radushkevich equation is used:

$$W = W_0 \exp(-k\varepsilon^2 / \beta^2) \qquad 2\text{-}5$$

where, W_0 is the limiting volume of the adsorbed space, which equals the micropore volume, β is the affinity coefficient characterizing the polarizability of the adsorbate and k is the Boltzmann constant. The affinity coefficient, β, is intended to be a shifting factor to bring the characteristic curves of all gases on the same adsorbent into a single curve. For adsorbents with large pores like carbon black, the following characteristic curve is used:

$$W = W_0 \exp(-k\,\varepsilon / \beta) \qquad 2\text{-}6$$

FHH Theory

The Slab theory [Frenkel (1946), Halsey (1948, 1952) and Hill (1949)]also called the Frenkel-Halsey-Hill (FHH) theory allows the adsorption potential to vary as the inverse cube of the distance from the surface. The simplest form of the FHH isotherm is:

$$\ln(P/P_0) = -\Delta\varepsilon_1 / n^3kT \qquad 2\text{-}7$$

where, n is the layer number, $-\Delta\varepsilon_1$ is the net interaction energy of the first layer and k is the Boltzmann constant. Layers are assumed to develop at discrete distances from the surface, thus the isotherm predicts that discrete steps exist, a fact that can be found in only a very few experimental cases.

In order to predict realistic multilayer isotherms the solid surface has to be heterogeneous, which means that the adsorption potential can no longer be a function of distance from the surface. One has to add the tangential variation of the potential. This changes the n^3 dependence to a θ^r dependence where θ is the surface coverage and r is a measure of the rate of decay of the gas-solid interaction energy. The value of r is slightly less than 3.

The heterogenity of the adsorbate can be handled by a perturbation technique. When the solid surface is homogeneous the θ^r dependence becomes θ^3 i.e. $r = 3$. Singelton and Halsey (1954) included a perturbation of the adsorbate by introducing two parameters:

1. A lateral interaction parameter, w.
2. A factor 'g' which measures the compatibility of the adsorbed film with the bulk adsorbate when perturbed by the adsorbent.

They proposed the following isotherm:

$$\ln (P/P_0) = -\Delta\varepsilon_1 / \theta^3 kT + w (1-g) / kT \qquad 2-8$$

where θ is the surface coverage and k is the Boltzmann constant. The empirical nature of parameters w and g is a major limitation of this theory.

EQUATION OF STATE APPROACH:

The theories based on the equation of state approach simplify the description of the fluid structure. The Hill-deBoer model assumes that the adsorbed layer can be represented by a two-dimensional van der Waals' fluid. The model of Barrer and Robins and the simplified local density model (SLD) assume that the fluid obeys the vdW equation of state and the fluid-wall potential used is some form of the integrated Lennard-Jones potential. Equation of state-based isotherms have been successfully used to model supercritical adsorbers [Akman and Sunol (1991)].

Hill-deBoer Theory

The Hill-deBoer theory is discussed in detail in the books by deBoer (1953) and Ross and Oliver (1964). In this model, the adsorbed film is considered to be a two dimensional gas. Unlike the Langmuir theory, the Hill-deBoer theory allows the adsorbed molecules to move laterally within the 2-D phase and desorption can take place from anywhere on the surface. Hence in this case the film is mobile.

The two dimensional gas is represented by a two dimensional van der Waals equation of state

$$(\pi + \alpha / \sigma^2)(\sigma - \beta) = kT \qquad 2\text{-}9$$

where, π is the two dimensional spreading pressure, σ is area per molecule, α and β are the 2-D analogs of a and b in the three dimensional van der Waals' equation of state and k is the Boltzmann constant.

The isotherm equation is :

$$p = K\,\theta/(1-\theta)\,\exp[\,\theta/(1-\theta) - 2\,\alpha\,\theta/(\,k\,T\,\beta\,)\,] \qquad 2\text{-}10$$

where, p is the pressure, K is a constant and θ is the fraction of surface covered by adsorbed molecules.

The Model of Barrer and Robins:

Barrer and Robins (1951), assumed that the adsorbate fluid obeyed van der Waals' equation of state and the interaction energy between the adsorbent and the fluid could be approximated by the integrated 9-3 Lennard Jones potential (the repulsive part was neglected). At equilibrium, the chemical potential of the bulk gas μ_b is equal to the chemical potential of the adsorbed gas μ, i.e.,

$$\mu = \mu_b \qquad 2-11$$

$$\theta/(1-\theta)\exp(\theta/(1-\theta) - 2a\theta/bRT - CN/r^3RT) = \theta_b/(1-\theta_b)\exp(\theta_b/(1-\theta_b) - 2a\theta_b/bRT) \qquad 2-12$$

where a and b are van der Waals constants, R is the universal gas constant, T is the temperature, N is total number of molecules in the system, n is the total number of moles in the system, θ is bn/V; the fraction of the total volume V occupied by closely packed molecules, θ_b is bn/V_b; the fraction of the total volume V_b occupied by closely packed molecules in the bulk of the fluid, r is the distance of the fluid molecule from the surface and C is an empirical constant.

Let v equal the molar volume of the fluid in contact with the adsorbent and let v_b equal the molar volume of the bulk fluid, then equation 2 - 12 may be rewritten in the more conventional form as follows :

$$1/(v-b)\exp[b/(v-b) - 2a/vRT - CN/r^3RT] = 1/(v_b-b)\exp[b/(v_b-b) - 2a/v_bRT] \qquad 2-13$$

This model predicts isotherms that give qualitative agreement with experimental results but in order to get quantitative agreement one needs to manipulate the value of C. One possible reason for this quantitative disagreement is the form of the fluid-wall interaction potential. Steele (1969) and Lee (1990) show that the 9-3 Lennard-Jones potential under predicts the interaction energy and suggest the use of the partially integrated 10-4 potential. Hill (1951) suggests further improvements for this model. Hill (1952), replaces the repulsive part of the van der Waals equation by Tonk's expression for hard spheres. Also the chemical potential at a distance r' from the surface is not determined from the local density contribution (as in the case of Barrer and Robins model) but from the entire density distribution. The disadvantage of this treatment is the fact that a nonlinear integral equation must be solved.

The Simplified Local Density Model:

This approach was developed by Rangarajan(1992). It is similar to the model of Barrer and Robins. The basic assumptions of this model are :

1) The fluid obeys the van der Waals' equation of state.

2) The fluid-wall potential is in the form of the 10-4 integrated Lennard-Jones potential, both the attractive and repulsive parts are considered in calculations.

3) The attractive van der Waals' parameter is forced to vary with distance from the adsorbing surface.

The model gives good qualitative predictions of adsorption isotherms, density profiles of the adsorbed fluid and phase transition near the surface of the adsorbent. To get quantitative agreement, the fluid - solid interaction parameter has to be adjusted. One reason could be that the van der Waals' equation of state is not good at predicting properties of liquids. More details of this theory will be discussed in Chapters 3 and 4.

CHEMICAL PHYSICAL MODELS :

These models are based on the principles of statistical mechanics. The Lattice Gas model predicts only monolayer coverage. The distribution function approach of Ross and Steele was one of the first multilayer theories. As the theory of liquid states advanced; a number of approaches based on solving the integral equations for the radial distribution function were developed. An entirely different approach is the various density functional theories. Vanderlick et al. (1989), have compared different density functional calculations with the BGY method. Evans et al. (1983) lists advantages and disadvantages of different density functional and integral equation theories.

Lattice Gas Model:

In the case of localized adsorption, the surface of the solid has sites on which fluid molecules are adsorbed. The adsorbed molecules vibrate around the sites. These sites are considered to be lattice points. This is the Lattice Gas Model which has been studied by Pandit et al. (1982). With simplifying assumptions this model gives the Langmuir isotherm and the BET isotherm.

Distribution function approach:

The distribution function approach was developed by Steele and Ross (1960). They treated a one-component fluid with two-body forces in an external field (the external field is generated by interaction between wall and fluid molecules) which is a function of position only. The total potential energy of the system of N atoms is

$$U\ (r_1,\ldots,r_N) = \Sigma\ u_s(r_i) + \Sigma u(r_{ij}) \qquad 2\text{-}14$$

where, $u_s(r_i)$ is the energy of the ith atom at position r_i due to the external field and $u(r_{ij})$ is the mutual interaction energy of atoms i and j in the fluid a distance r_{ij} apart.

For Steele's approach the singlet probability distribution function $\rho^1(r_1)$ and the pair probability distribution function $\rho^2(r_1,r_2)$ are considered. The potential energy of the ith molecule at its position ri is given by

$$U(r_i) = \rho^1(r_i)u_S(r_i) + \int \rho^2(r_i,r_j)\ u_2(r_i,r_j)\ dr_j \qquad 2\text{-}15$$

The relationship between the distribution function and the local pressure tensor $P_{XX}(r_i)$, $P_{YY}(r_i)$ and $P_{ZZ}(r_i)$ are derived. The component $P_{ZZ}(r_i)$ is normal to the plane of the surface of the fluid and is equal to the ordinary pressure exerted by a homogeneous phase in equilibrium with the adsorbed phase.

At equilibrium $P_{ZZ}(r_i)$ is independent of z_i, therefore the partial differential of $P_{ZZ}(r_i)$ w.r.t. z_i is zero, which results in an integral equation relating $\rho^1(r_i)$ to $\rho^2(r_i,r_j)$ in terms of the intermolecular forces. For given intermolecular potential functions $\rho^1(r_i)$ and $\rho^2(r_i,r_j)$ can be computed and hence the number of molecules adsorbed can be calculated. The calculations are exact for fluids with pairwise interactions. For low densities the distribution functions can be expanded in terms of the activity, which yields cluster integrals and virial expansions of equations. For higher adsorbate densities (in the case of multi-layer adsorption) the theory becomes more complicated. [Pierotti and Thomas (1971), Hill and Greenschlag (1961), Hill and Saito (1961)].

Integral Equation Theories:

The fluid near the wall behaves like a liquid, as the fluid moves away from the wall it behaves more like a gas. Therefore the equations used to calculate the fluid local density should represent the behavior of non-ideal fluids. One of the first attempts at calculating the local density was by using a virial expansion of the local density in terms of the bulk density [Pierotti and Thomas (1971)]. With advances in the theory of the liquid state, other approaches were developed.

The central idea in most modern theories of the liquid state is the radial distribution function, g(r). It is defined as [McQuarrie (1976)] :

$$g(r) = \frac{V^2 N!}{N^2 (N-2)!} \frac{\int \ldots \int e^{-\beta U_N} d\mathbf{r}_3 \ldots d\mathbf{r}_N}{Z_N} \qquad 2-16$$

where, there is a system of N particles in a volume V and at temperature T, Z_N is the configurational integral, $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 \ldots$ are coordinates in space and r is the intermolecular distance between two coordinates. If the total potential energy of an N-body system can be assumed to pair-wise additive, then all the thermodynamic properties of the system can be derived in terms of the radial distribution function.

A number of approximate equations have been derived for g(r). These different equations are collectively known as Integral Equations. Two approaches have been the most important; the hierarchy approach used to derive the Kirkwood integral equation and the Born-Green-Yvon (BGY) equation, and the direct correlation approach which includes the Ornstein-Ziernike equation, which can be used to derive the Percus-Yevick (PY) equation and the hypernetted chain (HNC) equation. Details of deriving these equations and comparisons of their predictions are discussed by McQuarrie (1976).

The use of the Ornstein-Ziernike equations for interface calculations has limited success. For the case of hard spheres in contact with a hard wall, the PY and the HNC closures yield density profiles which are in considerable error close to the wall. In this approach the the wall must be plane and cannot be allowed to show any atomic structure therefore this approach can never be used to model realistic fluid - solid situations.

Fischer and Methfessel (1980), developed the Born-Green-Yvon (BGY) approach to local densities of a fluid at interfaces. The local density of the non-uniform fluid was calculated from the first equation of the BGY hierarchy by modelling the pair correlation function. The mean force term was divided into a repulsive part and an attractive part. The repulsive part was approximated by a hard-sphere interaction and the pair correlation function was taken locally. The particles were assumed to be uncorrelated in the attractive part. They studied three cases : (a) the free liquid surface, (b) gas adsorption on a wall at low temperatures, and (c) a liquid in contact with a wall. In all three cases the results were in good agreement with computer simulations.

Density Functional Theory :

The key concept in the density functional theory is that there exists a functional Ω of the local number density $\rho(r)$, such that the equilibrium $\rho(r)$ minimizes Ω. This concept has been successfully applied to liquid helium and the electron gas, and an exact form of the functional can be calculated for classical fluids [Ebner et al. (1976); Ebner and Saam (1977) and Saam and Ebner (1977)].

In the density functional theory, a Helmholtz free energy functional F is minimized at equilibrium.

$$F = F\,(f(r),\, \rho(r),\, c(r_1,r_2)\,) \qquad 2 - 17$$

where, f(r) is the local free energy, $\rho(r)$ is the local density and $c(r_1,r_2)$ is the direct correlation function. At equilibrium F has a minimum value. This condition gives an integral equation for local density $\rho(r)$ in terms of the fluid-fluid and fluid-wall potentials and the direct correlation function.

Sullivan (1979), developed the van der Waals' model for adsorption, which can be considered to be an approximate form of the density functional theory. Teletzke et al. (1983), generalized Sullivan's model and applied it to predict wetting transitions for thin films. Tarazona and Evans (1984), developed a simple free energy functional which incorporated both 'local' thermodynamics and short ranged correlations.

Kierlik and Rosinberg (1990, 1991) proposed a simplified version of the free-energy density functional for the inhomogeneous hard-sphere fluid mixture, which requires four distinct weight functions and generates a triplet direct correlation function for the one component fluid. This theory gives results in good agreement with Monte Carlo simulation results and performs well in predicting the density profile of a hard-sphere fluid in contact with hard and soft walls.

SUMMARY

For the conceptual design of an adsorbent system, the knowledge of adsorption isotherms is required for adsorbent selection, adsorption configuration, selection of regenerant and in selection of pretreatment methods. Of the considerable number of theories to predict adsorption isotherms none are known to make satisfactory predictions in all conditions. For engineering design purposes a model needs to give an accurate representation of the equilibrium between the fluid phase and the solid surface, the accuracy of the molecular interactions is not always important.

This is why the early theories of adsorption such as the Langmuir theory, the BET theory and the Polanyi theory are used in calculations, even though their assumptions have limited validity. Unfortunately, these theories have limited applicability which is mainly due to their invalid assumptions. Another disadvantage is that in order to use any of these models one has to perform experiments to generate data to evaluate the parameters for the model. This can be a time consuming process which can not always be justified for conceptual design of the system.

It would be desirable to have a general theory of adsorption which can be applicable to all types of fluid-solid systems, this would require the theory to describe the molecular interactions with more precision. The interactions in an adsorption system is complex, it deals with matter density ranges from gas to dense liquids and even solids, also the surface of the adsorbent is heterogeneous and there is no uniformity of the potential. Advances in the field of chemical physics has lead to several molecular

theories of adsorption which discuss all these complex molecular interactions. Of the molecular theories, the different density functional theories seem to hold the most promise. However due to the lengthy calculations involved and the difficulty in obtaining parameters for different substances required for successful applications of these theories, their use in designing/modeling adsorption equipment has been avoided.

The equation of state based models are somewhere between the early empirical models and the advanced molecular theories based on chemical physics. These models recognize the idea that molecular interactions between the adsorbent and the adsorbate are important to get an accurate prediction of equilibrium conditions. However they simplify the description of the fluid structure by choosing an equation of state to represent fluid properties. This approach thus compromises accuracy of molecular interactions with simplicity. For design purposes one is primarily interested in the equilibrium characteristics and most popular equations of states can give excellent representation of equilibrium properties inspite of their inaccuracy on the molecular level. Therefore the model of Barrer and Robins or the SLD can be used to predict adsorption isotherms which would satisfy the needs for conceptual design of adsorption systems. One of the parameters in Barrer and Robins' model requires experimental data to determine it's value. The SLD does not require experimental data for it's parameters: it uses Lennard-Jones parameters for the adsorbent and adsorbate which are readily available or can be easily calculated using different correlations and the critical properties of the fluid which are also available in tabulated form.

Therefore the SLD model is a desirable candidate for predicting adsorption isotherms for use in design of adsorption systems. All the parameters used are easily available in literature so there is no need to perform adsorption experiments to obtain parameters. Due to the assumptions it makes on the molecular level it is applicable over a wide range of pressures and temperatures and is not limited to ideal gases. This thesis will study the application of the SLD and determine the range of pressures and temperatures where it is most applicable.

CHAPTER 3

THE SIMPLIFIED LOCAL DENSITY MODEL

The simplified local density model was proposed by Rangarajan (1992). A fluid molecule at any position from the solid interacts with the solid adsorbent and with the bulk fluid molecules. At equilibrium, these interactions are balanced. Therefore the chemical potential is uniform for the entire system. According to Rangarajan (1992), the chemical potential of the fluid at a position z from the solid wall can be written as:

$$\mu(z) = \mu_{ff}(z) + \mu_{fw}(z) = \mu_b \qquad 3\text{-}1$$

where, $\mu(z)$ is the chemical potential, $\mu_{ff}(z)$ is chemical potential due to fluid-fluid interactions, $\mu_{fw}(z)$ is the chemical potential due to fluid-solid wall interactions and μ_b is the chemical potential of the bulk fluid.

The Fluid-Solid Potential $\mu_{fw}(z)$

The fluid-solid potential is a function of the distance of the fluid molecule from the solid, but for a given position it is independent of the number of molecules at or around that position. The potential is also independent of the temperature of the system. The fluid-solid potential chosen is the partially integrated Lennard-Jones potential recommended by Lee (1990).

$$\mu_{fw}(z) = 4\,\pi\,\rho_a\,\varepsilon_{fw}\,\sigma_{fw}^6 \{ \sigma_{fw}^6/5/z^{10} - 1/2*1/\Sigma z_i^4 \} \qquad 3\text{-}2$$

where, ρ_a=density of solid, ε_{fw} and σ_{fw} are the Lennard-Jones parameters for the fluid-solid system, z is the distance from the solid and z_i is the distance from the ith layer of the solid.

The Lennard-Jones parameters for the fluid-solid system are determined as follows:

$$\sigma_{fw} = (\sigma_{ff} + \sigma_w)/2 \qquad 3-3$$

$$\varepsilon_{fw} = \sqrt{(\varepsilon_{ff}\, \varepsilon_w)} \qquad 3-4$$

where, the subscripts ff and w represent pure fluid and pure solid parameters, w is used instead of s to represent the fact that in the case of adsorption one is interested in the surface properties of the solid adsorbent and often the solid surface is referred to as a "wall".

The fluid-fluid potential $\mu_{ff}(z)$

As the distance from the solid increases, the effect of μ_{fw} decreases. When z is very large, the chemical potential $\mu(z)$ equals the chemical potential of the bulk fluid μ_b:

$$\mu(z) = \mu_{ff}(z) = \mu_b \qquad 3-5$$

For a fluid the chemical potential can be given by:

$$\mu_b = RT\ln f_b \qquad 3-6$$

where, f_b is the fugacity of the bulk fluid given by

$$\ln(f/P) = \int_0^P (v/RT-1/P)\, dP = \int_0^P (Z-1)/P\, dP \qquad 3-7$$

where, v is the molar volume, T is temperature, P is the pressure, R is the universal gas constant and $Z = Pv/RT$.

The integral can be determined for a known equation of state. Let the fluid properties be represented by the van der Waals' equation of state, then

$$\ln f_b = \ln(RT/(v_b-b)) + b/(v_b-b) - 2a_b/(v_bRT) \qquad 3-8$$

where, b is the close packed volume and a_b is related to the attractive potential between fluid molecules. The subscript b represents bulk properties. According to the pressure equation [McQuarrie (1976)] the constant "a" can be written as:

$$a = \sigma^3\varepsilon/6 * \int x(du/dx)\, g(x)\, 4\pi x^2\, dx \ , \quad x = r/\sigma \qquad 3 - 9$$

where, u is the fluid-fluid interaction potential. In the van der Waals' equation this is the Sutherland potential, which can be expressed as follows :

$$u(r) = \infty \qquad r < \sigma \qquad 3 - 10\,(a)$$

$$u(r) = \varepsilon\,(\sigma/r)^6 \quad \sigma < r < \infty \qquad 3 - 10\,(b)$$

where, r is the intermolecular distance and g(r) is the radial distribution function. Substituting in equation 3 - 9 we get :

$$a = (4/3)\,\pi\,\varepsilon\,\sigma^3 \qquad 3 - 11\,(a)$$

If instead of the pressure equation approach, one were to use the partition function approach, then we would have :

$$\mu_{ff} = \mu_{rep} + \mu_{att} \qquad 3 - 11\,(b)$$

where μ_{rep} is the contribution of repulsive forces and μ_{att} is the contribution of the attractive forces. Rangarajan (1992) uses this approach to calculate μ_{ff}. The difference between the pressure equation approach and the partition function approach appears in the attractive term 'a'

$$a = (2/3)\,\pi\,\varepsilon\,\sigma^3 \qquad 3 - 11\,(c)$$

Another complication is the value of ε and σ. For the fluid - solid potential Lennard - Jones parameters are used, but the vdW EOS assumes that the fluid molecules interact according to Sutherland potential so the ε and σ values for calculating 'a' are different. There is also some disagreement on the actual value of these parameters for pure substances. To avoid these problems we chose to calculate a and b from critical properties of the fluid as follows :

$$b = 0.125\, R\, T_c / P_c \qquad 3 - 12$$

$$a = 27 / 64\, (RT_c)^2 / P_c \qquad 3 - 13$$

The integral of equation 3 - 9, can be applied to any substance. van der Waals' assumed that the integral was independent of the number density ρ and the temperature T. The actual radial distribution function is a function of ρ and T, but it's value oscillates around unity and therefore when integrated it shows a weak density dependence.

For a homogeneous fluid the van der Waals' equation of state may be derived from the pressure equation of statistical mechanics [McQuarrie (1976)].

$$P/\rho kT = 1 - \rho/6kT\int r(du/dr)\, g(r)\, 4\pi r^2\, dr \qquad 3 - 14$$

or $$P/\rho kt = 1 - \rho\sigma^3\varepsilon/6kT\int x(du/dx)\, g(x)\, 4\pi x^2\, dx \qquad x=r/\sigma \qquad 3 - 15$$

where ρ is the number density and k is the Boltzmann constant.

