

# THE DENSITY PROFILES OF A LENNARD-JONES FLUID CONFINED TO A SLIT

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## Abstract

The structure of fluids confined by planar walls is studied using density functional theory. The density functional used is a generalized form of the hypernetted chain (HNC) functional which contains a term *third order* in the density. This term is chosen to ensure that the modified density functional gives the correct bulk pressure. The proposed density functional applied to a Lennard-Jones fluid confined to a slit for temperatures below the critical point. The agreement between the results of the density profiles obtained by the theory and computer simulation are good.

## Introduction

Following successes in the understanding of the properties of homogeneous fluids, there has been increasing activity directed at the understanding of inhomogeneous fluids, especially of the fluid-solid interface [1]. Such work is relevant to an appreciation of the structure and the behaviour of thin films, of wetting phenomena, of adhesion, of the electrical double layer, of catalysis and the properties of colloidal dispersions. This paper contains a contribution which follows earlier work on the structure of a fluid-solid interface, and supplements it.

In the previous papers [2,3], the modified density functional introduced by Rickayzen and Augousti [4] can improve the theory of the structure of a fluid close to a wall and gives the density profile of the fluid in better agreement with computer simulation. Powles, Rickayzen and Williams [5] used the same density functional to obtain the density profile of a Lennard-Jones, LJ 12-6, fluid confined to a slit. They showed that for a hard wall-LJ fluid system the agreement between their result and that of the computer simulation

for the temperature close and above the critical temperature is satisfactory, but it failed at a lower temperature or when the density at the wall is substantially lower than the bulk density. Powles et al. [5] also applied the proposed density functional to a LJ wall-LJ fluid system (wall with a '10-4-3' potential) for a temperature,  $T^*=1.35$  (above the critical temperature of the homogeneous fluid). At this temperature the results of the density profile are in good agreement with those obtained from computer simulation. Here we apply the same density functional method to a LJ 12-6 fluid for a different wall potential and a lower temperature, to find the density profiles and to compare them with the simulation results.

## The Density Integral Equation

We consider a fluid of spherically symmetric molecules confined to a slit where the external potential varies only in one dimension, the  $x$  direction, the thermodynamic potential per unit area at temperature  $T$  is given by [5].

$$\Omega[\rho] = \Omega[\rho_0] + K_B T \int dx_1 \rho(x_1) \ln \frac{\rho(x_1)}{\rho_0} - K_B T \int dx_1 \delta\phi(x_1)$$

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$$\begin{aligned}
 & -K_B T/2 \int dx_1 dx_2 C(x_1, x_2) \delta\rho(x_1) \delta\rho(x_2) \\
 & -K_B T \int dx_1 dx_2 dx_3 L(x_1, x_2, x_3) \delta\rho(x_1) \delta\rho(x_2) \delta\rho(x_3) \\
 & + \int dx_1 V(x_1) \rho(x_1), \tag{1}
 \end{aligned}$$

Where  $\rho(x)$  is the density,  $\rho_0$  is the bulk density,  $K_B$  is Boltzmann's constant and  $V(x_1)$  is the external potential,

$$\delta\rho(x_1) = \begin{cases} \rho(x_1) - \rho_0 & 0 < x_1 < h \\ -\rho_0 & \text{otherwise} \end{cases}, \tag{2}$$

here  $h$  is the separation of the walls. The function  $C(x_1, x_2)$  is related to the direct correlation function of the homogeneous fluid through the equation,

$$C(x_1, x_2) = \int dy_2 dz_2 c(r_1, r_2, \rho_0). \tag{3}$$

The function  $L(x_1, x_2, x_3)$  has been discussed

$$L(x_1, x_2, x_3) = B f(x_1 - x_2) f(x_2 - x_3) f(x_3 - x_1) \tag{4}$$

$$f(x) = \left(1 - \frac{x^2}{\sigma^2}\right) \Theta(\sigma - |x|), \tag{5}$$

here  $\sigma$  is the distance parameter of the Lennard-Jones fluid.