When the fluid is near the solid it is no longer homogeneous, therefore the number density should be put back in the integral. The two body potential is short ranged (~ r^{-6}) and the product of the density and the partial derivative of the potential with respect to x appears in the integral. The major contribution to the integral will be from the values of the potential and ρ near x. Therefore it might be possible to use the local density at x and pull ρ out of the integral. This is the local density approximation. This works because at distances far from x the two body interaction potential is negligible so there is no significant contribution to the integral.

Therefore at a distance z from the wall the chemical potential due to fluid-fluid interactions will be:

$$\mu_{ff}(z) - \mu_o = RT\ln(f(z)/f_o) \qquad 3 -16$$

$$\ln(f(z)) = \ln(RT/(v(z)-b)) + b/(v(z)-b) - 2a(z)/v(z)/R/T \qquad 3 -17$$

$$\ln(f(z)) = \ln(f_b) - N_A\mu_{fw} \qquad 3 -18$$

where, μ_o and f_o are respectively the chemical potential and the fugacity of the fluid at a fixed reference state.

The details of the calculation of a(z), v(z) and the computer program for adsorption calculations using this model are described by Rangarajan (1992). The attractive term a(z) is calculated as follows depending on the distance of the fluid molecule from the adsorbent.

At $0.5\,\sigma \le z \le 1.5\,\sigma$

$$a(z) = a_{bulk}\,[\,5/16 + (6/16)\,(z/\sigma)] \qquad 3-19$$

At $1.5\,\sigma \le z \le \infty$

$$a(z) = a_{bulk}\,[1 - (1/8)\{z/\sigma - 1/2\}^3] \qquad 3-20$$

where σ is the Lennard-Jones parameter "σ" which can be either σ_{ff} or σ_{fw}.

The value of v(z), is calculated from equation 3-17, using numerical techniques. However, below the critical point there maybe three values of v that satisfy the equation and the stable value of v is the one which gives the highest pressure. Rangarajan (1992) suggested the following methods to solve for the roots:

(1) Rewrite equation 3 - 17 as

$$v(z) = b + b/[\ln f(z)(v(z)-b)/RT) + 2a(z)/(v(z)RT)] \qquad 3-21$$

Using successive substitution this equation will provide a decreasing value of v(z). The initial guess is taken to be $v(z)=1.1*b$. This method will converge to a liquid root.

(2) Rewrite equation 3 - 17 as

$$v(z) = b + \{RT/f(z)\}\exp[\,b/(v(z)-b) - 2a(z)/(v(z)RT)] \qquad 3-22$$

Using successive substitution this converges to give the vapor root. The initial guess for v(z) used is $v(z) = RT/f(z)$. Once the roots are obtained they are arranged in increasing order of magnitude and the one that gives the highest value for pressure is selected. Stability test that $dP/dv < 0$ is made to ensure that the root selected is stable. Once the density profile is generated the surface excess is calculated using the following equation:

$$\Gamma^{ex} = \int_{z_0}^{\infty} [\rho(z) - \rho_{bulk}]\, dz \qquad 3-23$$

Reduced distance units : ETA and BETA

For the sake of convenience it was decided to use reduced distance units throughout the program code. To calculate fluid-wall interaction potential i.e. $\mu_{fw}(z)$, the reduced unit used was ETA which is calculated as follows :

$$ETA = z / \sigma_{fw} + 0.5\, \sigma_w / \sigma_{fw} \qquad 3-24$$

But for a(z) calculations one requires that the reduced distance units be in terms of the fluid-fluid parameters σ_{ff}. So for a(z) calculations the reduced unit BETA was used.

$$BETA = z / \sigma_{ff}. \qquad 3-25$$

The two reduced units can be interrelated as follows:

$$BETA = \{ ETA - 0.5\, \sigma_w / \sigma_{fw} \} * \sigma_{fw} / \sigma_{ff} \qquad 3-26$$

The modified SLD : PRSLD

To represent the fluid properties in the SLD model any equation of state may be used. The advantage of using the van der Waals' equation [Rangarajan (1992)], is that it is the simplest and most convenient equation of state that has a theoretical basis. The drawbacks are that it is not an accurate equation of state and gives poor predictions of vapor pressure and molar volume. The vdW equation does a good job in qualitative description of fluid behavior but it performs poorly in the field of quantitative predictions.

One of the objectives of this thesis was to improve the original SLD model by using a better equation of state to represent the fluid properties. As shown in equation 3 - 13, van der Waals assumed 'a' to be independent of temperature. Most improved equations of state propose semi-empirical corrections for 'a', and have the form a = a(T). Of these equations the Peng-Robinson (1976), equation of state gives the best representation of fluid properties such as saturation pressure and liquid densities. The Peng-Robinson equation is:

$$P = RT/(v-b) - a/(v^2+2bv-b^2) \qquad 3 - 27$$

where:

$$b = 0.0778\, T_c R / P_c \qquad 3 - 28$$

$$a = 0.45724\, (RT_c)^2\, \alpha / P_c \qquad 3 - 29$$

$$\alpha = [1+(0.37464+1.54226\omega-0.26992\omega^2)(1-(T_r)\hat{}0.5)]^2 \qquad 3 - 30$$

$$\omega = -1 - \log_{10}(P^{sat}/P_c)\,|_{Tr=0.7} \qquad 3 - 31$$

where, ω is the acentric factor, P^{sat} is the saturation pressure or the vapor pressure of the fluid, T_r is the reduced temperature, $T_r = T/T_c$.

This equation can be rewritten as

$$Z^3 - (1-B)Z^2 + (A-3B-2B)Z - (AB-B^2-B^3) = 0 \qquad 3 - 32$$

where:

$$A = aP/R^2T^2 \qquad 3 - 33$$

$$B = bP/RT \qquad 3 - 34$$

$$Z = vP/RT \qquad 3 - 35$$

The fugacity of a Peng-Robinson fluid may be calculated from the following equation:

$$\ln(f/P) = Z-1-\ln(Z-B)-A/(2.824B)*\ln((Z+2.414B)/(Z-0.414B)) \qquad 3 - 36$$

The attractive term a(z) is calculated using equations 3 - 19 and 3 - 20. The value of a_{bulk} in these equations is calculated using equations 3 - 29 thru 3 - 31. The same type of algorithms are used to calculate v(z) the corresponding equations are as follows:

For method (1) the equation equivalent to equation 3 - 21 is :

$$v(z) = b + b/DENO \tag{3 - 37}$$

$$\begin{aligned} DENO = \{&\ln f(z) + \ln(v(z)-b)/RT + a(z)v(z)/(RT(v(z)^2+2bv(z)-b^2)) \\ &+a(z)/(2.824RTb)^{*} \ln[(v(z)+2.414b)/(v(z)-0.414b)]\} \end{aligned} \tag{3 - 38}$$

For method (2) the corresponding equation for a Peng - Robinson fluid is:

$$v(z) = b+RT/f(z) \exp FUNC \tag{3 - 39}$$

$$\begin{aligned} FUNC = \{&b/(v(z)-b) - a(z)v(z)/[RT(v(z)^2+2bv(z)-b^2)] + a(z)/[2.824RTb] \\ &{}^{*}\ln[(v(z)-0.414b)/(v(z)+2.414b)]\} \end{aligned} \tag{3 - 40}$$

The computer program used to calculate surface excess using the PRSLD is described in Appendix B.

The PR equation of state is better at predicting vapor pressure and molar volume than the vdW equation, it was expected that by using the PR equation in the SLD would improve the quantitative aspect of the predicted adsorption isotherms. This is because the PR equation predicts more realistic values of fluid densities near the solid - fluid interface and also predicts more accurate values of the vapor pressure for subcritical temperatures. Figures 3 - 1, 3 - 2 and 3 - 3 compare the adsorption isotherms predicted for carbon dioxide, ethane and ethylene, using vdW and PR equations of state.

The PRSLD model predicts higher adsorption than the vdWSLD for the same value at ε_{fw} at same T and P. The reason is that the PRSLD predicts a higher value of density at each position from the wall, $\rho(z)$, than the vdWSLD. Thus the term $(\rho(z)-\rho_{bulk})$ is higher at each position from the wall for the PRSLD model. As seen in Figure 3 - 4 the PRSLD predicts higher density values near the solid wall than the vdWSLD. This is because the vdW equation under predicts liquid densities. A comparison between experimental saturation densities for ethylene (Angus et. al., 1974) and values predicted using the vdW and PR equations of state are shown in Table 3 - 1.

Table 3 - 1 : A comparison of the experimental values of bulk saturation liquid densities for ethylene (Tc = 282.4 K, Pc = 50.4 bar) with values predicted by the vdW and PR equations of state.

T (K)	Bulk saturation liquid density (mol/cu.m)		
	Expt.	vdW	PR
269.000	12937.9496	7231.86069	12189.9189
255.000	14640.6454	7929.71104	14573.9878
241.000	15907.8617	8487.16317	16372.6949
225.000	17077.9609	9042.00009	18030.5907
211.000	17965.2552	9485.14626	19247.7591

Comparison of the vdWSLD, the PRSLD and experimental isotherms is complicated by the differences in predicted vapor pressure values given by the vdW and PR equations respectively and the experimentally obtained value of the vapor pressure. The predicted adsorption isotherms depend on the efw value chosen. Since the relationship between abulk and eff is uncertain it was decided to let efw be an adjustable parameter. Figures 3 - 5, 3 - 6 and 3 - 7 compare predicted isotherms of vdWSLD and PRSLD models against experimental values of Findenegg (1983) for ethylene on Graphon. The efw value for the best fit was the same for each model for all temperatures, 350 for vdWSLD and 150 for PRSLD.

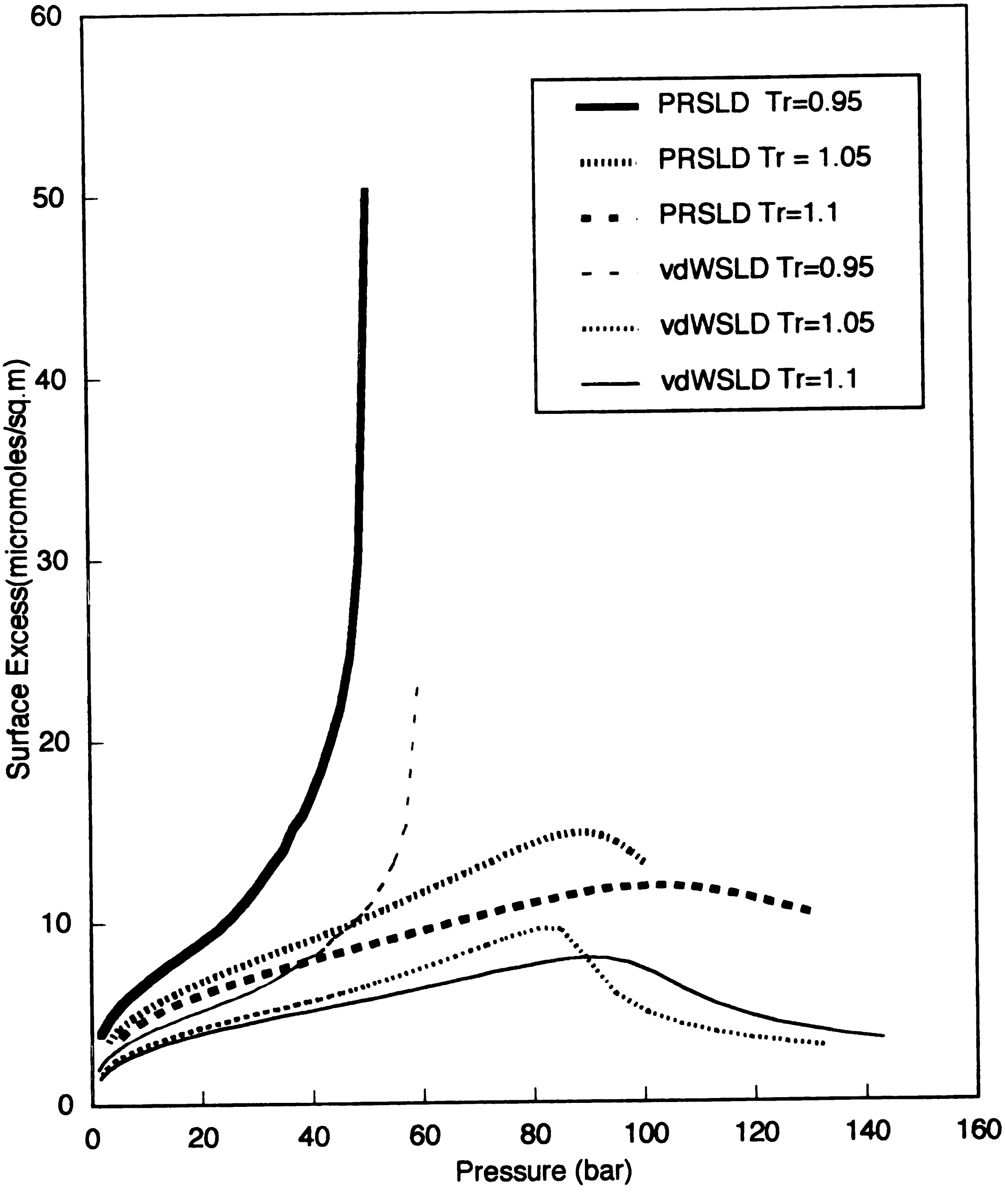

Figure 3-1 : Adsorption isotherms predicted using the vdWSLD & PRSLD models for Carbon dioxide (Tc=304.1 K, Pc=73.8 bar) for the ratio $\varepsilon_{W} / \varepsilon_{FF} = 0.25$.

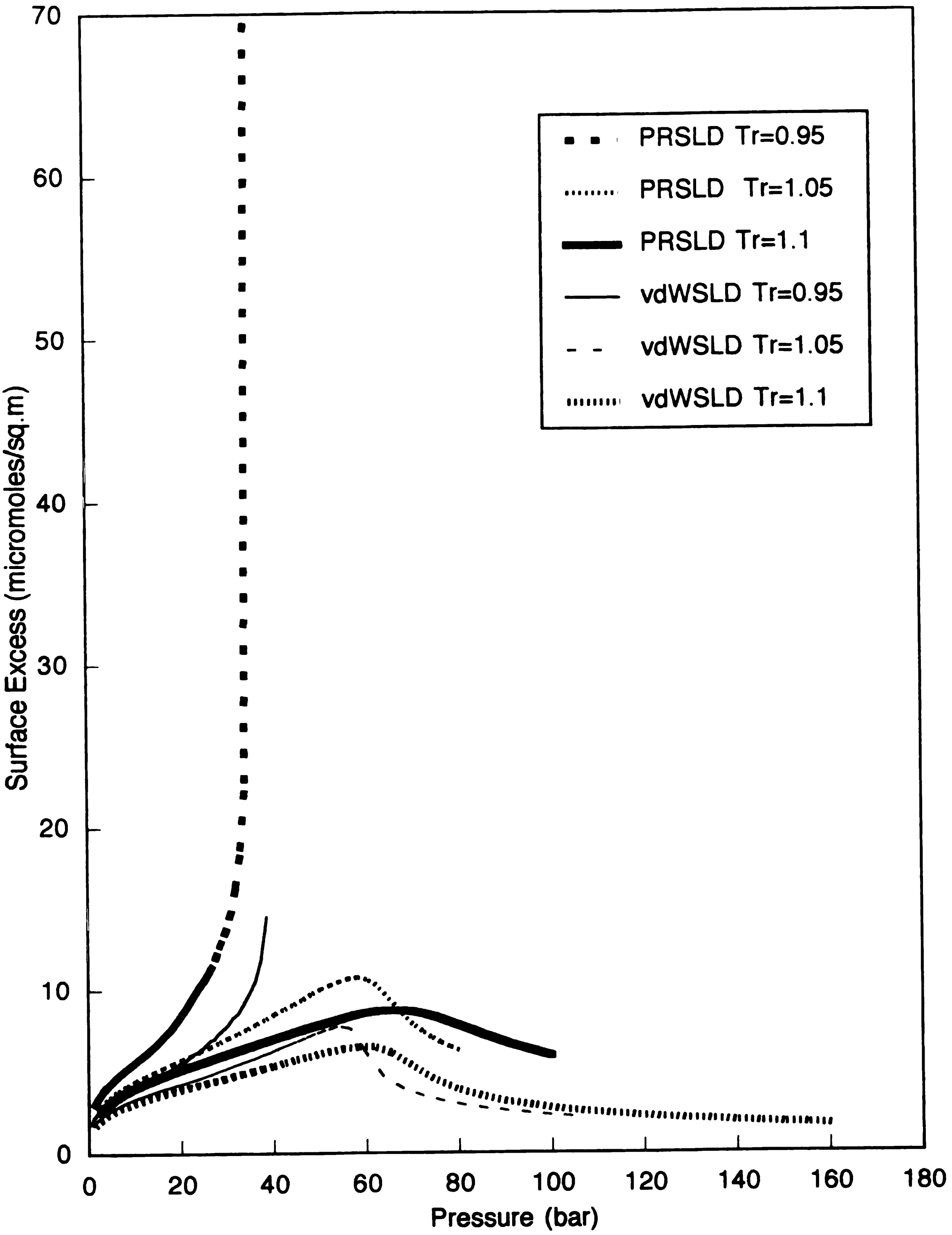

Figure 3-2 : Adsorption isotherms predicted using the vdWSLD & PRSLD models for Ethane (Tc = 305.4 K,Pc = 48.8 bar) for the ratios $\varepsilon_W / \varepsilon_{FF} = 0.25$.

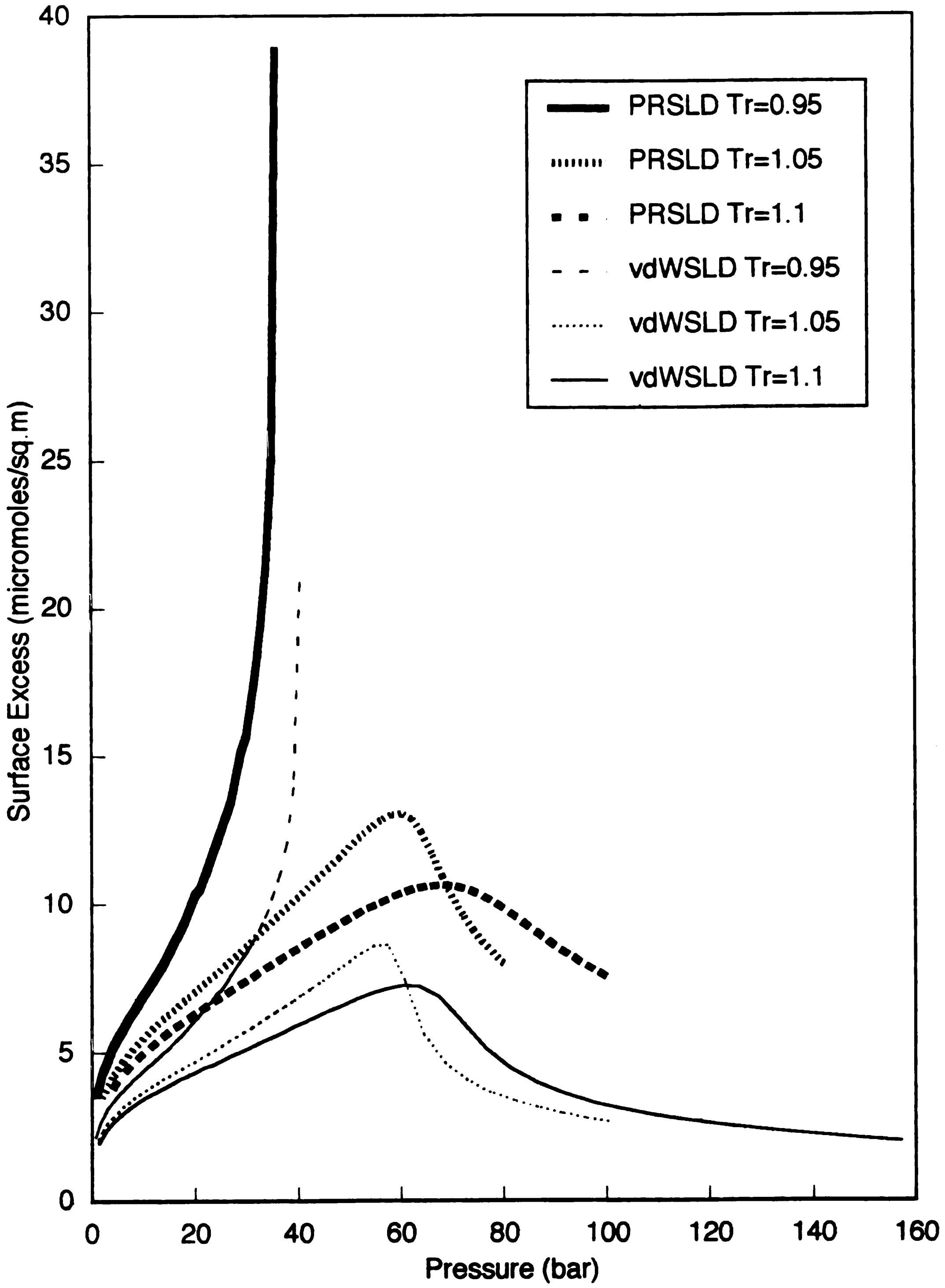

Figure 3-3 : Adsorption isotherms predicted using the vdWSLD & PRSLD models for Ethylene (Tc = 282.4 K, Pc = 50.4 bar) for the ratios $\varepsilon_W / \varepsilon_{FF} = 0.25$.