Parameter  $B$  is chosen such that, the density functional, equation (1), leads to the correct bulk pressure at far distances from the wall,

$$\frac{P}{k_B T} = \rho_0 - \rho_0 \int_{-\infty}^{\infty} dx_2 \left[ \frac{\rho_0}{2} C(x_1, x_2) - \rho_0^2 \int_{-\infty}^{\infty} dx_3 L(x_1, x_2, x_3) \right] \tag{6}$$

The equilibrium density of the fluid minimizes the thermodynamic potential and satisfies the integral equation below;

$$\begin{aligned}
 \ln \frac{\rho(x_1)}{\rho_0} &= \int dx_2 C(x_1, x_2) \delta\rho(x_2) \\
 &+ 3 \int dx_2 dx_3 L(x_1, x_2, x_3) \delta\rho(x_2) \delta\rho(x_3) - \frac{V(x_1)}{K_B T} \tag{7}
 \end{aligned}$$

To solve the integral equation (7), the homogeneous direct correlation function and the bulk pressure are required.

### The Bulk Direct Correlation Function and the Bulk Pressure of a Cut-off and Shifted LJ Fluid.

The cut-off and shifted LJ 12-6 fluid is studied here. The intermolecular potential for this fluid is

$$u(r) = \begin{cases} u_{LJ}(r) - u_{LJ}(r_c) & r \leq r_c \\ 0 & r > r_c \end{cases}, \tag{8}$$

here  $r_c$  is cut-off distance and

$$u_{LJ}(r) = 4\epsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right], \tag{9}$$

Where  $\epsilon$  and  $\sigma$  are the Lennard-Jones Fluid Parameters.

We use Goldman's parametrized equation [6] for the pair distribution function,  $g(\rho, T, r)$ , to find the direct correlation function as a numerical solution of the Ornstein-Zernike equation. Vogelsang and Hoheisel [7] extended the Baxter factorization method using the pair correlation function obtained by computer simulation, then they used the PY closure to continue the pair correlation function,  $g(r)$ , to larger  $r$ . The same procedure is used here, to find the bulk direct correlation function,  $c(r_1, r_2)$ , for a cut-off and shifted LJ potential. The procedure below is applied to find,  $C(x_1, x_2)$  or  $c(x)$  directly from auxiliary function,  $q(t)$ , [7]. Then one does not need to perform the double integral in equation (3) numerically.

Therefore:

$$C(x) = 2\pi \int_{|x|}^R dr r c(r) \tag{10}$$

the direct correlation function,  $c(r)$ , is zero between  $r_c$  and  $R$  whereas  $g(r)$  is not zero and from reference [7]:

$$rc(r) = -q'(r) + 2\pi\rho_0 \int_0^{R-r} dt q(t)q'(r+t). \tag{11}$$

Substitution of equation (11) into equation (10) yields

$$C(x) = -2\pi \int_{|x|}^R q'(r) + (2\pi)^2 \rho_0 \int_{|x|}^R dr \int_0^{R-r} dt q(t)q'(r+t) \tag{12}$$

$$= 2\pi q(|x|) + (2\pi)^2 \rho_0 \int_0^{R-|x|} dt \int_{|x|}^{R-t} dr q(t)q'(r+t)$$

$$= 2\pi q(|x|) + (2\pi)^2 \rho_0 \int_0^{R-|x|} dt q(t) \int_{|x|+t}^R ds q'(s).$$

Then  $C(x)$  is given by

$$C(x) = 2\pi q(|x|) + (2\pi)^2 \rho_0 \int_0^{R-|x|} dt q(t)q(|x|+t). \tag{13}$$

The pressure can be obtained from a 33-constant modified Benedict-Webb-Rubin (MBWR) equation of state for a LJ fluid obtained by Nicholas et al. [8] which gives the pressure of a full LJ fluid. The correction to the pressure due to the cut-off and shifted potential is given by [9]

$$\Delta P = \frac{1}{6} \rho_0^2 \int_{r_c}^{\infty} r \frac{du_{LJ}}{dr} g(r) dr. \quad (14)$$

If we assume that, for  $r > r_c$ ;  $g(r) = 1$ , then

$$\Delta P = \frac{2\pi}{3} \rho_0^2 \left[ \frac{8.0\sigma^6}{r_c^3} - \frac{16.0\sigma^{12}}{3r_c^9} \right].$$

thus [9]

$$P(\text{sp}) = P_N(T, \rho) + \Delta P \quad (15)$$

where  $P(\text{sp})$  is the pressure of the cut-off and shifted LJ fluid and  $P_N(T, \rho)$  is the pressure of the full LJ fluid obtained by Nicholas et al.