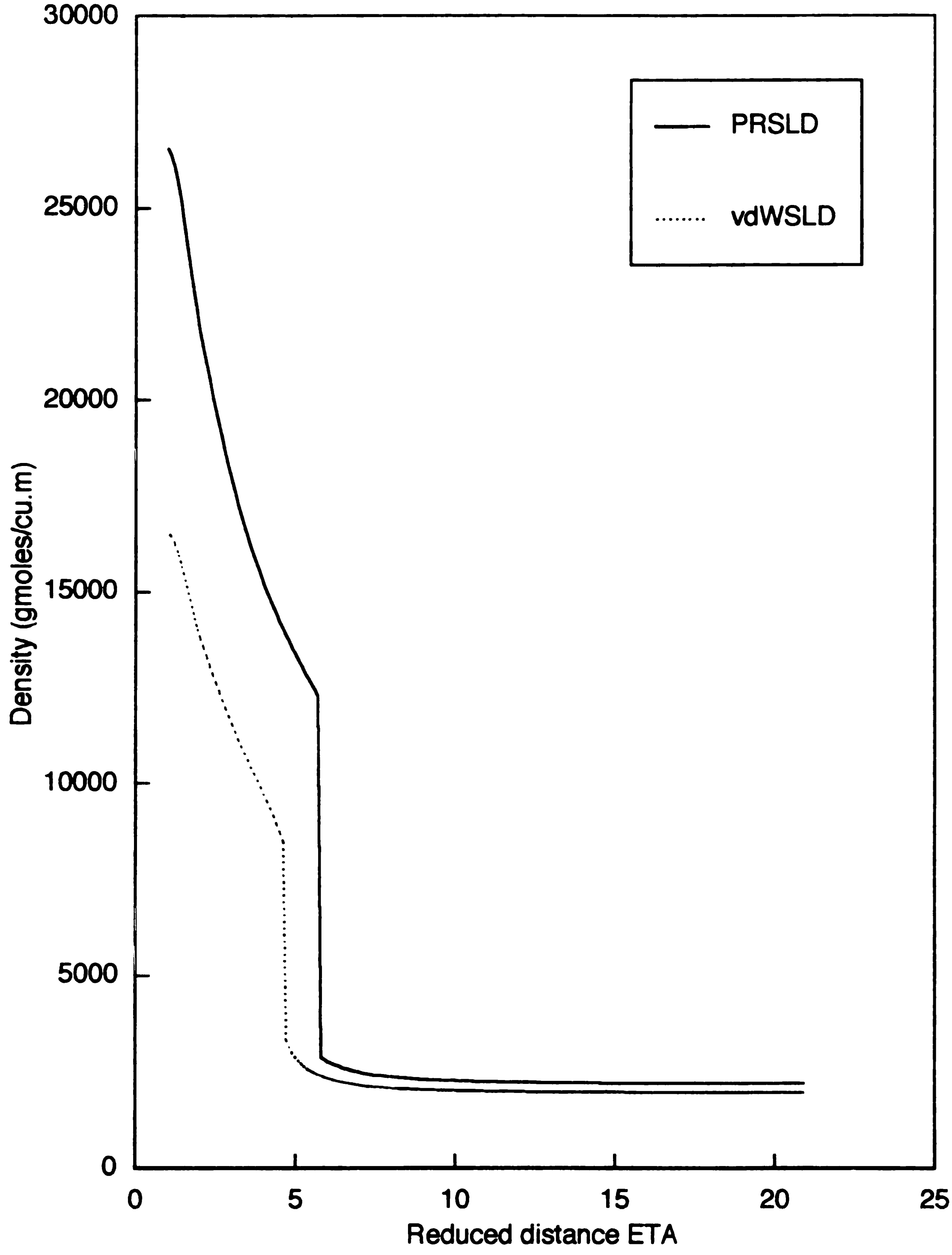

Figure 3-4 : Comparision of the density profiles generated by vdWSLD & PRSLD for Ethylene (Tc=282.4 K, Pc= 50.4 bar) on a solid at Tr=0.95 and the ratio $\varepsilon_W / \varepsilon_{FF} = 2.0$.

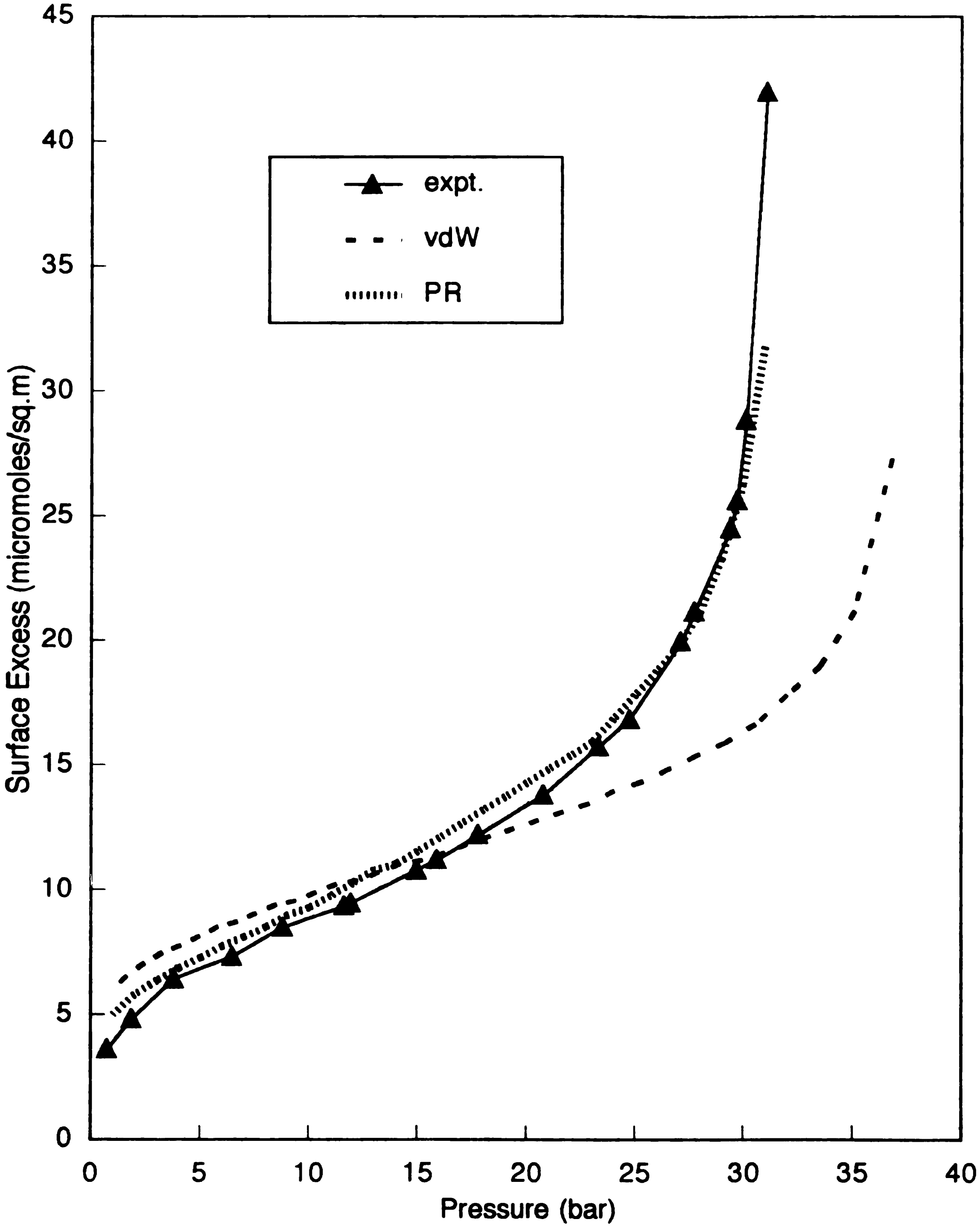

Figure 3-5 : A comparison of adsorption isotherms predicted using the vdWSLD & PRSLD models for Ethylene (Tc=282.4 K, Pc=50.4 bar) versus the experimental data at 263K.

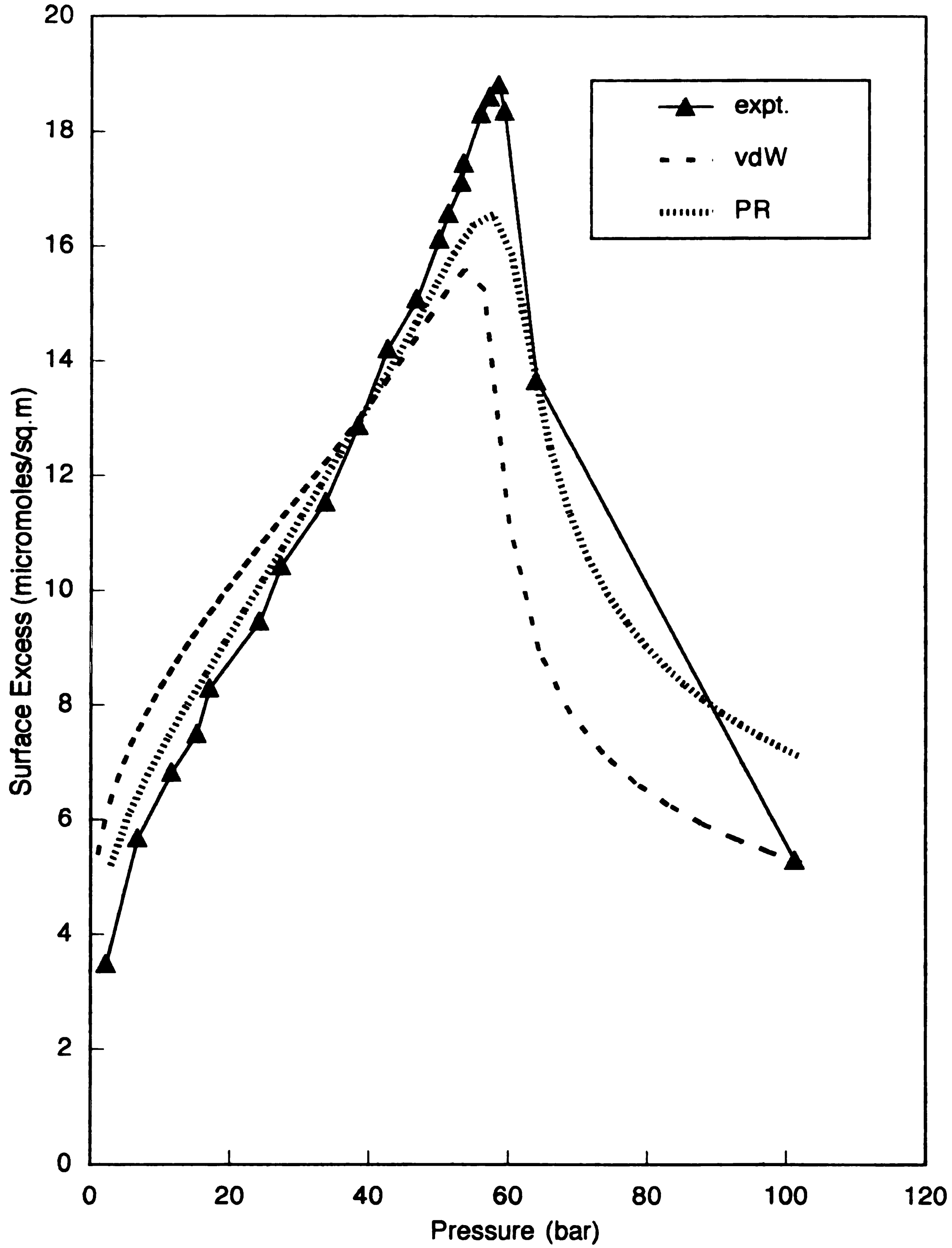

Figure 3-6 : A comparison of adsorption isotherms predicted using the vdWSLD & PRSLD models for Ethylene (Tc=282.4 K, Pc=50.4 bar) versus the experimental data at 293K.

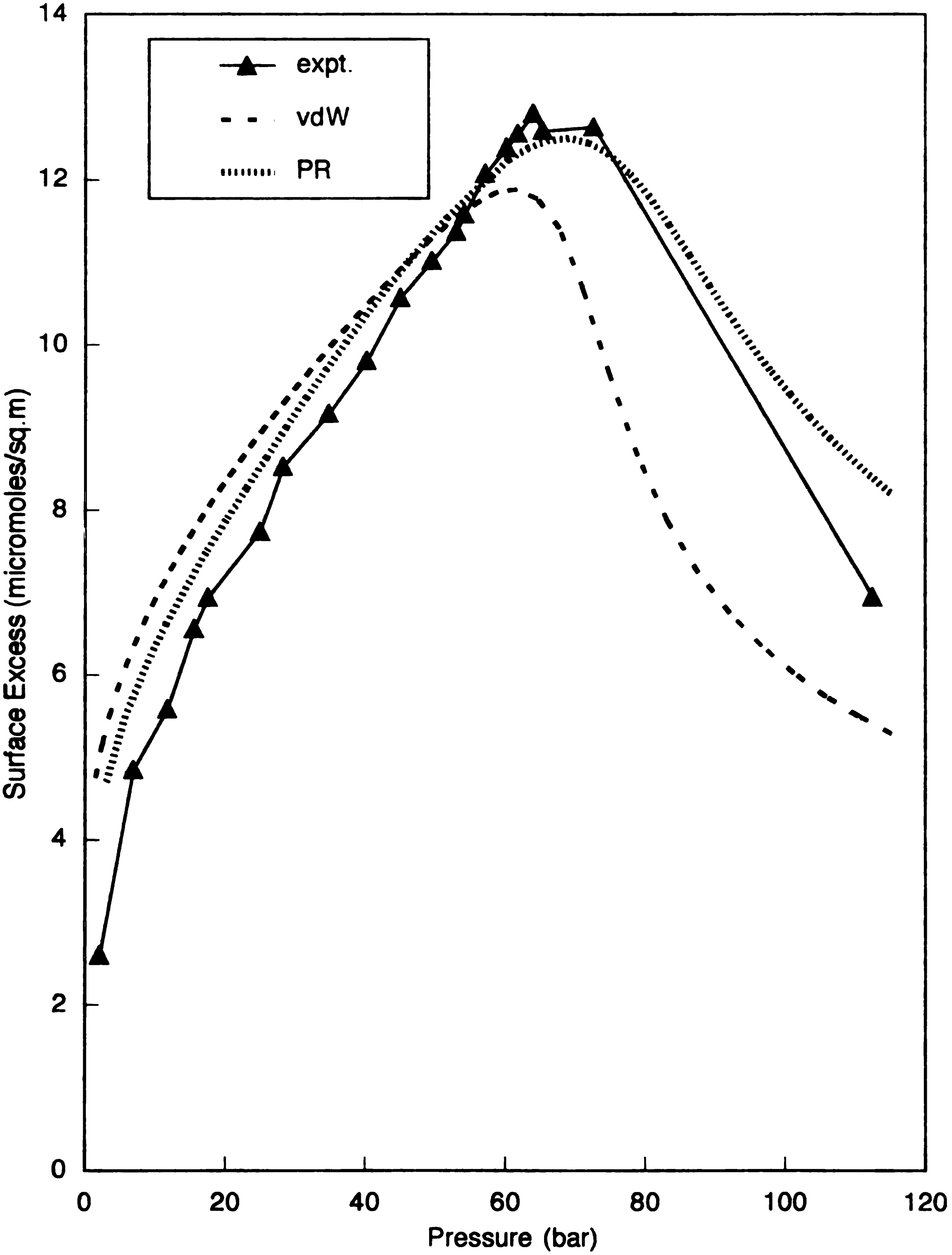

Figure 3-7 : A comparison of adsorption isotherms predicted using the vdWSLD & PRSLD models for Ethylene (Tc=282.4 K, Pc=50.4 bar) versus the experimental data at 313K.

CHAPTER 4

THE INTEGRAL EQUATION

The simplified local density model of Rangarajan (1992) and the model of Barrer and Robins (1951) assume that the fluid chemical potential can be calculated with the local density of the fluid. Actually the entire density profile is required to find the true fluid-fluid potential. This approach requires the solution of an integral equation and will be referred to as the Integral Equation (IE) approach. The details of the equations used in this approach are described in appendix A and the computer program is in appendix C.

If a molecule is at a distance z' from the wall or in terms of reduced units η it is at a reduced distance of η' from the wall, where $\eta = z/\sigma$, $\eta' = z'/\sigma$ and 'σ' is the molecular diameter of the fluid molecule; the chemical potential of that molecule is :

For $0.5 \le \eta' \le 1.5$

$$\ln f(\eta') = \ln\left(\frac{RT}{v(\eta')-b}\right) + \frac{b}{v(\eta')-b} - \frac{3\,a_{bulk}}{4\,RT}\left| \int_{1/2}^{\eta'+1} \rho(\eta)\,d\eta + \int_{\eta'+1}^{\infty} \frac{\rho(\eta)\,d\eta}{(\eta-\eta')^4} \right| \tag{4-1}$$

When $\eta' \ge 1.5$

$$\ln f(\eta') = \ln\left(\frac{RT}{v(\eta')-b}\right) + \frac{b}{v(\eta')-b} - \frac{3\,a_{bulk}}{4\,RT}\left| \int_{1/2}^{\eta'+1} \frac{\rho(\eta)\,d\eta}{(\eta-\eta')^4} + \int_{\eta'-1}^{\eta'+1} \rho(\eta)\,d\eta + \int_{\eta'+1}^{\infty} \frac{\rho(\eta)\,d\eta}{(\eta-\eta')^4} \right| \tag{4-2}$$

To solve for η' we first need to solve the density profile integrals. This can be done numerically. A first guess of the density profile is required. This can be obtained from the SLD.

Instead of integrating the function $\rho(\eta) / (\eta-\eta')^4$ to ∞ we need a finite limit. In order to obtain that finite limit one has to determine to what distance the value of the integral has a significant contribution. As the distance $(\eta-\eta')$ increases the contribution to the integral decreases. In order to obtain maximum distance to which the function $\rho(\eta) / (\eta-\eta')^4$ has to be integrated the case of a vapor-liquid interface was solved. For this case the following density profile equation applies :

$$I = \left| \int_{-\infty}^{\eta'-1} \frac{\rho(\eta)\, d\eta}{(\eta-\eta')^4} + \int_{\eta'-1}^{\eta'+1} \rho(\eta)\, d\eta + \int_{\eta'+1}^{\infty} \frac{\rho(\eta)\, d\eta}{(\eta-\eta')^4} \right| \qquad 4\text{-}3$$

$$\ln f(\eta') = \ln\left(\frac{RT}{v(\eta')-b}\right) + \frac{b}{v(\eta')-b} - \frac{3\, a_{bulk}}{4\, RT}\, I \qquad 4\text{-}4$$

The initial profile used is shown in the Figure 4-1 which is the type generated by the SLD model. On solving the IE we get a profile of the type shown in Figure 4-2. For this case $\rho(-\infty) = \rho_{liquid}$ and $\rho(+\infty) = \rho_{vapor}$. Assume that at a certain distance η'-x, $\rho(\eta'-x) \approx \rho(+\infty) = \rho_{vapor}$. Then instead of integrating from$(-\infty)$ to $+\infty$ we need to integrate from the finite distances of $(\eta'-x)$ to $(\eta'+x)$. To find these finite distances we substituted different values of 'x' to solve the integral. If 'x' was such that $\rho(\eta'-x) < \rho_{liquid}$ and $\rho(\eta'+x) > \rho_{vapor}$. So we continued to increase the value of 'x' until

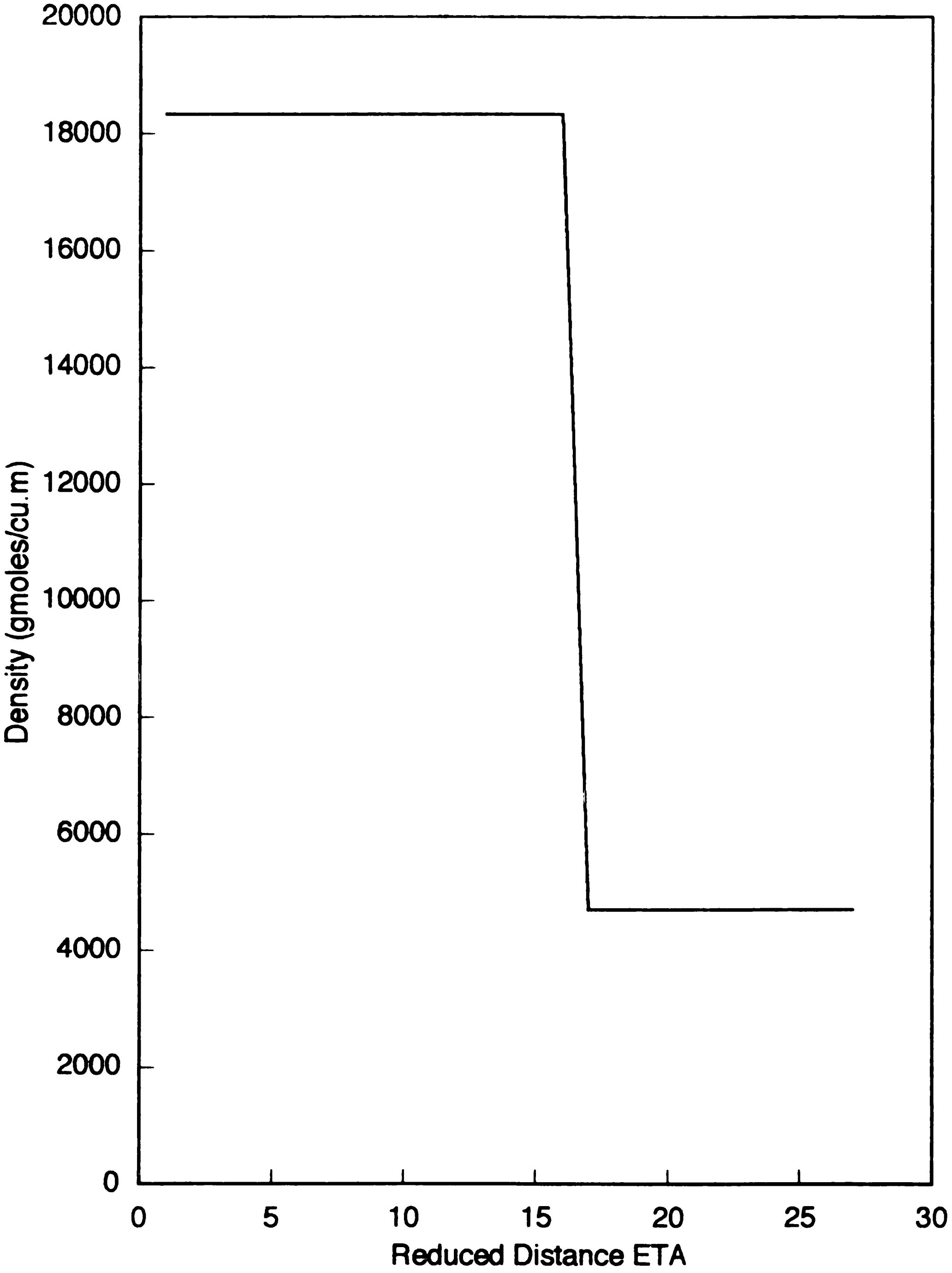

Figure 4-1 : Example of a typical density profile generated by the SLD model for the case of vapor liquid interface