### Results and Discussion

The external potential,  $V(x)$ , in equation (7) is the contribution from both walls;

$$V(x) = \begin{cases} u_1(h-x) + u_1(x) & 0 < x < h \\ \infty & \text{otherwise} \end{cases} \quad (16)$$

The integral equation (7) has been solved for two different kinds of the wall-potentials,  $u_1(x)$ .

#### a) Walls with a '10-4' potential, case I,

The interaction energy between the wall and the fluid is [10]

$$u_1(x) = 2\pi\epsilon_n \sum_{i=1}^2 [X(x_i) - X(l_c)] \quad (17)$$

where  $x_i$  is the perpendicular distance of the fluid atom from the  $i$ th plane of the wall,  $l_c$  is the truncation range of the interaction (we use  $l_c = 2.37$ ),

$$X(x_i) = \frac{2}{5} \frac{\sigma^{12}}{x_i^{10}} - \frac{\sigma^6}{x_i^4},$$

the case when  $n\sigma^2 = 0.8$ ,  $x_i = x$  and  $x_2 = x + 2.69\text{\AA}$  is used here. We compare the density profile obtained by the solution of the integral equation (7) with the result of computer simulation (MC) [10] obtained by Abraham. The LJ potential is truncated at,  $r_c = 2.37$  for both methods. Also the average number density and the temperature are given below.

$$\tilde{\rho} = \frac{\int_0^h \rho(x) dx}{h} = 0.6, \quad \rho_0 = 0.555 \quad T = 1.0.$$

All the parameters are given in terms of the LJ fluid parameters  $\epsilon$  and  $\sigma$ . The distances are measured in units of  $\sigma$ , densities in units of  $\sigma^{-3}$  and temperature in units of  $\epsilon/K_B$ . In both methods the separation of the walls,  $h$ , has been chosen sufficiently large to ignore the effect of one wall on the other. The separation of the walls used in our calculation is

$$h = 11.2$$

The comparison is displayed in figure (1).

#### b) Walls with a '10-4' potential, case II,

The interaction of the wall and a given liquid particle is given by [11]

$$u_1(x) = 2\pi\epsilon \left( \frac{4}{5} \right) \left[ \frac{2}{5} \left( \frac{\sigma}{x} \right)^{10} - \left( \frac{\sigma}{x} \right)^4 \right]. \quad (18)$$

In this case we compare the result obtained by equation (7) with the one obtained by Magda, Tirrell and Davis [11] using molecular dynamics simulation. The separation of the two walls and the temperature are:

$$h = 11.57 \quad T = 0.97.$$

Also the cut-off distance and the average density are given by

$$r_c = 2.37 \quad \tilde{\rho} = 0.67 \pm .01.$$

The comparison is shown in figure (2).

The temperature used by Powles et al. [5], for the case of the LJ wall-LJ fluid system, was above the critical one,  $T = 1.35 > T_c = 1.119$  when  $r_c = 2.5$ . The critical temperature for  $r_c = 2.37$  is calculated below.