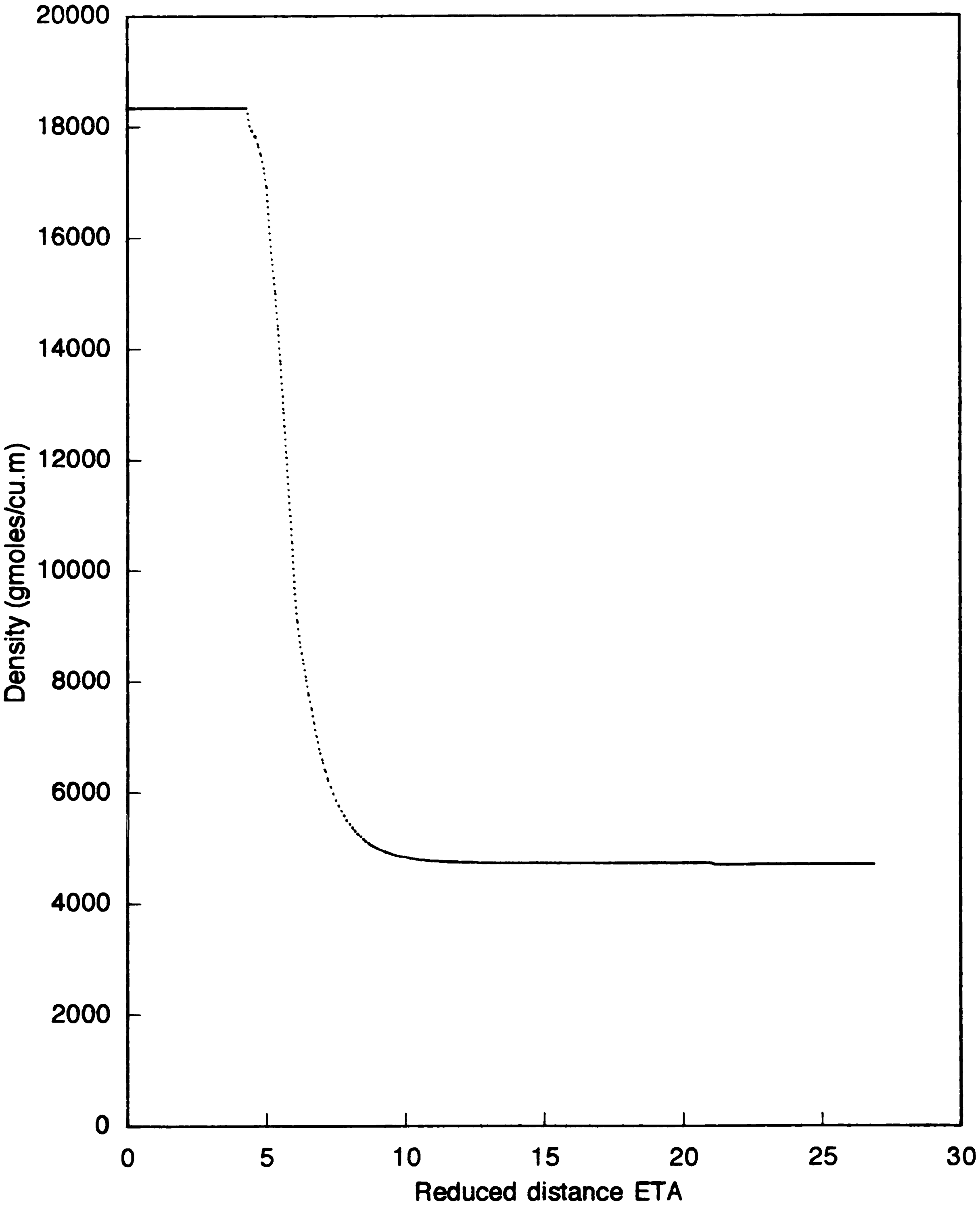

Figure 4 - 2 : Example of a typical density profile generated by solving the IE for the case of a vapor liquid interface.

$\rho(\eta'-x) \approx \rho_{liquid}$ and $\rho(\eta'+x) \approx \rho_{vapor}$ within a ± 0.001% error. This was done for water and ethylene for the range of reduced temperatures of $0.3 \leq T_r \leq 0.9$. The results are tabulated in Table 4 - 1.

The relation between T_r and X can not be generalized and needs to be determined for each fluid one is interested in. Based on these calculations it was decided to use the limit of $\eta'+17$ for the case of adsorption of ethylene, ethane and carbon dioxide on a graphon wall (lower limit for adsorption case is 1/2). Figure 4 - 3 compares density profiles generated by vdWSLD and IE for the adsorption of a fluid (Tc = 282.2 K, Pc = 51.07 bar, σ_{ff} = 3.79 Å) on a solid σ_w = 3.4 Å with a solid - fluid attraction of ε_{fw} = 75.21 at 1 bar pressure.

Table 4 - 1 : "X" values for Water (Tc = 647.3 K, Pc = 22.34 bar) and Ethylene (Tc = 282.4 K, Pc = 51.07 bar) at different reduced temperatures.

Ethylene		Water	
T_r	X	T_r	X
0.3	7	0.3	6
0.4	7	0.4	6
0.5	7	0.5	6
0.6	9	0.6	6
0.7	6	0.7	5
0.8	16	0.8	4
0.9	17	0.9	4

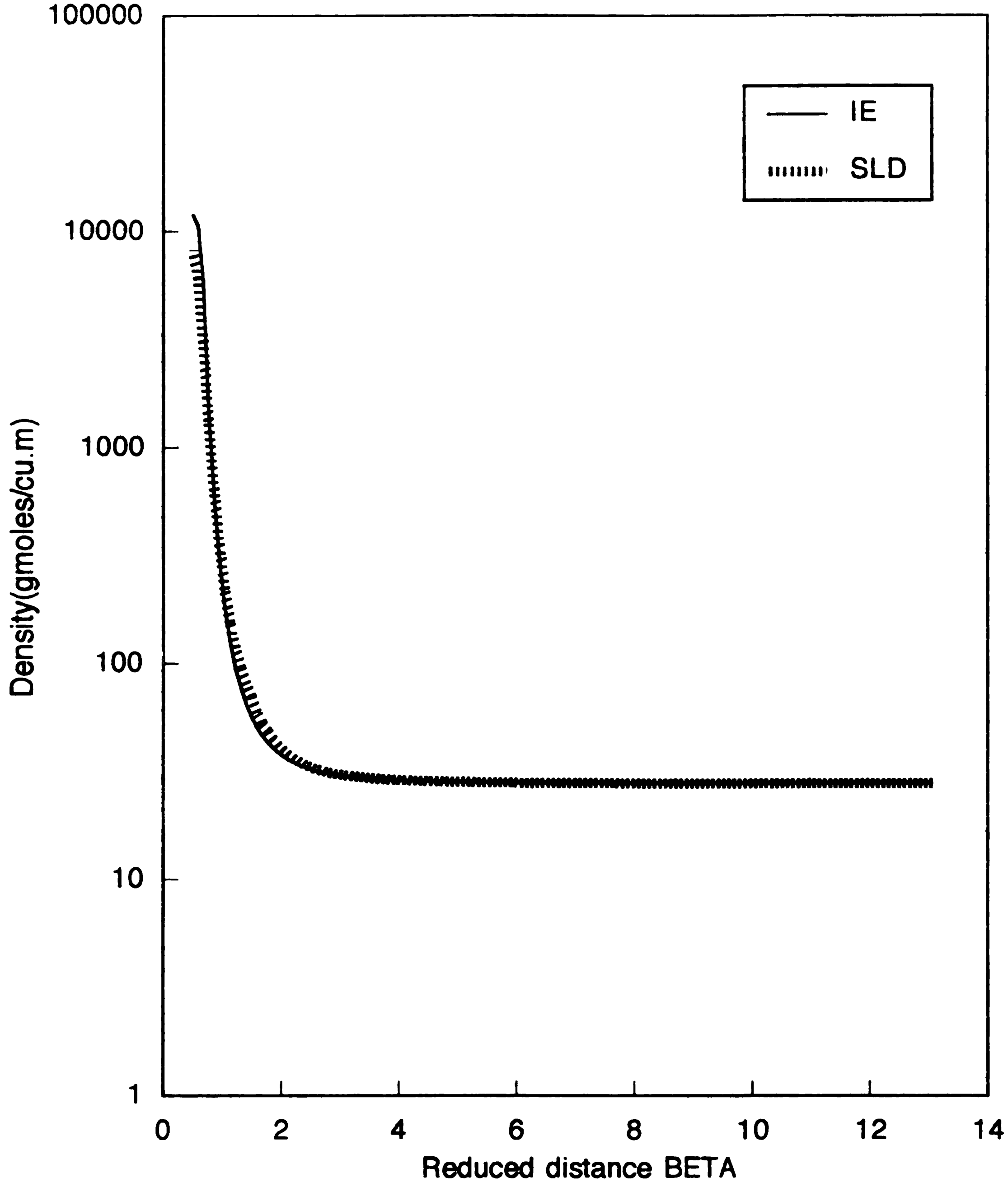

Figure 4-3 : Comparison of the density profiles generated by SLD & IE for Ethylene (Tc=282.4 K, Pc=50.4 bar) on a solid at Tr=0.95 and the ratio $\varepsilon_W / \varepsilon_{FF} = 0.1$.

The other point to consider is the number of iterations required to solve for the density profile. Once the integrals are solved then then the chemical potential is solved numerically for obtaining the new densities. Let the original be represented by $\rho_0(\eta')$ and the new density be represented by $\rho_n(\eta')$ then if, $\rho_0(\eta') - \rho_n(\eta') / \rho_0(\eta') < 0.001$, the new profile is accepted if not the iteration continues. Thus the iteration is considered complete only when the two profiles differ at each position by less than ± 0.1%.

One of the objectives of this thesis is to determine, if the density profile generated by the SLD is a good first guess for solving the IE. To measure how good a first guess the SLD was it was decided to use the % error which is defined as :

$$\% \text{ error} = \frac{\Gamma_{SLD} - \Gamma_{IE}}{\Gamma_{SLD}} * 100 \qquad 4-5$$

where, Γ_{SLD}= Surface excess obtained from the SLD model

Γ_{IE} = Surface excess obtained from the IE model.

Low values of % error indicate a first good guess. For the case of adsorption of fluid on a wall three fluids were chosen : Ethylene, Ethane and Carbon dioxide. Three different reduced temperatures selected were T_r=0.95, T_r = 1.05 & T_r=1.10. For each fluid at each reduced temperature three solids were selected such that the relative solid - fluid attractions (measured by $\varepsilon_w/\varepsilon_{ff}$) were 0.25 (low solid - fluid attraction), 1.0 (solid - fluid attraction in the same range of fluid - fluid attraction) and 2.0 (solid - fluid attraction much higher than fluid - fluid attraction). The hard core diameter of the solid was taken to be : σ_w = 3.4Å. These different parameters are summarized in Tables 4 - 2, 4 - 3 and 4 - 4 [Reid et al. (1987)].

Table 4 - 2 : The σ_{ff}, ε_{ff} values for ethylene, ethane and carbon dioxide.

Fluid	T_c(K)	P_c(bar)	ε_{ff}(K)	σ_{ff}(Å)
Ethylene	282.4	50.4	224.7	4.163
Ethane	305.4	48.8	215.7	4.443
Carbon dioxide	304.1	73.8	195.2	3.941

Table 4 - 3 : Different reduced temperatures (in K) selected for ethylene, ethane and carbon dioxide.

Ethylene		Ethane	Carbon dioxide
Tr	T	T	T
0.95	268.28	290.13	288.895
1.05	296.52	320.775	319.305
1.1.	310.64	335.94	334.51

Table 4 - 4 : ε values for ethylene, ethane and carbon dioxide

	Ethylene		Ethane		Carbon dioxide	
$\varepsilon_w/\varepsilon_{ff}$	ε_w	ε_{fw}	ε_w	ε_{fw}	ε_w	ε_{fw}
0.25	56.175	112.35	53.925	107.85	48.8	97.6
1.0	224.7	224.7	215.7	215.7	195.2	195.2
2.0	449.4	317.773	431.4	305.05	390.4	276.05

The range of the % error for different reduced pressures (or P/Psat for subcritical temperatures) for these different conditions are tabulated in Tables 4 - 5 thru 4 - 13. These values are approximate and are meant as a guide for developing generalizations only. Figures 4 - 4 thru 4 - 12 show the effect of temperature and $\varepsilon_w/\varepsilon_{ff}$ on the % error for different fluids. For the SLD to be a good first guess for solving the IE, the absolute value of the % error should below 20%. For the conditions chosen the SLD is a good first guess in certain regions for each fluid-wall system.

<u>The general trends indicate that</u> :

(1) The % error is a function of the fluid - solid system chosen (represented by the ratio $\varepsilon_w/\varepsilon_{FF}$) and the temperature and pressure of the system.

(2) When the temperature of a chosen fluid - solid system increases from near critical to super critical the absolute value of the % error is lowered.

(3) The SLD is a good first guess for super critical fluids when the reduced pressure(P/Pc) is between 0.1 and 0.6. The % error increases drastically when Pr > 0.7. For subcritical fluids the SLD is a good first guess (i.e. the absolute value of the % error is below 20%) when the ratio of P/Psat is less than 0.7.

(4) On increasing the ratio of $\varepsilon_w/\varepsilon_{FF}$ for the same system temperature and pressure, the absolute value of the % error lowers, i.e. SLD is a better first guess when the fluid-wall potential is higher than the fluid-fluid potential

The IE for the PR equation is difficult to formulate. In the case of the vdW equation one can equate the attractive term with the attractive term in the pressure equation to get :

$$-a/v^2 = -2\pi\varepsilon_{ff}\sigma^3 N_A^2/(3v^2) \qquad 4-6$$

Thus, $a = 2\pi\varepsilon_{ff}\sigma^3 N_A^2/3$ 4 - 7

The corresponding activity results in the equation

$$-a_{PR}/(v^2+2b_{PR}v-b_{PR}^2) = -2\pi\varepsilon_{ff}\sigma^3 N_A^2/(3v^2) \qquad 4-8$$

where the subscript PR stands for Peng - Robinson. The problem with the relation in equation 4 - 8 is that it is difficult to obtain a straightforward relation between a_{PR} and ε_{ff} and σ which is independent of the molar volume v and the repulsive term b_{PR}. Also, the assumptions of vdW are known and can be rewritten as an integral, the assumptions of the PR equation are not known well enough to be rewritten in the form of an integral.

Table 4 - 5 : The % error values for Carbon dioxide at Tr = 0.95 for different values of the ratio $\varepsilon_w/\varepsilon_{ff}$.

P/Psat	$\varepsilon_w/\varepsilon_{ff}$=0.25	$\varepsilon_w/\varepsilon_{ff}$=1.0	$\varepsilon_w/\varepsilon_{ff}$=2.0
<0.1	42 ~ 20	8.0 ~ -1.0	3.0 ~ -4.0
0.1-0.2	2.0 ~ 9.0	-1.0 ~ -6.0	-4.0 ~ -7.0
0.2-0.3	9.0 ~ 1.0	-6.0 ~ -9.0	-7.0 ~ -10.0
0.3-0.4	1.0 ~ -3.0	-9.0 ~ -11.0	-10.0 ~ -12.0
0.4-0.5	-3.0 ~ -9.0	-11.0 ~ -14.0	-12.0 ~ -13.0
0.5-0.6	-9.0 ~ -12.0	-14.0 ~ -15.0	-13.0 ~ -15.0
0.6-0.7	-12.0 ~ -15.0	-15.0 ~ -17.0	-15.0 ~ -17.0
> 0.7	-15.0 ~ -50.0	-17.0 ~ -43.0	-17.0 ~ -44.0

Table 4 - 6 : The % error values for Ethylene at Tr = 0.95 for different values of the ratio $\varepsilon_w/\varepsilon_{ff}$.

P/Psat	$\varepsilon_w/\varepsilon_{ff}=0.25$	$\varepsilon_w/\varepsilon_{ff}=1.0$	$\varepsilon_w/\varepsilon_{ff}=2.0$
<0.1	23 ~ 9.0	4.0 ~ -4.0	-0.3 ~ -6.0
0.1-0.2	9.0 ~ 1.0	-4.0 ~ -7.0	-6.0 ~ -8.0
0.2-0.3	1.0 ~ -5.0	-7.0 ~ -10.0	-8.0 ~ -10.0
0.3-0.4	-5.0 ~ -9.0	-10.0 ~ -12.0	-10.0 ~ -12.0
0.4-0.5	-9.0 ~ -13.0	-12.0 ~ -15.0	-12.0 ~ -14.0
0.5-0.6	-13.0 ~ -16.0	-15.0 ~ -16.0	-14.0 ~ -16.0
0.6-0.7	-16.0 ~ -20.0	-16.0 ~ -20.0	-16.0 ~ -18.0
>0.7	-20.0 ~ -61.0	-20.0 ~ -50.0	-18.0 ~ -47.0

Table 4 - 7 : The % error values for Ethane at Tr = 0.95 for different values of the ratio $\varepsilon_w/\varepsilon_{ff}$.

P/Psat	$\varepsilon_w/\varepsilon_{ff}=0.25$	$\varepsilon_w/\varepsilon_{ff}=1.0$	$\varepsilon_w/\varepsilon_{ff}=2.0$
<0.1	26.0 ~ 11.0	4.0 ~ -3.0	0.3 ~ -5.0
0.1-0.2	11.0 ~ 2.0	-3.0 ~ -8.0	-5.0 ~ -9.0
0.2-0.3	2.0 ~ -4.0	-8.0 ~ -11.0	-9.0 ~ -12.0
0.3-0.4	-4.0 ~ -10.0	-11.0 ~ -13.0	-12.0 ~ -13.0
0.4-0.5	-10.0 ~ -15.0	-13.0 ~ -16.0	-13.0 ~ -16.0
0.5-0.6	-15.0 ~ -19.0	-16.0 ~ -19.0	-16.0 ~ -19.0
0.6-0.7	-19.0 ~ -23.0	-19.0 ~ -23.0	-19.0 ~ -22.0
>0.7	-23.0 ~ -67.0	-23.0 ~ -61.0	-22.0 ~ -57.0

Table 4 - 8 : The % error values for Carbon dioxide at Tr = 1.05 for different values of the ratio $\varepsilon_w/\varepsilon_{ff}$.

Pr	$\varepsilon_w/\varepsilon_{ff}=0.25$	$\varepsilon_w/\varepsilon_{ff}=1.0$	$\varepsilon_w/\varepsilon_{ff}=2.0$
<0.1	42.0 ~ 18.0	9.0 ~ -1.0	3.0 ~ -4.0
0.1-0.2	18.0 ~ 8.0	-1.0 ~ -5.0	-4.0 ~ -7.0
0.2-0.3	8.0 ~ 0.5	-5.0 ~ -9.0	-7.0 ~ -10.0
0.3-0.4	0.5 ~ -4.0	-9.0 ~ -11.0	-10.0 ~ -12.0
0.4-0.5	-4.0 ~ -9.0	-11.0 ~ -13.0	-12.0 ~ -13.0
0.5-0.6	-9.0 ~ -13.0	-13.0 ~ -15.0	-13.0 ~ -15.0
0.6-0.7	-13.0 ~ -17.0	-15.0 ~ -18.0	-15.0 ~ -17.0
>0.7	-17.0 ~ -50.0	-18.0 ~ -39.0	-17.0 ~ -36.0

Table 4 - 9 : The % error values for Ethylene at Tr = 1.05 for different values of the ratio $\varepsilon_w/\varepsilon_{ff}$.

Pr	$\varepsilon_w/\varepsilon_{ff}=0.25$	$\varepsilon_w/\varepsilon_{ff}=1.0$	$\varepsilon_w/\varepsilon_{ff}=2.0$
<0.1	23.0 ~ 10.0	4.0 ~ -3.0	-0.3 ~ -5.0
0.1-0.2	10.0 ~ 1.0	-3.0 ~ -8.0	-5.0 ~ -8.0
0.2-0.3	1.0 ~ -4.0	-8.0 ~ -10.0	-8.0 ~ -10.0
0.3-0.4	-4.0 ~ -10.0	-10.0 ~ -12.0	-10.0 ~ -12.0
0.4-0.5	-10.0 ~ -13.0	-12.0 ~ -14.0	-12.0 ~ -14.0
0.5-0.6	-13.0 ~ -16.0	-14.0 ~ -16.0	-14.0 ~ -15.0
0.6-0.7	-16.0 ~ -19.0	-16.0 ~ -18.0	-15.0 ~ -17.0
>0.7	-19.0 ~ -52.0	-18.0 ~ -42.0	-17.0 ~ -35.0

Table 4 - 10 : The % error values for Ethane at Tr = 1.05 for different values of the ratio $\varepsilon_w/\varepsilon_{ff}$.

Pr	$\varepsilon_w/\varepsilon_{ff}$=0.25	$\varepsilon_w/\varepsilon_{ff}$=1.0	$\varepsilon_w/\varepsilon_{ff}$=2.0
<0.1	25.0 ~ 11.0	5.0 ~ -3.0	0.6 ~ -5.0
0.1-0.2	11.0 ~ 0.1	-3.0 ~ -8.0	-5.0 ~ -9.0
0.2-0.3	0.1 ~ -5.0	-8.0 ~ -11.0	-9.0 ~ -11.0
0.3-0.4	-5.0 ~ -10.0	-11.0 ~ -14.0	-11.0 ~ -13.0
0.4-0.5	-10.0 ~ -15.0	-14.0 ~ -16.0	-13.0 ~ -15.0
0.5-0.6	-15.0 ~ -18.0	-16.0 ~ -19.0	-15.0 ~ -18.0
0.6-0.7	-18.0 ~ -22.0	-19.0 ~ -21.0	-18.0 ~ -20.0
>0.7	-22.0 ~ -61.0	21.0 ~ -51.0	-20.0 ~ -45.0

Table 4 - 11 : The % error values for Carbon dioxide at Tr = 1.10 for different values of the ratio $\varepsilon_w/\varepsilon_{ff}$.

Pr	$\varepsilon_w/\varepsilon_{ff}$=0.25	$\varepsilon_w/\varepsilon_{ff}$=1.0	$\varepsilon_w/\varepsilon_{ff}$=2.0
<0.1	42.0 ~ 20.0	9.0 ~ 1.0	3.0 ~ -3.0
0.1-0.2	20.0 ~ 11.0	1.00 ~ -4.0	-3.0 ~ -6.0
0.2-0.3	11.0 ~ 4.0	-4.0 ~ -7.0	-6.0 ~ -8.0
0.3-0.4	4.0 ~ -2.0	-7.0 ~ -10.0	-8.0 ~ -10.0
0.4-0.5	-2.0 ~ -6.0	-10.0 ~ -12.0	-10.0 ~ -12.0
0.5-0.6	-6.0 ~ -10.0	-12.0 ~ -13.0	-12.0 ~ -13.0
0.6-0.7	-10.0 ~ -13.0	-13.0 ~ -16.0	-13.0 ~ -15.0
>0.7	-13.0 ~ -49.0	-16.0 ~ -36.0	-15.0 ~ -31.0

Table 4 - 12 : The % error values for Ethylene at Tr = 1.10 for different values of the ratio $\varepsilon_w/\varepsilon_{ff}$.

Pr	$\varepsilon_w/\varepsilon_{ff}=0.25$	$\varepsilon_w/\varepsilon_{ff}=1.0$	$\varepsilon_w/\varepsilon_{ff}=2.0$
<0.1	22.0 ~ 9.0	3.0 ~ -2.0	-0.7 ~ -5.0
0.1-0.2	9.0 ~ 2.0	-2.0 ~ -6.0	-5.0 ~ -7.0
0.2-0.3	2.0 ~ -3.0	-6.0 ~ -9.0	-7.0 ~ -10.0
0.3-0.4	-3.0 ~ -7.0	-9.0 ~ -11.0	-10.0 ~ -11.0
0.4-0.5	-7.0 ~ -10.0	-11.0 ~ -13.0	-11.0 ~ -12.0
0.5-0.6	-10.0 ~ -13.0	-13.0 ~ -14.0	-12.0 ~ -14.0
0.6-0.7	-13.0 ~ -17.0	-14.0 ~ -16.0	-14.0 ~ -16.0
>0.7	-17.0 ~ -50.0	16.0 ~ -36.0	-16.0 ~ -33.0

Table 4 - 13 : The % error values for Ethane at Tr = 1.10 for different values of the ratio $\varepsilon_w/\varepsilon_{ff}$.

Pr	$\varepsilon_w/\varepsilon_{ff}=0.25$	$\varepsilon_w/\varepsilon_{ff}=1.0$	$\varepsilon_w/\varepsilon_{ff}=2.0$
<0.1	23 ~ 10.0	4.0 ~ -2.0	0.4 ~ -5.0
0.1-0.2	10.0 ~ 4.0	-2.0 ~ -6.0	-5.0 ~ -8.0
0.2-0.3	4.0 ~ -2.0	-6.0 ~ -10.0	-8.0 ~ -10.0
0.3-0.4	-2.0 ~ -7.0	-10.0 ~ -12.0	-10.0 ~ -12.0
0.4-0.5	-7.0 ~ -12.0	-12.0 ~ -14.0	-12.0 ~ -14.0
0.5-0.6	-12.0 ~ -15.0	-14.0 ~ -16.0	-14.0 ~ -15.0
0.6-0.7	-15.0 ~ -20.0	-16.0 ~ -19.0	-15.0 ~ -18.0
>0.7	-20.0 ~ -58.0	-19.0 ~ -44.0	-18.0 ~ -39.0

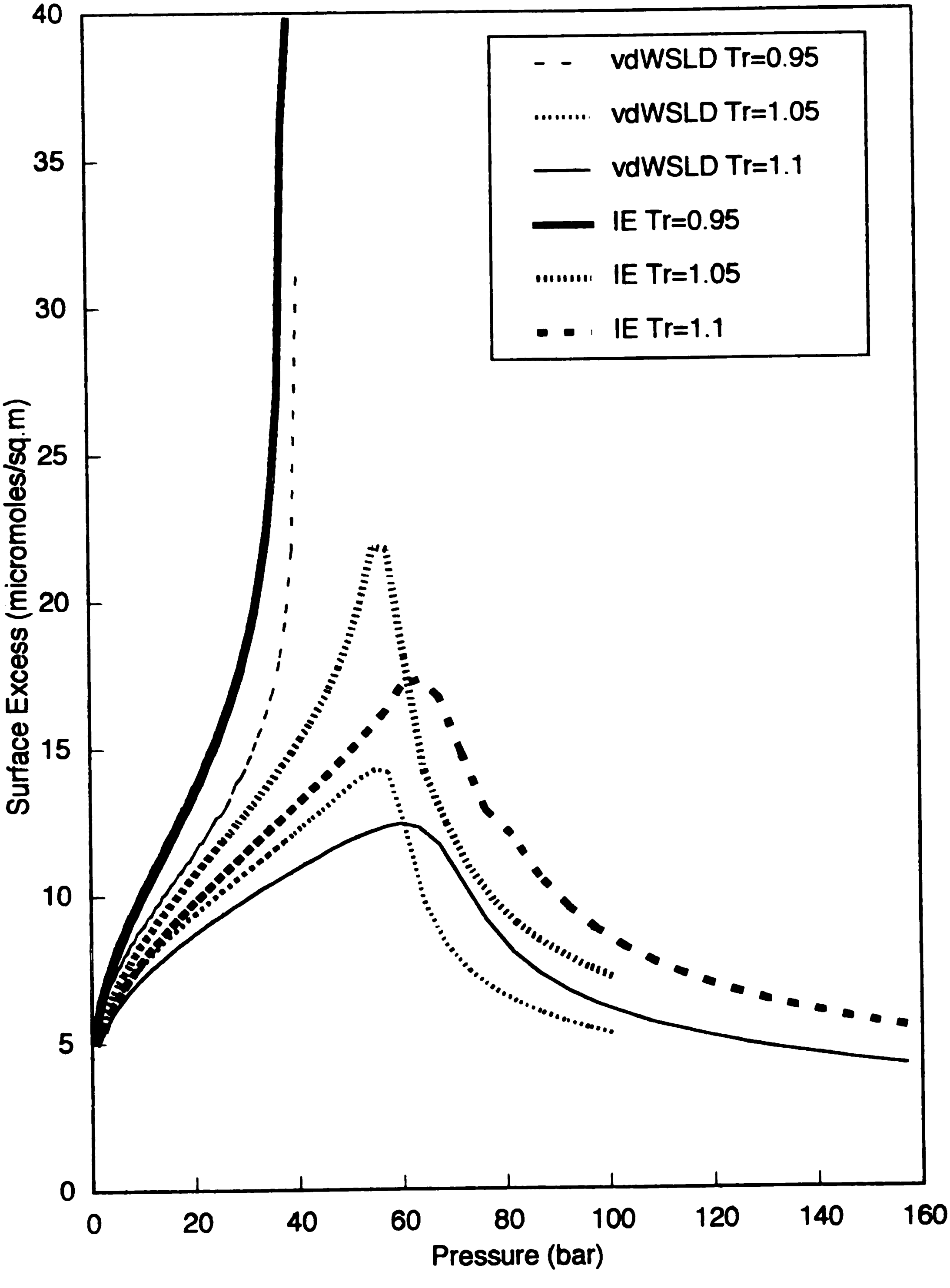

Figure 4-4 : Adsorption isotherms predicted using the IE & vdWSLD models for Ethylene (Tc=282.4 KPc = 50.4 bar) for the ratios $\varepsilon_W / \varepsilon_{FF} = 2.0$.

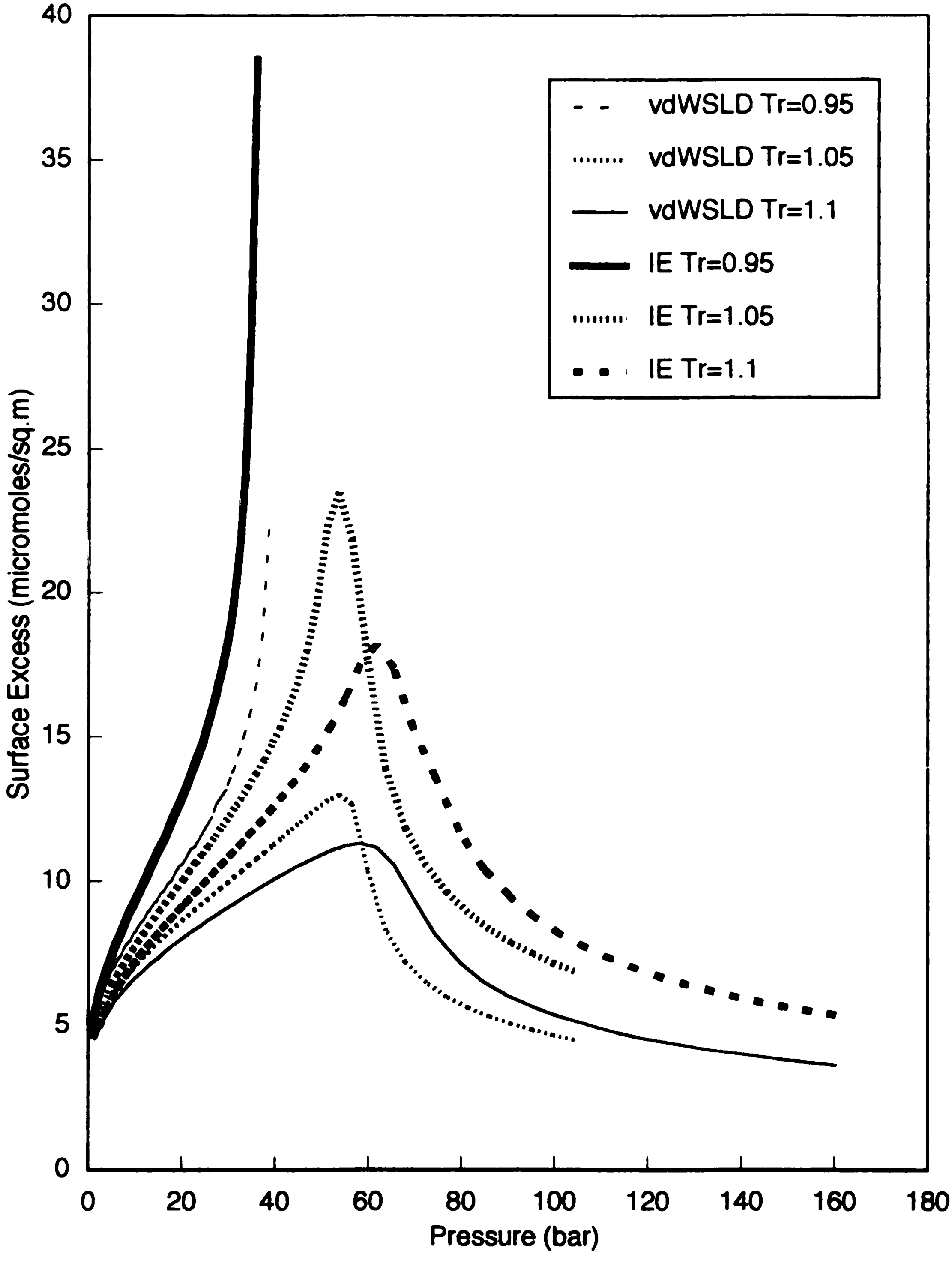

Figure 4-5 : Adsorption isotherms predicted using the IE & vdWSLD models for Ethane (Tc=305.4 K, Pc=48.8 bar) for the ratios $\varepsilon_W / \varepsilon_{FF}$=2.0 .

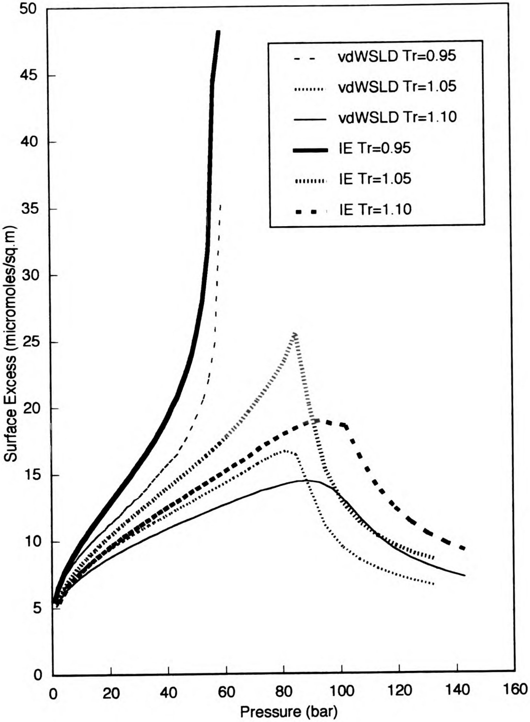

Figure 4-6 : Adsorption isotherms predicted using the IE & vdWSLD models for Carbon dioxide(Tc=304.1 K, Pc= 73.8 bar) for the ratios $\varepsilon_W / \varepsilon_{FF} = 2.0$.

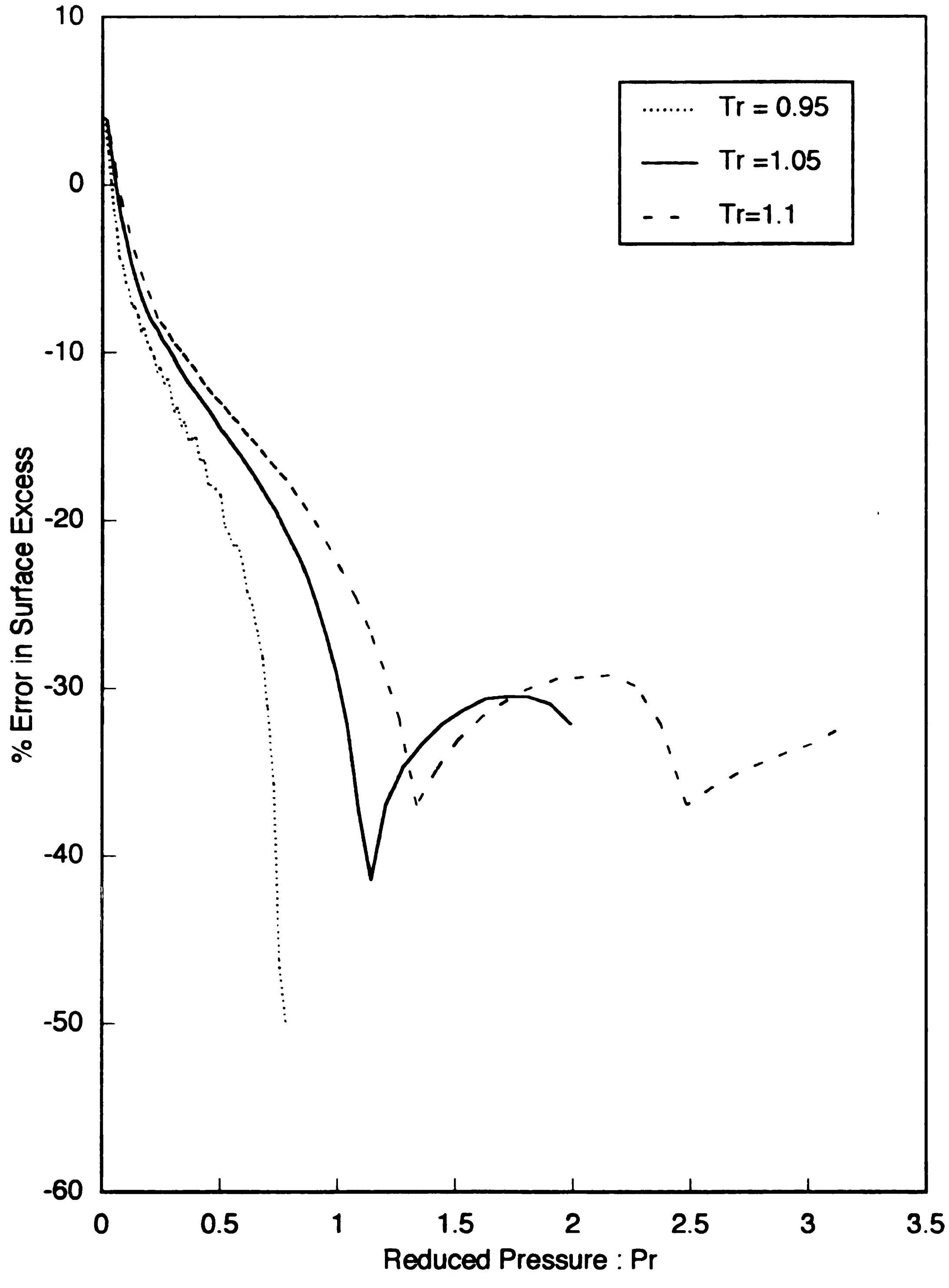

Figure 4-7 : Effect of temperature on % error for the ratio $\varepsilon_W / \varepsilon_{FF} = 1.0$, for Ethylene (Tc=282.4 K, Pc= 50.4 bar).

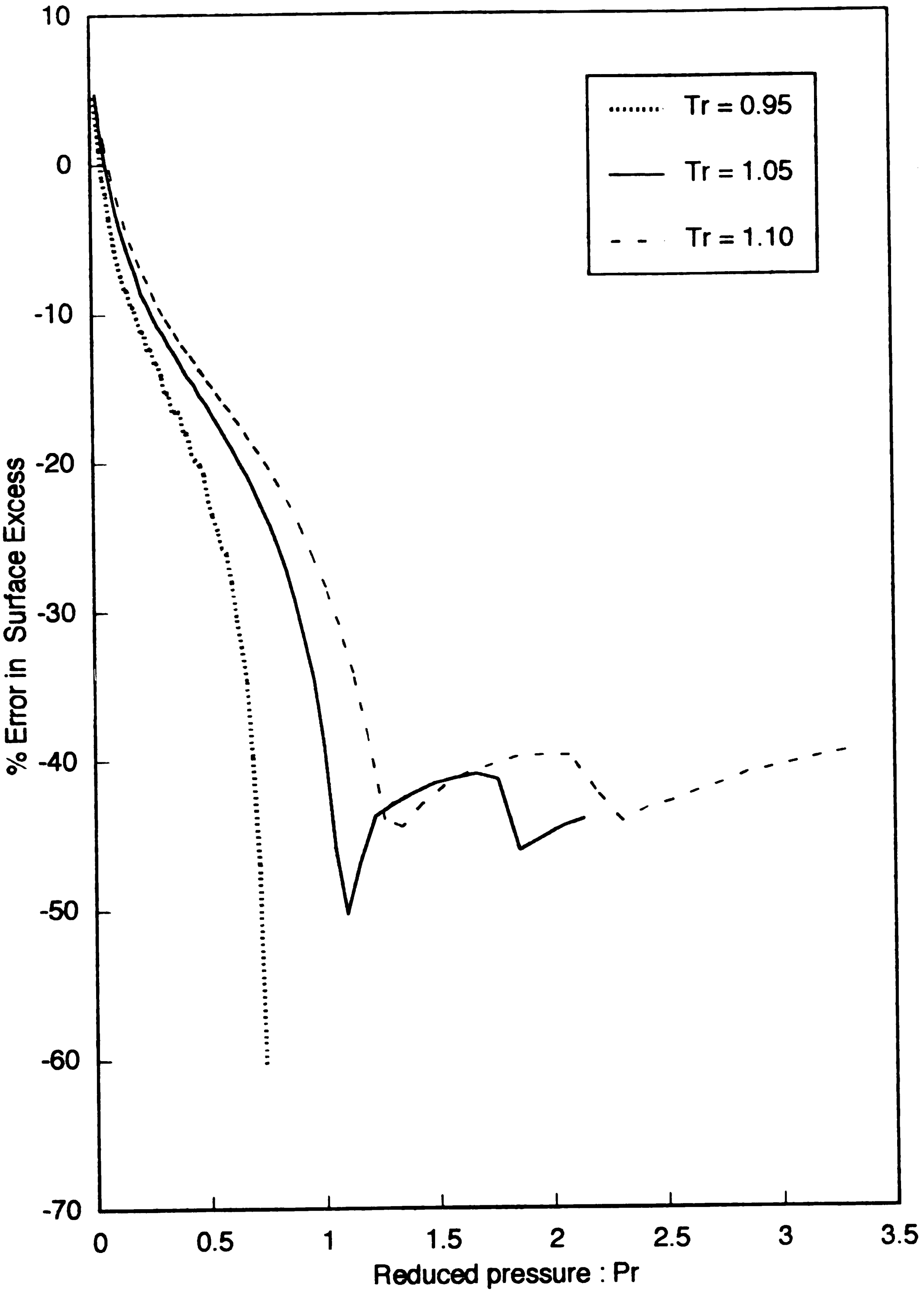

Figure 4-8 : Effect of temperature on % error for the ratio $\varepsilon_W / \varepsilon_{FF} = 1.0$, for Ethane (Tc=305.4 K, Pc=48.4 bar) .