The correction to the pressure due to the cut-off is given by equation (14), if we assume that  $g(r) = 1$  for  $r > r_c$  and then ignore very small terms, [9]

$$\Delta P = \frac{16\pi}{3} r_c^{-3} \rho_0^2. \quad (19)$$

The critical temperature and density must satisfy the equations:

$$\frac{dP}{d\rho} = 0, \quad \frac{d^2 P}{d^2 \rho} = 0, \quad (20)$$

on substitution of equation (19) and (15) into equations (20) the difference in the critical temperature and density of the cut-off and shifted LJ fluid and the critical temperature and density of full LJ fluid can be obtained by

$$\frac{d\Delta P}{d\rho} = \frac{32\pi\rho_0}{3r_c^3} = A\Delta T_c + B\Delta\rho_c \quad (21)$$

$$\frac{d^2\Delta P}{d\rho^2} = \frac{32\pi}{3r_c^3} = C\Delta T_c + D\Delta\rho_c, \quad (22)$$

Where A, B, C, and D are constants. Thus

$$\Delta T_c \propto r_c^{-3}, \quad \Delta\rho_c \propto r_c^{-3} \quad (23)$$

Powles has already obtained the critical temperature for two different cut-off potentials ( $r_c=2.5, 3.0$ ) and also the critical temperature for full Lennard-Jones is available. Therefore we can use equation (23) and these temperatures to find the critical temperature for

$$r_c=2.37;$$

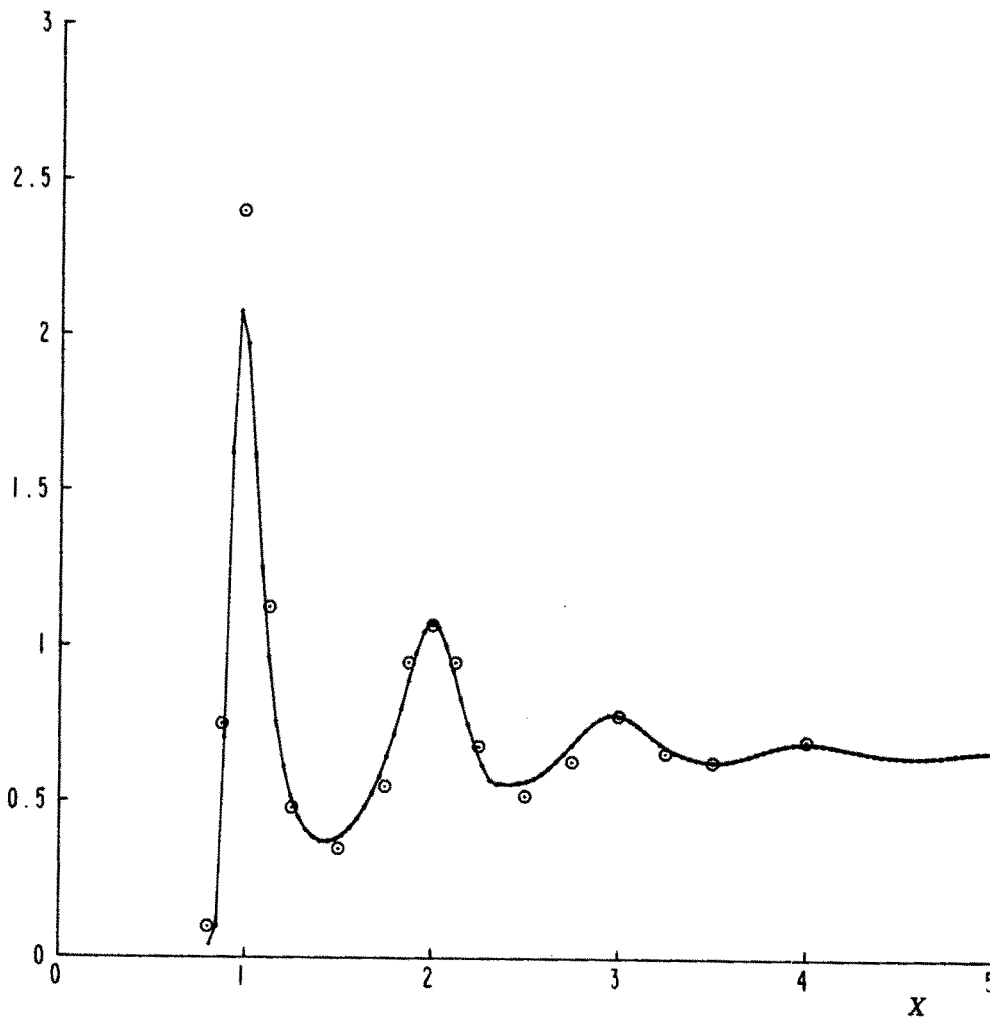
$$(T_c)_{r_c=2.37} = 1.08,$$

which means both temperatures used to find the density profile are below the critical temperature of the homogeneous fluid.