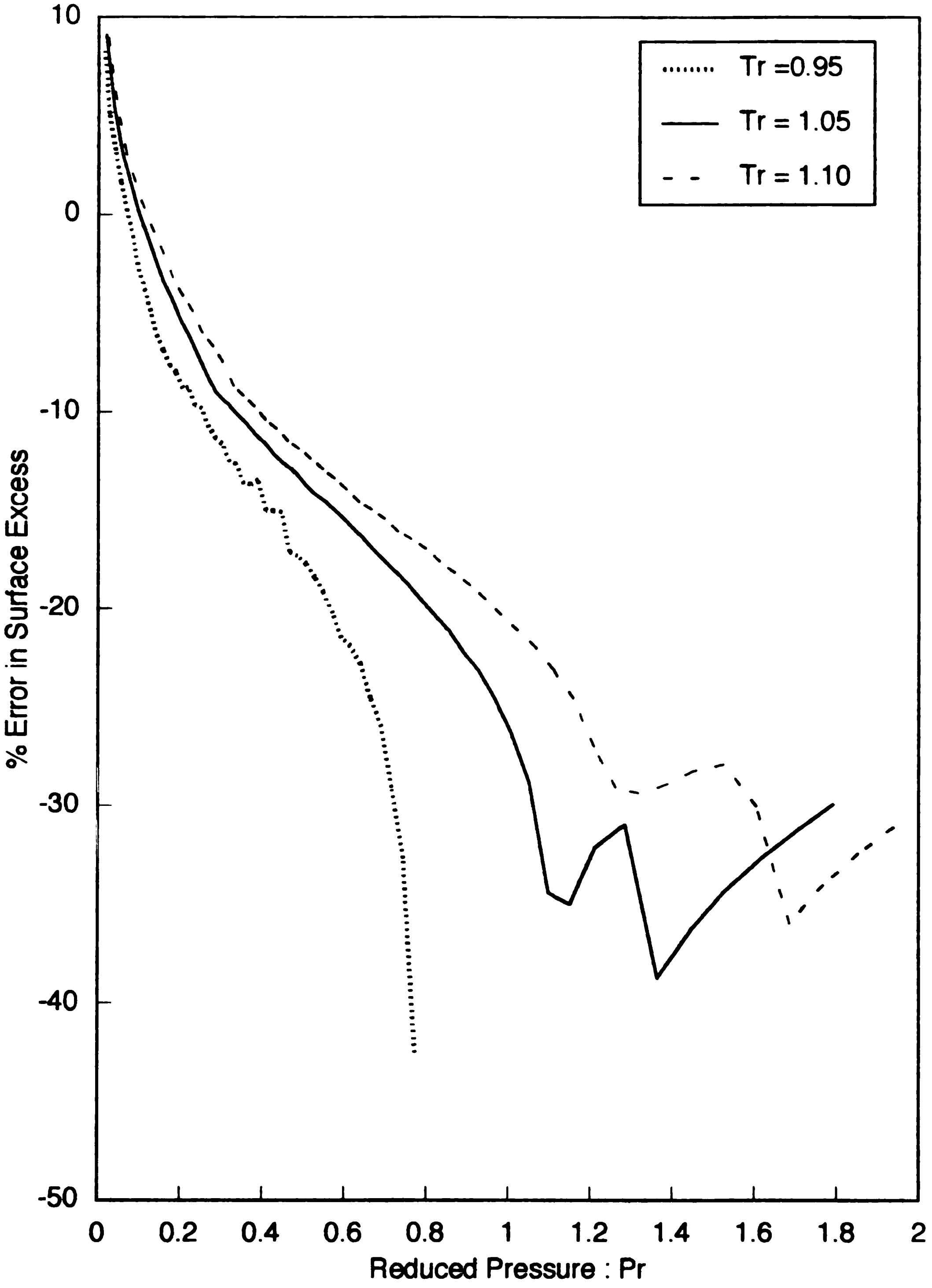

Figure 4-9 : Effect of temperature on % error for the ratio $\varepsilon_W / \varepsilon_{FF} = 1.0$, for Carbon dioxide (Tc=304.1 K, Pc= 73.8 bar).

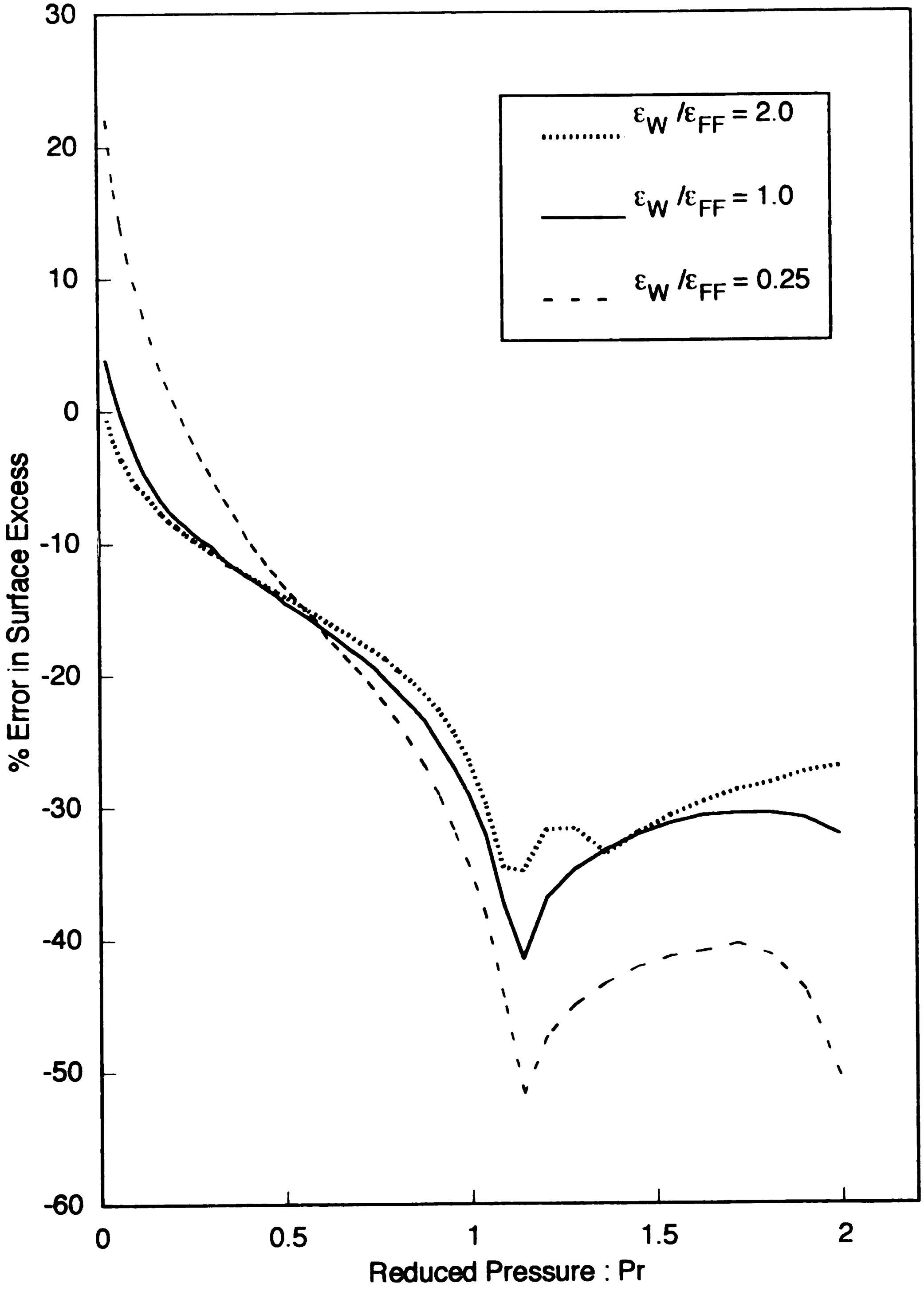

Figure 4-10 : Effect of the ratio $\varepsilon_W/\varepsilon_{FF}$ on % error at Tr =1.05 for Ethylene (Tc=282.4 K, Pc = 50.4 bar)

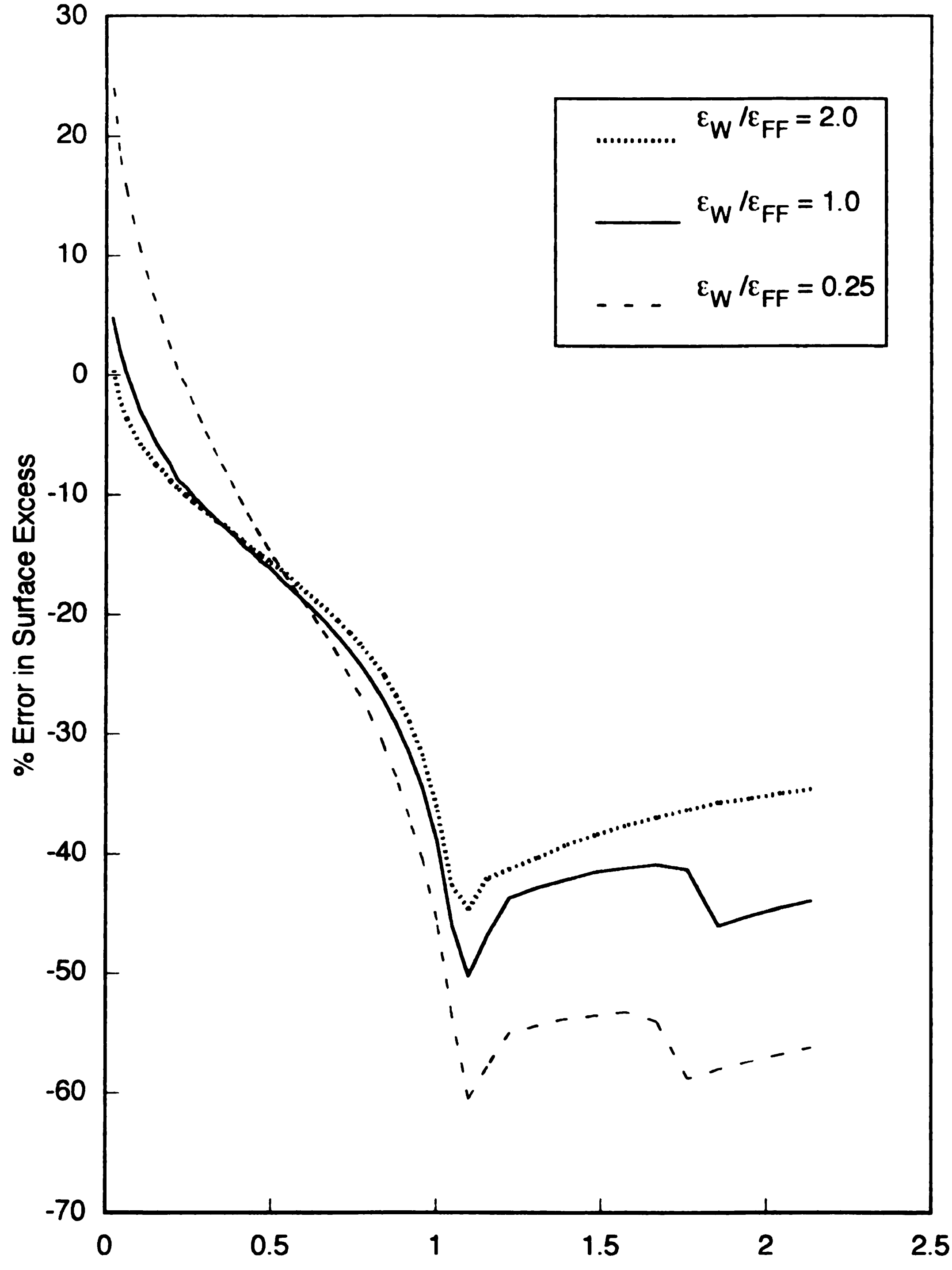

Figure 4-11 : Effect of the ratio $\varepsilon_W/\varepsilon_{FF}$ on % error at Tr =1.05 for Ethane (Tc=305.4 K, Pc = 48.4 bar).

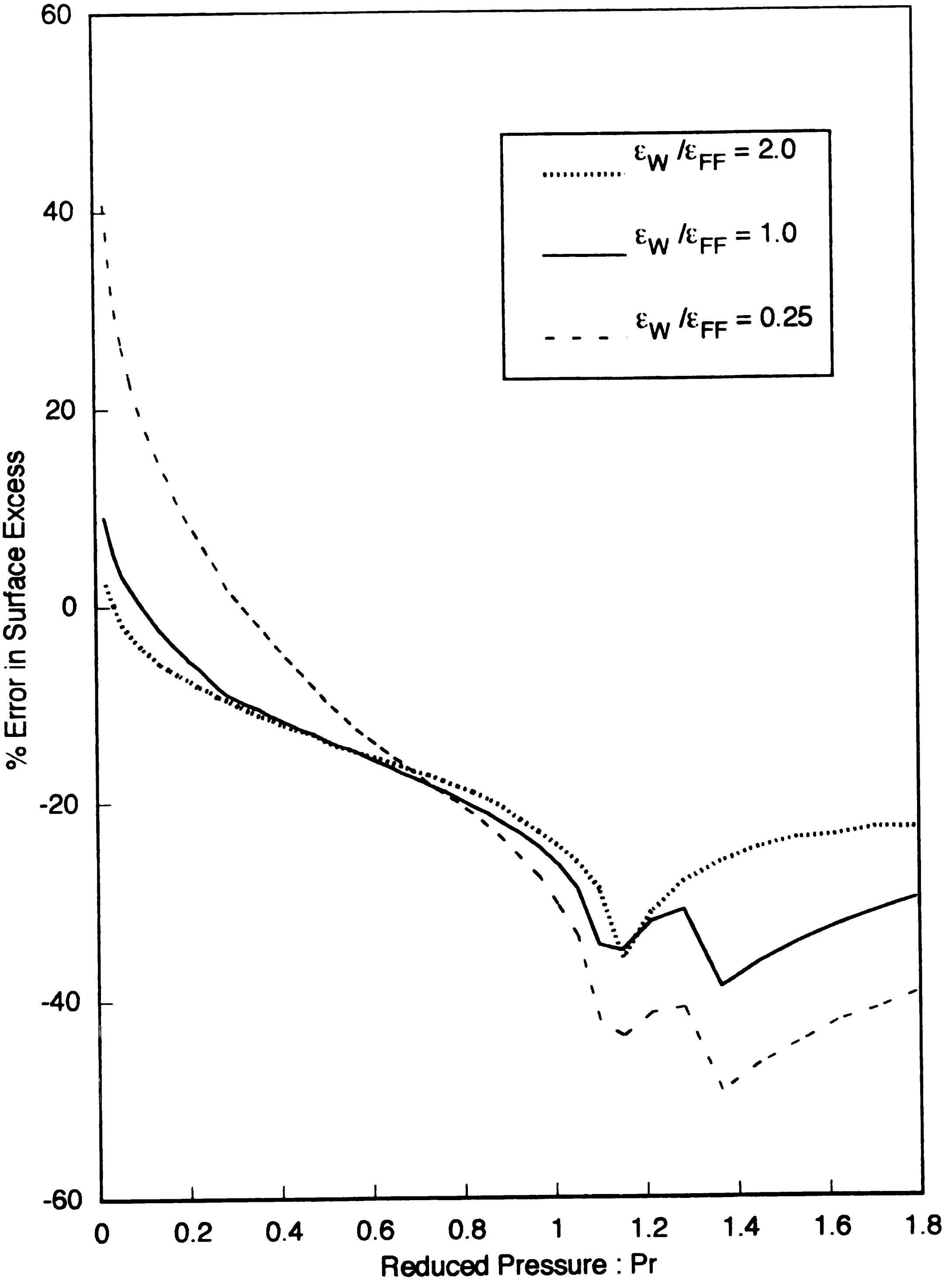

Figure 4-12 : Effect of the ratio $\varepsilon_W / \varepsilon_{FF}$ on % error atTr =1.05 for Carbon dioxide (Tc=304.1 K, Pc =73.8 bar).

CHAPTER 5

SUMMARY AND CONCLUSION

The objectives of this thesis as stated in Chapter 1, were to modify the simplified local density (SLD) model by using the Peng-Robinson equation of state to calculate the fluid properties and to investigate whether the SLD density profiles are good first approximations for solving the the integral equation (IE).

In chapter 2 the different adsorption models were described and in the end it was emphasized that for the conceptual design of adsorption systems the desirable characteristics of an adsorption model are:

(1) dependable prediction of equilibrium conditions at a wide range of temperatures and pressures for different kinds of fluid - solid systems.

(2) easy availability of the different parameters required to calculate adsorption isotherms.

(3) quick calculations and readily understandable results.

The SLD was modified in chapter 3 by introducing the Peng - Robinson equation of state to represent the fluid properties. The original SLD model used the van der Waals' equation and was thus named the vdWSLD, while the modified form was called the PRSLD. The adsorption isotherms predicted by these two models were compared for different fluids at different temperatures. For the same solid - fluid interaction parameter ε_{fw}, the PRSLD predicted higher Γ values than the vdWSLD. Adsorption isotherms predicted by the PRSLD and the vdWSLD were also compared with experimental data. The ε_{fw} parameter was adjusted for both SLD models to get the best fit isotherm. Over a difference of 50 C the efw value for the best fit isotherm was the same. The PRSLD gave better quantitaive agreement.

In chapter 4 a different approach was taken. The density profile generated by the SLD was used as a first guess to solve an integral equation to obtain a more accurate density profile. This approach was called the IE approach. It is similar to the mean - field approach developed in density functional theories. Here the aim was to find out in which ranges of temperature and pressure the SLD will be a good first guess for solving the IE. The adsorption isotherms generated using the SLD and the IE were compared for ethylene, ethane and carbon dioxide on three different types of adsorbents : low solid - fluid interaction potential, comparable potential and high potential. Three different temperatures were selected for each fluid, one to represent subcritical range, one to represent near critical range and one to represent supercritical range. Based on these comparisons it was concluded that the SLD is a good first guess when:

(1) for super critical fluids when the reduced pressure(P/Pc) is between 0.1 and 0.6 and for subcritical fluids when the ratio of P/Psat is less than 0.7.

(2) when the fluid-wall potential is higher than the fluid-fluid potential.

Also the SLD performs better when the temperature is in the supercritical region.

In the above mentioned comparisons between the SLD and IE only the vdWSLD could be used. It is difficult to formulate an IE solution corresponding to the PRSLD. This is because it is difficult to obtain a relation between the attractive term, a_{PR} and ε_{ff} and σ which is independent of the molar volume v and the repulsive term b_{PR}.

In conclusion the SLD developed by Rangarajan (1992) predicts adsorption isotherms in qualitative agreement with experimental data. Quantitative agreement is improved by modifying it with the Peng - Robinson equation of state. Another approach to improving it's predictions is by using it as a first guess to solve an integral equation i.e. the IE approach.

Future Work :

More work needs to be done in the following areas :

(1) The SLD should be extended to the case of a mixture of fluids contacting a solid adsorbent. When comparing predictions with experimental data, the best fit value of the ε_{fw} parameter should be obtained and used.

(2) A relation between a_{PR} and ε_{ff} and σ needs to be developed which is independent of v and b_{PR} in order that the corresponding IE can be formed for the PRSLD. If a relation can not be formed then some method of solving the existing relation needs to be formed so that the IE can be formulated.

APPENDIX A

APPENDIX A

Details of solving the Integral Equation

Rangarajan (1992), solved the fluid-fluid interaction potential for a non-homogeneous fluid by considering the following two cases :

(1) A fluid molecule in the vicinity of the wall $0.5\,\sigma \leq z \leq 1.5\,\sigma$

(2) A fluid molecule far form the wall $1.5\,\sigma \leq z \leq \infty$

where σ is the molecular diameter

z is the distance from the wall.

While performing the integration the simplified local density (SLD) assumption was used $\rho(x) = \rho(z)$ (where "x" is the axial distance coordinate in the cylindrical system with "r" as the radial distance coordinate). For the integral equation approach the entire density profile is required not just the local density. In this approach the fluid configurational integral will be solved in a slightly different manner. For a van der Waals' fluid the fugacity can be written as

$$\ln f = \ln(RT/\,(v-b)\,) + b/(v-b) - 2a/vRT \qquad \text{A - 1}$$

where R = universal gas constant

T = temperature

v = molar volume

f = fugacity

$$b = 0.125\,RT_c\,/\,P_c \qquad \text{A - 2}$$

$$a = \frac{27}{64}\,(RT_c/P_c)^2 \qquad \text{A - 3}$$

Or $$a = \sigma^3 \varepsilon/\sigma \int x \frac{du}{dx} g(x) 4\pi x^2 dx \qquad \text{A - 4}$$

where $x = r / \sigma$

σ = Hard core diameter

ε = Fluid-fluid interaction potential

$$u(r) = \infty \qquad r < \sigma \qquad \text{A - 5}$$

$$u(r) = \varepsilon\,(\sigma / r)^6 \qquad \sigma < r < \infty \qquad \text{A - 6}$$

The fluid-fluid interaction contribution to the fugacity equation can also be written as :

$$\frac{-a}{vRT} = -\frac{1\,N_A}{kT} \int_v -\varepsilon(\sigma / r_d)^6 \frac{1\,dv}{v(z)} \qquad \text{A - 7}$$

$$\frac{-a}{vRT} = -\frac{1\,N_A}{2\,kT} \int_v -\varepsilon(\sigma / r_d)^6\, dv \int_v \frac{1\,dv}{v(z)} \qquad \text{A - 8}$$

where r_d is the distance from the center of molecule. So the fluid - fluid interaction contribution consists of an integration of the Sutherland potential and an integration of the density profile.

Consider the integral $$\int_v \frac{-\varepsilon\,\sigma^6}{r_d^6}\, dv \qquad \text{A - 9}$$

Let y = distance from the center of the fluid molecule.

σ = diameter of the fluid molecule.

ε = maximum energy of attraction between pair of fluid molecules.

This integral is solved in cylindrical coordinates where r is the radial distance and x is the axial distance. Hence we have:

$$\int_0^\infty \int_0^\infty \frac{-2\pi\varepsilon\sigma^6 r}{(x^2+r^2)^3}\, dr\, dx \qquad \text{A - 10}$$

This integral will be solved in two parts $0 \le y \le \sigma$ and $\sigma \le y \le \infty$

For $0 \le y \le \sigma$

$$2\pi\varepsilon\sigma^6 \int_0^y \int_{\sqrt{(r^2-x^2)}}^{\infty} \frac{-r\,dr\,dx}{(x^2+r^2)^3}$$

$$= 2\pi\varepsilon\sigma^6 \int_0^y \frac{r\,dx}{4(r^2+x^2)^2} \Big|_{\sqrt{(\sigma^2-x^2)}}^{\infty}$$

$$= \frac{\pi\varepsilon\sigma^2 y}{2} \qquad \text{A - 11}$$

For $\sigma \le y \le \infty$

$$\frac{-\pi\varepsilon\sigma^3}{2} + 2\pi\int_\sigma^y \int_0^\infty \frac{-\varepsilon\sigma^6\,r\,dr\,dx}{(r^2+x^2)^3}$$

$$= \frac{-\pi\varepsilon\sigma^3}{2} + \frac{\pi}{2}\int_\sigma^y \frac{-\varepsilon\sigma^6\,dr\,dx}{(r^2+x^2)^2} \Big|_0^\infty$$

$$= \frac{-\pi\varepsilon\sigma^3}{2} + \frac{\pi\varepsilon\sigma^3}{2}\int_\sigma^y \frac{-1\,dx}{x^4} = \pi\varepsilon\sigma^3 + \frac{\pi\varepsilon\sigma^6}{6}(1/x^3) \Big|_\sigma^y$$

$$= -\frac{2\pi\varepsilon\sigma^3}{3} + \frac{\pi\varepsilon\sigma^6}{6\,y^3}$$

$$= -\frac{2\pi\varepsilon\sigma^3}{3}(1 - \sigma^3/\,4y^3) \qquad \text{A - 12}$$

So we have $\int_v -\varepsilon\,(\sigma/r_d)^6\,dv$

$$= \frac{\pi\varepsilon\sigma^2 y}{2} \qquad (0 \le y \le \sigma) \qquad \text{A - 13}$$

$$= -\frac{2\pi\varepsilon\sigma^3}{3}(1 - \sigma^3/\,4y^3) \qquad (\sigma \le y \le \infty) \qquad \text{A - 14}$$

But for a van der Waals' fluid we know that when $r < \sigma$ the potential is ∞. So the integral of the Sutherland potential becomes for $y = \infty$.

$$-\frac{2\pi\varepsilon\sigma^3 x^2}{3} = -\frac{4\pi\varepsilon\sigma^3}{3} \qquad \text{A - 15}$$

Now we have $\int_v -\varepsilon\,(\sigma/r_d)^6 \,\frac{1dv}{v(z)}$ A - 16

Consider a molecule at an axial distance z' from the wall. It will be assumed that the potential is most influential at distance σ the molecule at z'. Here σ is equal to the diameter of the molecule. The Sutherland potential becomes

$$-\frac{\pi\varepsilon\sigma^2}{2}\,\sigma = -\frac{\pi\varepsilon\sigma^3}{2} \qquad \text{A - 17}$$

Now our molecule of interest is located at a distance z' from the wall. To integrate the density profile $\rho(z)$ or $1/v(z)$ around z' where z is the distance of any other molecule from the wall, we need to split the integral. When z' is very near the wall i.e. $\sigma/2 < z' < 1.5\,\sigma$, where σ is diameter of the molecule, the density profile may be integrated as follows :

$$\int_{\sigma/2}^{z'+\sigma} \rho(z)dz + \int_{z'+\sigma}^{\infty} \frac{\rho(z)\,dz}{(z-z')^4} \qquad \text{A - 18}$$

When z' is far from the wall i.e. $z' > 1.5\sigma$, the density profile is integrated as

$$\int_{\sigma/2}^{z'-\sigma} \frac{\rho(z)\,dz}{(z-z')^4} + \int_{z-\sigma}^{z'+\sigma} \rho(z)dz + \int_{z+\sigma}^{\infty} \frac{\rho(z)\,dz}{(z-z')^4} \qquad \text{A - 19}$$

Using reduced units of distance = η, where $\eta = z/\sigma$, $\eta' = z'/\sigma$ we get :

When $0.5 < \eta' < 1.5$

$$\int_{1/2}^{\eta'+1} \rho(\eta)\,d\eta + \int_{\eta'+1}^{\infty} \frac{\rho(\eta)\,d\eta}{(\eta-\eta')^4} \qquad \text{A - 20}$$

And when $\eta' > 1.5$

$$\int_{1/2}^{\eta'-1} \frac{\rho(\eta)\,d\eta}{(\eta-\eta')4} + \int_{\eta'-1}^{\eta'+1} \rho(\eta)\,d\eta + \int_{\eta'+1}^{\infty} \frac{\rho(\eta)\,d\eta}{(\eta-\eta')4} \qquad \text{A - 21}$$

The vdW $\frac{a(z)}{v(z)RT}$ term can be replaced as follows:

When $0.5 < \eta' < 1.5$

$$\frac{-1\,N_A}{2\,kT} \left| -\frac{\pi\varepsilon\sigma^3}{2} \int_{1/2}^{\eta'-1} \rho(\eta)\,d\eta - \frac{\pi\varepsilon\sigma^3}{2} \int_{\eta'-1}^{\infty} \frac{\rho(\eta)\,d\eta}{(\eta-\eta')^4} \right| \qquad \text{A - 22}$$

When $\eta' > 1.5$

$$\frac{-1\,N_A}{2\,kT} \left| -\frac{\pi\varepsilon\sigma^3}{2} \int_{1/2}^{\eta'-1} \frac{\rho(\eta)\,d\eta}{(\eta-\eta')^4} - \frac{\pi\varepsilon\sigma^3}{2} \int_{\eta'-1}^{\eta'+1} \rho(\eta)\,d\eta - \frac{\pi\varepsilon\sigma^3}{2} \int_{\eta'+1}^{\infty} \frac{\rho(\eta)\,d\eta}{(\eta-\eta')^4} \right. \qquad \text{A - 23}$$

For a homogeneous fluid the density is uniform so

$$\frac{a_{bulk}}{vRT} = \frac{-1 * N_A * 1}{2 * kT * v} \int_V -\varepsilon(\sigma/r_d)^6\,dv \qquad \text{A - 24}$$

$$\frac{a_{bulk}}{vRT} = \frac{1 * N_A * 1}{2 * kT * v} * \frac{4\pi\varepsilon\sigma^3}{3} \qquad \text{A - 25}$$

$$\frac{\pi\varepsilon\sigma^3}{2} = \frac{a_{bulk}}{R} * \frac{3}{4} * \frac{k}{N_A} \qquad \text{A - 26}$$

$$\frac{\pi\varepsilon\sigma^3}{2} = \frac{3}{4} * \frac{a_{bulk}}{R} * \frac{k}{N_A} \qquad \text{A - 27}$$

Using this relation we substitute for $\frac{\pi\varepsilon\sigma^3}{2}$

For $0.5 \le \eta' \le 1.5$

$$\frac{3\,a_{bulk}}{8\,RT} \left| \int_{1/2}^{\eta'+1} \rho(\eta)\,d\eta + \int_{\eta'+1}^{\infty} \frac{\rho(\eta)\,d\eta}{(\eta-\eta')^4} \right| \qquad \text{A - 28}$$

For $\eta' \geq 1.5$

$$\frac{3\,a_{bulk}}{8\,RT}\;\left|\int_{1/2}^{\eta'-1}\frac{\rho(\eta)\,d\eta}{(\eta-\eta')^4}+\int_{\eta'-1}^{\eta'+1}\rho(\eta)\,d\eta+\int_{\eta'+1}^{\infty}\frac{\rho(\eta)\,d\eta}{(\eta-\eta')^4}\right| \qquad \text{A - 29}$$

$$\ln f(\eta') = \ln\left(\frac{RT}{v(\eta')-b}\right)+\frac{b}{v(\eta')-b}-\frac{2a(\eta')}{v(\eta')RT} \qquad \text{A - 30}$$

For $0.5 \leq \eta' \leq 1.5$ we have,

$$\ln f(\eta') = \ln\left(\frac{RT}{v(\eta')-b}\right)+\frac{b}{v(\eta')-b}-\frac{3\,a_{bulk}}{4\,RT}\;\left|\int_{1/2}^{\eta'+1}\rho(\eta)\,d\eta+\int_{\eta'+1}^{\infty}\frac{\rho(\eta)\,d\eta}{(\eta-\eta')^4}\right| \qquad \text{A - 31}$$

And $\eta' \geq 1.5$

$$\ln f(\eta') = \ln\left(\frac{RT}{v(\eta')-b}\right)+\frac{b}{v(\eta')-b}-\frac{3\,a_{bulk}}{4\,RT}\;\left|\int_{1/2}^{\eta'+1}\frac{\rho(\eta)\,d\eta}{(\eta-\eta')^4}+\int_{\eta'-1}^{\eta'+1}\rho(\eta)\,d\eta+\int_{\eta'+1}^{\infty}\frac{\rho(\eta)\,d\eta}{(\eta-\eta')^4}\right|$$