Figures (1) and (2) show good agreement between the theory and simulation at temperatures below, although close to,  $T_c$ . This extends the range of temperature over which the theory provides satisfactory results.

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**Figure 1** The density profile for a LJ fluid (case D); the circles are the results of simulation and solid line is obtained from density functional approximation.

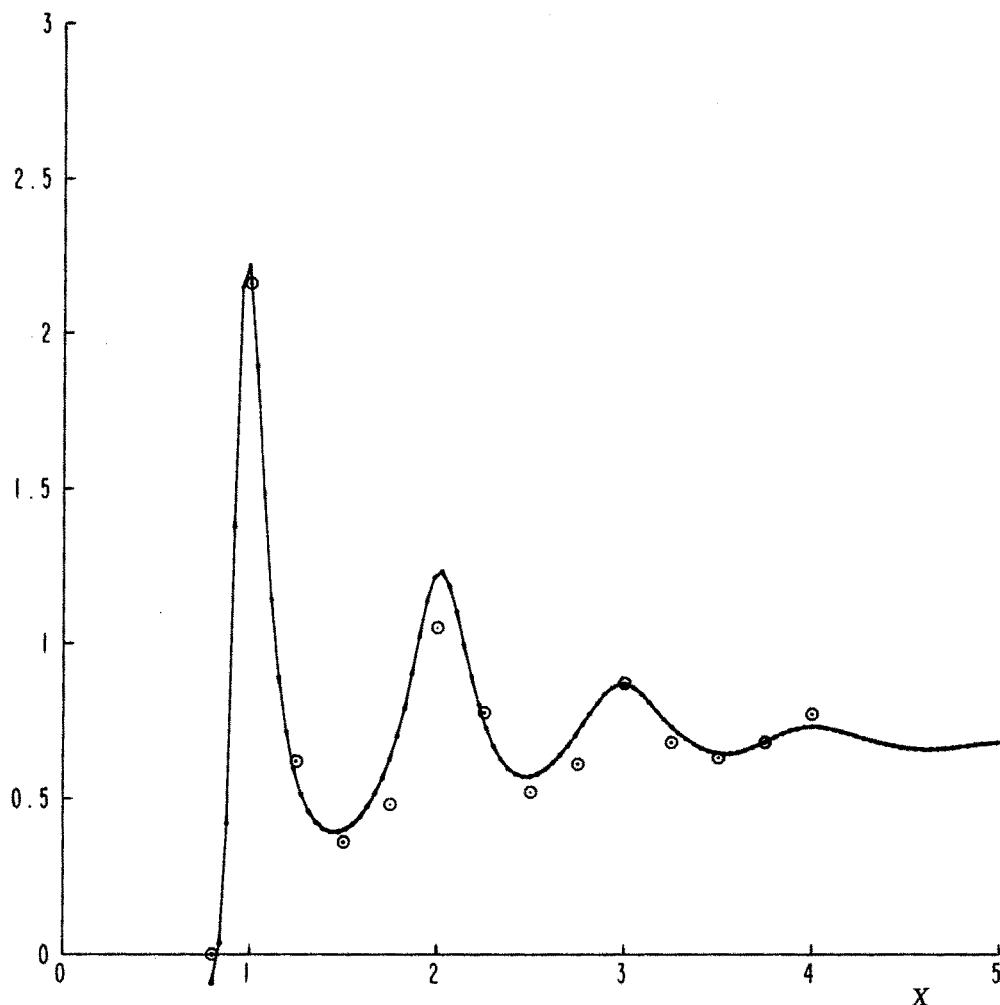


Figure 2 The density profile for a LJ fluid (case II), the notation is as in figure (1)

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