A - 32

APPENDIX B

APPENDIX B

Program code for calculating surface excess using PRSLD

```
C*************************************************************
C234567
C Program to calculate surface excess or adsorption isotherms
C
C The program uses Peng Robinson equation of state, with a
C modified a to account for exclusion. The strength of the
C adsorption potential and its dependence on position
C is given by Psi.
C       The fluid-fluid potential uff = u total - u ads.
C From this potential the various fluid properties
C are calculated.
C
C
C       The variables used are defined below.
C       All units used are SI unless otherwise stated.
C
        COMMON R,TC,PC,OMEGA
C
C       Define Psi as a statement function
C       Use a 10-4 potential where PSI is the negative of the
```

```
C     intermolecular potential.
C     SIGFW = sigma fluid-wall, in Angstroms.


C     EPSFW is the fluid-wall potential in K
C     ALPHA is the ratio of the spacing of the graphite
C     basal planes (3.35 A) to SIGFW.
C     The number density of C atoms in graphite is
C     0.382 atoms/A^2.
C     The equation used is that suggested by Lee (1.5).

      PSI(ETA)=4.0*3.1415926*0.382*SIGFW*SIGFW*EPSFW*(-0.2
     1/ETA**10+0.5/ETA**4+0.5/(ETA+ALPHA)**4+0.5/(ETA+2.0*
     *ALPHA)**4+0.5/(ETA+3.0*ALPHA)**4+0.5/(ETA+4.0*ALPHA)
     ***4)

      OPEN(UNIT=3,FILE='ADSORP.DAT',STATUS='UNKNOWN')
      OPEN(UNIT=7,FILE='DENPRO.DAT',STATUS='UNKNOWN')
      OPEN(UNIT=8,FILE='EXCESS.DAT',STATUS='UNKNOWN')
      OPEN(UNIT=4,FILE='V1CAL.DAT',STATUS='UNKNOWN')
      OPEN(UNIT=2,FILE='P.DAT',STATUS='UNKNOWN')

C     R = Gas constant J/K/mol
C     Tc = Critical Temperature K
C     Pc = Critical Pressure    N/m2
```

```
C       OMEGA = Acentric Factor
C       SIGMA = Sigma gas-solid in m.
C       T = Temperature K
C       PLIM = Bulk pressure limit.
C       EPSFW = Gas-solid potential well depth in K
C       SIGFW = Sigma gas-solid in Angstroms
C       ALPHA = Spacing of graphite planes / Siggs
C       SIGFF = Sigma fluid-fluid in Angstroms
C       SIGWW = Sigma wall-wall in Angstroms
C       AB = Bulk Peng-Robinson 'a'
C       BB = Bulk Peng-Robinson 'b'

        R=8.314
        TC=304.1
        PC=73.8E5
       OMEGA = 0.239
       FOMEGA = 0.37464+1.54226*OMEGA-0.26992*(OMEGA**2)
       T=334.51
        TR=T/TC
         PLIM=130E5
         EPSFW=97.6
        SIGFF = 4.163
        SIGWW = 3.4
        SIGFW = (SIGWW+SIGFF)/2
        SIGMA = SIGFW*1E-10
```

```
         ALPHA=3.35/SIGFW

C        Calculate a bulk and b
         AB=0.45724*(R*TC*(1+FOMEG*(1-SQRT(TR))))**2/PC
         BB=0.07780*R*TC/PC
C        Write parameters to files
         PCB=PC/1.0E5
         WRITE(7,*) TC
         WRITE(7,*) PC
         WRITE(7,*) SIGMA
         WRITE(7,*) SIGWW
         WRITE(7,*) SIGFW
         WRITE(7,*) SIGFF
         WRITE(7,*) AB
         WRITE(7,*) BB
         WRITE(7,*) T
C       CHECK WHETHER CONDITIONS ARE SUBCRITICAL OR
C        SUPERCRITICAL
          IF(TR.GE.1) GOTO 2
C        IF SUBCRITICAL FIND SATURATION PRESSURE, FUGACITY
C        AND VAPOR AND LIQUID DENSITIES.
           CALL FSAT(AB,BB,T,FUGS,PS,VV,VL)
 2                 DELP=PLIM/40.
C                LOOP FOR BULK PRESSURE
                 PB=0.0E5
```

```
                  J = 0
C         FOR EACH BULK PRESSURE VALUE
 5                            PB=PB+DELP
                              B=BB
                              A=AB
C        FIRST CALCULATE BULK DENSITY (DENB) and BULK
C        FUGACITY (FB)


                             CALL BVCAL(A,B,T,PB,PS,V,FB)
                              CALL PV(A,B,T,V,P)

                              DENB=1.0/V
                              BP=P

     WRITE(7,*) P
     WRITE(7,*) DENB
     WRITE(2,*)P/1E5, DENB, ALOG(FB)

                              DELETA=0.1
                              ETA=.9
                              EXCESS=0.0
                                       K=0
 6                                             ETA=ETA+DELETA
```

```
C     Calculate local fugacity
C       Use the following formula to get the local
C       fugacity (F), for a given position ETA.
C                                              F=FB*EXP(PSI(ETA)/T)
                                               ALNFB=ALOG(FB)
                                               ALNF=ALNFB+PSI(ETA)/T
                                               PSIV=PSI(ETA)
C                                              Calculate local a
      CALL ACALC(ETA,AB,A,SIGWW,SIGFW,SIGFF)
C  Using local parameters calculate V and local density DENL


        CALL VCALC(A,B,T,ALNF,BP,PS,V)
                       DENL=1.0/V


            EXCESS=SIGMA*(DENL-DENB)*DELETA*1.E6+EXCESS
C       DENLG is the density in gmoles/cc
                      DENLG=DENL/1.0E6
                      WRITE (7,102)ETA,DENL,ALNF
              K = K+1
         IF(K.LT.200) GOTO 6
              BP=P/1.0E5
              DENBG=DENB/1.E6
              WRITE(3,*)BP,EXCESS
               WRITE(8,*) BP
```

```
            J = J+1
         IF(J.LT.40)  GOTO 5
 102 FORMAT(1X,F8.2,2X,F12.5,2X,F10.5)
        END

C************************************************************
C234567
C      SUBROUTINES
C************************************************************
C     THIS SUBROUTINE CALCULATES BULK FUGACITY & DENSITY

       SUBROUTINE  BVCAL(A,B,T,P,PS,V,FB)

       COMMON  R,TC,PC,OMEGA

       PMX = 0
       PMN = 0
      ASTAR = A*P/(R*T)**2
      BSTAR = B*P/R/T
       A2 = BSTAR-1
       A1 = ASTAR-BSTAR*(2+3*BSTAR)
       A0 = BSTAR*(BSTAR**2+BSTAR-ASTAR)

      CALL  CUBIC(A2,A1,A0,R1,R2,R3,C1,C2,C3,IFLAG)
         WRITE(2,*)'IFLAG',IFLAG
```

```
IF (IFLAG.EQ.1) THEN
      ZV=R1
       V= ZV*R*T/P
 ALNF=A/2.82/R/T/B*ALOG((V-0.414*B)/(V+2.414*B))
ALNF=ALNF+ALOG(R*T/(V-B))+B/(V-B)
ALNF=ALNF-A*V/R/T/(V*V+2*B*V-B*B)
      FB = EXP(ALNF)
ELSE IF(IFLAG.EQ.2) THEN
      ZL = R1
      IF(ZL.GT.R2)  ZL=R2
      ZV = R1



       IF(ZV.LT.R2)  ZV=R2
     ELSE
         CALL ARANGE(R1,R2,R3)
            ZL = R3
            ZV = R1
  ENDIF

  IF (IFLAG.EQ.1) GOTO 14
   VMAX=ZV*R*T/P
    VMIN=ZL*R*T/P
     VB=1.1*B
   WRITE(2,*) VMAX,VMIN
```

```
         CALL PV(A,B,T,VMAX,PMX)
         CALL PV(A,B,T,VMIN,PMN)
          V = VMIN
         CALL DPDV(A,B,T,VMAX,IDPDV1)
             IF(VMIN.EQ.0)  GOTO 11
          CALL DPDV(A,B,T,VMIN,IDPDV3)

11      IF (P.LE.PS)  V=VMAX
           IF (VMIN.EQ.0)   V=VMAX
          FUGF1=(A/2.8284)*ALOG((V-0.414*B)/(V+2.414*B))
         ALNFMX=ALOG(R*T/(V-B))+B/(V-B)+FUGF1/B/R/T
         ALNFMX=ALNFMX-A*V/R/T/(V**2+2*B*V-B*B)


           FB = EXP(ALNFMX)
14        WRITE(6,*)1/V,FB
            CONTINUE
             RETURN
            END

C*************************************************************
C      THIS SUBROUTINE CALCULATES THE LOCAL VOLUME (WHICH
C       IS USED TO CALCULATE THE LOCAL DENSITY)
```

```
      SUBROUTINE VCALC(A,B,T,ALNF,BP,PS,V)
      COMMON R,TC,PC,OMEGA

      IV=1
       IV3=1
       DPDV1=1
       DPDV3=1
       P1=0
       P3=0
       V=0
       CALL V1CALC(A,B,T,ALNF,V1,IV1)
         IF(IV1.EQ.1)  GOTO 10
        CALL DPDV(A,B,T,V1,IDPDV1)
         IF(IDPDV1.EQ.1)  GOTO 10
10     CONTINUE



         CALL V3CALC(A,B,T,ALNF,V3,IV3)
          IF (IV3.EQ.1)  GOTO 14
         CALL DPDV(A,B,T,V3,IDPDV3)
          IF(IDPDV3.EQ.0)  THEN
              CALL PV(A,B,T,V3,P3)
            ELSE
          CONTINUE
         ENDIF
```

```
 14     CONTINUE
          IF  (P1.GT.P3)  THEN
           V=V1
          ELSE
             V=V3
            ENDIF
           CONTINUE
           GOTO 15
 15      RETURN
       END

C*************************************************************
C  THIS SUBROUTINE CALCULATES SATURATION FUGACITY
C  FOR SUBCRITICAL CONDITIONS
        SUBROUTINE  FSAT(A,B,T,FUGS,PS,VMX,VMN)
             COMMON  R,TC,PC,OMEGA
         TR = T/TC



         SLOPE=-(1+OMEGA)/0.4286
          FPR=(SLOPE/TR)-SLOPE
          PR=10**FPR
           P=PR*PC
 20      CONTINUE
            K = 0
```

```
       BSTAR=B*P/R/T
       ASTAR=A*P/(R*T)**2
       A2=BSTAR-1
       A1=ASTAR-BSTAR*(2+3*BSTAR)
       A0=BSTAR*(BSTAR**2+BSTAR-ASTAR)
       CALL CUBIC(A2,A1,A0,R1,R2,R3,C1,C2,C3,IFLAG)
       IF (IFLAG.EQ.1)  GOTO 32
        COTINUE
        IF(IFLAG.EQ.2) THEN
            ZL = R1
            IF(R1.GT.R2)  ZL=R2
              ZV = R1
              IF(ZV.LT.R2)  ZV=2
          ELSE
        CALL ARANGE(R1,R2,R3)
            ZL = R3
           ZV = R1
        ENDIF
       VL=ZL*R*T/P



      VV=ZV*R*T/P
 RLT=ALOG((2*ZV+BSTAR*(2.+8.**0.5))/(2*ZL+BSTAR*(2.+
18.**0.5)))
      IF  (BSTAR.GE.ZV)  THEN
```

```
            STOP
         ENDIF
         RLT2=ALOG(ZV-BSTAR)
         RLNPHI=(ZV-1)-RLT2-ASTAR*RLT/BSTAR/(8.**0.5)
         FUGV=EXP(RLNPHI)*P
     RLT=ALOG((2*ZL+BSTAR*(2+8**0.5))/(2*ZL+BSTAR*(2-
    18**0.5)))
        IF(BSTAR.GE.ZL)  THEN
             STOP
        ENDIF
        RLT2=ALOG(ZL-BSTAR)
        RLNPHI=(ZL-1)-RLT2-ASTAR*RLT/BSTAR/(8**0.5)
         FUGL=EXP(RLNPHI)*P
           K = K+1
           IF(K.GT.200)   THEN
             GOTO  31
          ENDIF
         TEST=ABS(1-FUGL/FUGV)
          IF(TEST.LT.0.001)  GOTO 30
           P=P*FUGL/FUGV
            GOTO  20
31      WRITE(6,*) 'NOT ITERATED'
            STOP
32       Z = R1
            VV= Z*R*T/P
```

```
            VL=VV
          RLT=ALOG((Z+2.414*BSTAR)/(Z-0.414*BSTAR)
          RLT2=ALOG(Z-BSTAR)
          RLNPHI=Z-1-RLT2-RLT*ASTAR/2.82/BSTAR
          FUGS=EXP(RLNPHI)*P
 30       FUGS=FUGL
           VMX=VV
            VMN=VL
             PS=P
              WRITE(6,*)ALOG(FUGL),ALOG(FUGV),VL,VV
             RETURN
             END

C************************************************************
      SUBROUTINE CONV(A,B,T,ALNF,V1,V3,V,ERROR)
      COMMON R

C     This subroutine iterates between values VLOW = V1
C     and VHIGH = V3 for a V which is satisfactory.
C     This subroutine uses a linear interpolation scheme
C     (Secant or Regula-Falsi) method and can be very slow.

      ALNF1C=B/(V1-B)-A*V1/R/T/(V1*V1+2*B*V1-B*B)
      ALNF1C=ALNF1C+ALOG(R*T/(V1-B))
      ALNF1C=ALNF1C+A/2.824*ALOG((V1-0.414*B)/(V1+2.414*B))/
```

```
     *B/R/T
      ALNF1=ALNF1C-ALNF
      F1=EXP(ALNF1)

      ALNF3C=B/(V3-B)-A*V3/R/T/(V3*V3+2*B*V3-B*B)
      ALNF3C=ALNF3C+ALOG(R*T/(V3-B))
       ALNFC3=ALNFC3+A/2.824*ALOG((V3-0.414*B)/(V3+2.414*B))/
     *B/R/T
      ALNF3=ALNF3C-ALNF
      F3=EXP(ALNF3)

17    V=(V3-V1)/(F3-F1)+(V1*F3-V3*F1)/(F3-F1)
      ALNFC=B/(V-B)-2.0*A/R/T/V
      ALNFC=ALNFC+ALOG(R*T/(V-B))
      ERROR=EXP(ALNFC-ALNF)-1.0
      IF (ABS(ERROR).LE.0.001) GOTO 40
      IF (ERROR.LE.0) THEN
        V3=V
        F3=EXP(ALNFC-ALNF)
      ELSE
        V1=V
        F1=EXP(ALNFC-ALNF)
      ENDIF
      GOTO 17
40    CONTINUE
```

```
      RETURN
      END

C ******************************************************
C234567
      SUBROUTINE DPDV(A,B,T,V,IDPDV)
      COMMON R

C     Input A,B,T,V and Output = IDPDV
C     THIS SUBROUTINE EVALUATES THE DERIVATIVE dP/dv
C     AND RETURNS A VALUE OF 1 FOR IDPDV IF THE SLOPE
C     IS POSITIVE, i.e. THE ROOT IS UNSTABLE.
      IDPDV=0
      DP=-R*T/(V-B)/(V-B)+2.0*A*(V+B)/((V*V+2*B*V-B*B)**2)
      IF (DP.GT.0) IDPDV=1
      RETURN
      END

C**************************************************************
        SUBROUTINE V1CALC(A,B,T,ALNF,V1,IV1)
C     This subroutine uses a successive substituion method
C     to get the small root V1.
C     Inputs A,B,T,ALNF and Output V1, IV1
        COMMON R,TC,PC,OMEGA
       IV1=0
```

```
C  Starting guess for calculating v
    V1=1.1*B
C   Iterate 60 times

    DO 20 I = 1,60
        ARG=(V1-B)/R/T
        IF((V1.LE.B).OR.(ARG.LE.0.0)) THEN
            IV1=1
            GOTO 30
        ELSE
     DENO=ALNF+ALOG(ARG)+A*V1/R/T/(V1**2+2*B*V1-B**2)
   DENO=DENO+A/2.82/R/T/B*ALOG((V1+2.414*B)/(V1-0.414*B))
            V1=B+B/DENO
        ENDIF
20 CONTINUE
   ALNFC=B/(V1-B)-A*V1/R/T/(V1*V1-2*B*V1*B*B)
   ALNFC=ALNFC+ALOG(R*T/(V1-B))

   ALNFC=ALNFC+A/2.82/R/T/B*ALOG((V10.414*B)/(V1+2.414*B))
   ERROR=EXP(ALNFC-ALNF)-1.0
   IF (ABS(ERROR).GE.0.001) IV1=1
30 CONTINUE
   RETURN
   END
```

```
C*************************************************************
C234567


      SUBROUTINE V3CALC(A,B,T,ALNF,V3,IV3)


      COMMON R,TC,PC,OMEGA
      IV3=0
C     STARTING GUESS FOR V3 = RT/F
      ALNV3=ALOG(R*T)-ALNF
      V3=EXP(ALNV3)
C     ITERATE TILL DONE OR 40 TIMES
      DO 20 I=1,40
        IF (V3.LE.B) THEN
        IV3=1
        GOTO 30
        ENDIF
        ARG=B/(V3-B)-A*V3/R/T/(V3**2+2*B*V3-B**2)
        IF(ARG.GT.40.) THEN
C         D3=1./V3
          IV3=1
          GOTO 30
        ELSE
          DENO=A/2.824/R/T/B*ALOG((V3-0.414*B)/(V3+2.414*B))
         ALNV3B=ALOG(R*T)-ALNF+ARG+DENO
```

```
          V3=B+EXP(ALNV3B)
         ENDIF
 20     CONTINUE
        ALNFC=B/(V3-B)-A*V3/R/T/(V3*V3+2*V3*B-B*B)



        ALNFC=ALNFC+ALOG(R*T/(V3-B))
       ALNFC=ALNFC+A/2.824*ALOG((V3-0.414*B)/(V3+2.414*B)/
      *B/R/T
        ERROR=EXP(ALNFC-ALNF)-1.0
        IF(ABS(ERROR).GE.0.001) IV3=1
 30     CONTINUE
        RETURN
        END

C*************************************************************
C234567
         SUBROUTINE PV(A,B,T,V,P)
         COMMON R
C        This subroutine returns the value of P given a,b,T,v
C        using the Peng-Robinson equation of state.

         P=R*T/(V-B)-A/(V8V+2*B*V-B*B)
         RETURN
         END
```

```
C***********************************************************
C234567
      SUBROUTINE ARANGE(R1,R2,R3)
C     PROGRAM TO PUT 3 NUMBERS IN DESCENDING ORDER
      DO 20 J=1,3
        IF(R2.GT.R1) THEN



           TEMP=R1
           R1=R2
           R2=TEMP
        ENDIF
        IF(R3.GT.R2) THEN
           TEMP=R2
           R2=R3
           R3=TEMP
        ENDIF
 20   CONTINUE
      RETURN
      END

C**************************************************
C234567
        SUBROUTINE ACALC(ETA,AB,A,SIGWW,SIGFW,SIGFF)
C       This subroutine calculates the 'a' term
```

```
C        after taking into account the effect of exclusion.
C        AB = Value of a in the bulk
C        ETA = reduced distance from the center of wall
C       The main program sends a reduced distance ETA based on
C       the distance from the center of the wall molecule to
C       the center of the first fluid molecule(SIGFW), which
C        is the basis for the integrated 9-3 potential.
C      However the integrations for configurational energy
C       have been done from the edge of the wall molecule.
C       Therefore it is necessary to translate the
C       coordinate. BETA is the distance from the edge of the
C       wall in reduced units
C        If the wall molecule and the fluid molecule were of
C        the same size
C         BETA = ETA - 0.5
C         However, the wall molecules and the fluid molecules
C         are of different sizes, hence the conversion is
C         slightly complicated.

        BETA = (ETA - (0.5*SIGWW/SIGFW))*(SIGFW/SIGFF)
        IF (BETA.LE.1.5) THEN
                A=AB*(5.0+6.0*BETA)/16.0
        ELSE
                A=AB*(1.0-1.0/8.0/(BETA-0.5)**3)
        ENDIF
```

```
      RETURN
      END

C*************************************************************
*************************************************************

C**************************************************************
C                    SUBROUTINE CUBIC
C**************************************************************
C* THIS SUBROUTINE FINDS THE ROOTS OF A CUBIC EQUATION OF  *
C* THE FORM  X**3 + A2*X**2 + A1*X + A0 = 0 ANALYTICALLY.  *

C**************************************************************

C* VARIABLES                                                  *
C**************************************************************
C* A0 ------ THE ZEROETH ORDER TERM OF THE NORMALIZED CUBIC *
C*            EQUATION                                        *
C* A1 ------ THE FIRST ORDER TERM OF THE NORMALIZED CUBIC   *
C*            EQUATION                                        *
C* A2 ------ THE SECOND ORDER TERM OF THE NORMALIZED CUBIC  *
C*            EQUATION                                        *
C* C1 ------ THE COMPLEX ARGUMENT OF ROOT #1 OF THE EQUATION*
C* C2 ------ THE COMPLEX ARGUMENT OF ROOT #2 OF THE EQUATION*
C* C3 ------ THE COMPLEX ARGUMENT OF ROOT #3 OF THE EQUATION*
C* CCHECK -- THE SAME AS "CHECK" BUT CONVERTED TO COMPLEX   *
C*           NUMBER FORMAT                                    *
C* CHECK --- Q**3 + R**2, USED TO CHECK FOR THE CASE OF THE *
C*           SOLUTION AND IN FINDING THE ROOTS OF THE        *
C*           EQUATION, DOUBLE PRECISION                       *
C* DA0 ----- "A0" CONVERTED TO DOUBLE PRECSION                *
C* DA1 ----- "A1" CONVERTED TO DOUBLE PRECSION                *
```

```
C* DA2 ----- "A2" CONVERTED TO DOUBLE PRECSION                 *
C* ES1 ----- AN INTERMEDIATE CALCULATION TO USED IN THE        *
C*           CALCULATION OF "S1"                               *
C* ES2 ----- AN INTERMEDIATE CALCULATION TO USED IN THE        *
C*           CALCULATION OF "S2"                               *
C* IFLAG --- A FLAG TO INDICATE THE CASE OF THE SOLUTION OF *
C*           THE EQUATION:=1 ONE REAL + TWO COMPLEX ROOTS,     *
C*                         =2 REAL ROOTS,AT LEAST TWO THE SAME *
C*                         =3 THREE DISTINCT REAL ROOTS        *
C* P1 ----- AN INTERMEDIATE SUM USED IN THE CALCULATION OF     *
C*          "SS1"                                              *
C* P2 ----- AN INTERMEDIATE SUM USED IN THE CALCULATION OF     *
C*          "SS2"                                              *
C* Q ------ AN INTERMEDIATE SUM USED IN CALCULATING "CHECK" *
C* R ------ AN INTERMEDIATE SUM USED IN CALCULATING "CHECK" *
C* R1 ----- THE REAL ARGUMENT OF ROOT #1 OF THE EQUATION       *
C* R2 ----- THE REAL ARGUMENT OF ROOT #2 OF THE EQUATION       *
C* R3 ----- THE REAL ARGUMENT OF ROOT #3 OF THE EQUATION       *
C* RECK --- THE SAME AS "CHECK", BUT SINGLE PRECISION REAL     *
C* S1 ----- AN INTERMEDIATE VALUE USED TO FIND THE ROOTS OF *
C*          THE EQUATION, COMPLEX NUMBER                       *
C* S2 ----- AN INTERMEDIATE VALUE USED TO FIND THE ROOTS OF *
C*          THE EQUATION, COMPLEX NUMBER                       *
C* SS1 ---- THE SAME AS S1 BUT DOUBLE PRECSION REAL            *
C* SS2 ---- THE SAME AS S2 BUT DOUBLE PRECSION REAL            *
C* Z1 ----- ROOT #1 OF THE EQUATION, COMPLEX NUMBER            *
C* Z2 ----- ROOT #2 OF THE EQUATION, COMPLEX NUMBER            *
C* Z3 ----- ROOT #3 OF THE EQUATION, COMPLEX NUMBER            *
C*************************************************************


      SUBROUTINE CUBIC(A2,A1,A0,R1,R2,R3,C1,C2,C3,IFLAG)

         DOUBLE PRECISION CHECK,DA0,DA1,DA2,P1,P2,Q,R,SS1,SS2
```

```
COMPLEX ES1,ES2,S1,S2,Z1,Z2,Z3,CCHECK
 DA0 = DBLE(A0)
 DA1 = DBLE(A1)
 DA2 = DBLE(A2)
 Q = DA1/3.D00 - DA2*DA2/9.D00
 R = (DA1*DA2 - 3.D00*DA0)/6.D00 - (DA2/3.D00)**3
 CHECK = Q**3 + R*R
 IF (CHECK.GT.0.0) THEN
       IFLAG = 1
       P1 = R + DSQRT(CHECK)
       P2 = R - DSQRT(CHECK)
       IF (P1.LT.0.0) THEN
             SS1 = -DEXP((DLOG(-1.D00*P1))/3.D00)
          ELSE
             SS1 = DEXP((DLOG(P1))/3.D00)
          ENDIF
       IF (P2.LT.0.0) THEN
             SS2 = -DEXP((DLOG(-1.D00*P2))/3.D00)
          ELSE
             SS2 = DEXP((DLOG(P2))/3.D00)
          ENDIF
       R1 = SS1 + SS2 - DA2/3.D00
       R2 = -(SS1 + SS2) - DA2/3.D00
       R3 = R2
       C1 = 0.0
```

```
            C2 = (SQRT(3.))*(SS1 - SS2)/2.D00
            C3 = -C2
         ELSE IF (CHECK.LT.0.0) THEN
            IFLAG = 3
            RR = 1.*R
            RECK = 1.*CHECK
            CCHECK = CMPLX(RECK,0.0)
            ES1 = CLOG(RR + CSQRT(CCHECK))/3.
            ES2 = CLOG(RR - CSQRT(CCHECK))/3.
            S1 = CEXP(ES1)
            S2 = CEXP(ES2)
     Z2 = -(S1 + S2)/2 - A2/3 + (CMPLX(0.0,3**.5))*(S1 -
   *S2)/2
     Z3 = -(S1 + S2)/2 - A2/3 - (CMPLX(0.0,3**.5))*(S1 -
   *S2)/2
            R1 = REAL(Z1)
            R2 = REAL(Z2)
            R3 = REAL(Z3)
            C1 = 0.0
            C2 = C1
            C3 = C1
         ELSE
C************************************************************
C * IF THE ROOTS OF THE EQUATION ARE VERY, VERY SMALL AND   *
C * VERY, VERY CLOSE TOGETHER, THIS SUBROUTINE MAY          *
```

```
C * ERRONEOUSLY REPORT THAT THE EQUATION HAS ONLY ONE       *
C * ROOT NEAR ZERO                                          *
C************************************************************
               IFLAG = 2
              IF (R.LT.0.0) THEN
                     SS1 = -DEXP((DLOG(-1.D00*R))/3.D00)
                  ELSE IF (R.EQ.0.0) THEN
                     SS1 = 0.0
                  ELSE
                     SS1 = DEXP((DLOG(R))/3.D00)
                  ENDIF
               SS2 = SS1
               R1 = SS1 + SS2 - DA2/3.D00
               R2 = -(SS1 + SS2)/2 - DA2/3.D00
               R3 = R2
               C1 = 0.0
               C2 = C1
               C3 = C2
            ENDIF
         RETURN
         END
```

APPENDIX C

APPENDIX C

Program code for calculating the surface excess using the density profile calculated from the vdWSLD as a first guess to solve the integral equation

```
C                    ADPRO.F
C This program calculates density profile and surface excess.
C Some of the constants used are R=8.314 J/K*mol, ETA is the
C dimensionless distance, DEN is the density, ALNF is the
C natural log of fugacity. BETA is corrected reduced
C distance, BULD is bulk density.

      REAL*8 ETA(261),DEN(261),A(261),ANS1,ANS2,ANS3,ER,ANS,TC
      REAL*8 V1(261),V2,E,Y(151),X(151),T,DEN19261),EXCESS
      REAL*8 PC,AB,BB,P,DENB,BETA(261),ALNF(261),DEN2(261)
      INTEGER I,K2,K3,K4,K,J,L,N,N2,IFAIL,N1,M
      EXTERNAL D01GAF

C      D01GAF IS A NAG SUBROUTINE WHICH PERFORMS
C       NUMERICAL INTEGRATION.
        OPEN(UNIT=3,FILE='DENPRO.DAT',STATUS='UNKNOWN')
```

```
C DENPRO.DAT is the data file generated by
C the VdWSLD program.
       OPEN(UNIT=4,FILE='EXCES.DAT',STATUS='UNKNOWN')
C      This file stores surface excess data.

         OPEN(8,STATUS='UNKNOWN', FILE='IE3. DAT')
         OPEN(2,STATUS='UNKNOWN', FILE='D3. DAT')

C       TC=Critical temperature, K
C        PC=Critical pressure. N/m**2
C        SIGMA=Sigma fluid - wall, m
C        SIGWW=Sigma wall - wall,Angstroms
C        SIGFW=Sigma fluid - wall, Angstorms
C        SIGFF= Sigma fluid - fluid, Angstorms

           READ(3,*)TC
           READ(3,*)PC
           READ(3,*)SIGMA
           READ(3,*)SIGWW
           READ(3,*)SIGFW
           READ(3,*)SIGFF
           READ(3,*)AB
           READ(3,*)BB
           READ(3,*)T
           IER=0.0
```

```
C          T=temperature,K
C          P=pressure, N/m**2
C          BULD=bulk density,gmol/m**3

    10      READ(3,*,END=11)P
              READ(3,*)DENB

              DO 25 I=1,200
                READ(3,102,END=12)ETA(I),DEN(I),ALNF(I)
      12 BETA(I)=(ETA(I)-0.5*(SIGWW/SIGFW) )*(SIGFW/SIGFF)
C     12        BETA(I)=ETA(I)-0.5
                DEN1 (I)=DEN(I)
    25        CONTINUE
C   'C'   IS A LOOP COUNTER
                C=1

C   NOW THE FUNCTION VALUES ARE CALCULATED
   5        DO  45   I=1,140
                     K2=I-10
                     K3=I+10
                      K4=I+60

             IF  (BETA(I).GT. 1.5)  GOTO  66
```

```
               DO  55   J=1,K3
                        A(J)=DEN(J)
                            JJ=J-1+1
                       X(JJ)=A(J)
55            CONTINUE

C NOW THE INTEGRAL IS CALCULATED USING  D01GAF
                N=K3-1+1
                IFAIL=0
             CALL  DO1GIF (X,Y,N,ANS1,ER,IFAIL)

             DO  65  K=K3,K4
                     A(K)=DEN(K)/( (BETA(I) )**4)
                      KK=K-K3+1
                     X(KK)=BETA(K)
                      Y(KK)=A(K)
  65        CONTINUE
                     N1=K4-K3+1
                     IFAIL=0
               CALL  DO1GIF  (X,Y.ANS2,ER,IFAIL)

              ANS=ANS1+ANS2
              GOTO 35
C  DO1GAF  CAN'T BE USED IF THERE ARE LESS THAN FOUR DATA
C    POINTS FOR THIS CASE USE TRAPEZOIDAL RULE
```

```
66         IF (K2-1.LT.4)  GOTO 67


              DO  75  L=1,K2
                   A(L)=DEN(L)/( (BETA(L)-BETA(I) )**4 )
                     LL=L-1+1
                   X(LL)=BETA(L)
                   Y(LL)=A(L)
 73          CONTINUE
                   N=K2-1+1
                   IFAIL=0
               CALL DO1GAF(X,Y,N,ANS1,ER,IFAIL)


 67           SUM=0.0
                 DO 76 L=1,K2
                    A(L)=DEN(L)/( ( BETA(L)-BETA(I) )**4 )
                    SUM=SUM+A(L)
76            CONTINUE
                  H= (BETA(K2)-BETA(1) )/(K2-1+1)
                  SUM1=SUM- (A (1) +A(K2) )/2
                  ANS1=H*SUM1
                DO  85  M=K2,K3
                       A(M)=DEN(M)
                        MM=M-K2+1
                       X(MM)=BETA(M)
                       Y(MM)=A(M)
```

```
   85           CONTINUE
                          IFAIL=0
                          N1=K3-K2+1
                   CALL D01GAF(X,Y,N1,ANS2,ER,IFAIL)

                 DO  95  N=K3,K4
                   A(N)=DEN(N) / ( ( BETA(N)-BETA(I) )**4 )
                   NN=N-K3+1
                   Y(NN)=A(N)
                     X(NN)=BETA(N)
   95          CONTINUE
                            IFAIL=0
                             N2=K4-K3+1
                CALL   D01GAF(X,Y,N2,ANS3,ER,IFAIL)

              ANS=ANS1+ANS2+ANS3

C  THE NEW DENSITIES ARE CALCULATED
   35        F=ALNF(I)-LOG( (8.314*T) )
               E=(ANS*.75) / (T*8.314)*AB

               V1 (I)= 1/DEN(1)
   400       FUN=LOG(V1 (I)-BB )+F+E-BB/ (V1(I)-BB)
                 DFUN=V1(I)/((V1(I)-BB)**2)
```

```
68          V2=V1  (I)-FUN/DFUN
                  IF(ABS(V1  (I)-V2 ).LT.1E-6 )   GOTO 77
               V1  (I)=V2
              GOTO  400
77          DEN2  (I)=1/V1(I)
45          CONTINUE

C   CONDITION FOR ENDING IS THE NUMBER OF LOOPS SHOULD NOT
C   EXCEED  100 AND THE DIFFERENCE BETWEEN VALUES IN OLD
C   AND NEW PROFILE SHOULD NOT EXCEED 0.1%

            C=C+1
           IF(C.GT.101)    GOTO   19
            DO  7   KM=1,140
               DIFF=(ABS(DEN(KM)-DEN2(KM)  )/DEN(KM)
               DIFFP = DIFF*100
                IF    (DIFFP.GT.0.1)     GOTO 8
7         CONTINUE
            GOTO 190
8         CONTINUE

           DO  18  KJ=1,140
                     DEN(KJ)=DEN2(KJ)
18        CONTINUE
                GOTO  5
```

```
          DO 17 KL 141,200
               DEN(KL) = DEN(140)
   17     CONTINUE
               GOTO 5
C   IF THE LOOP DOES NOT CONVERGE AFTER 100 ITERATIONS IER=1
   19       IER=1.0
              WRITE(6,*)'IER',IER
   190      EXCESS=0.0
               EXC1=0.0
               DENERR=0.0
                SUM=0.0
               SUM1=0.0
                DO  9  I=1,140
                              DEN(I)=DEN2(I)

        EXCESS=SIGMA*0.1*(DEN(I)-DENB)*1E6+EXCESS
         EXC1=SIGMA*0.1*(DEN1(I)-DENB)*1E6+EXC1

                              SUM=DEN(I)-DENB+SUM
                              SUM1=DEN1(I)-DENB+SUM1
                              DENERR=1-SUM/SUM1
C                            WRITE(6,*)'C',C
                                WRITE(2,*) ETA(I),DEN(I)
   9          CONTINUE
              EXERR=(1-(EXC1/EXCESS) )*100
```

```
          WRITE(8,*)P,EXC1,EXCESS
                   PDENER=DENERR*100
           WRITE (4,*)P,EXERR
           GOTO  10
11        WRITE(6,*)'END OF PROGRAM
              WRITE(6,*)IER

102        FORMAT(1X,F8.2,2X,F12.5,2X,F10.5)
103       FORMAT(1X,F8.2,2X,F12.5,2X,F12.5)

                 END
```

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BIBLIOGRAPHY

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