

## One Particle and Two Particle Distributions in the Liquid-Vapour Interface

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Liquid-vapour interface for a simple fluid modelled by the Lennard-Jones potential was treated by the first two members of the Born-Green-Yvon-Bogolyubov hierarchy. The pair of coupled integral equations was solved numerically to get the density profile and the pair correlation function in the inhomogeneous region. It was found that one can get a significant result for the pair correlation function if the monotonous density profile is inserted in the equation determining the pair correlation function. On the other hand, we did not succeed in getting a convergent solution for the density profile. This means that some further efforts will be necessary to overcome the difficulties connected with the unstable numerical procedures.

### 1. INTRODUCTION

The question of the behaviour of the liquid-vapour interface is not yet fully settled. Early results obtained either by computer simulation techniques or by integral equation theories gave oscillatory profiles for simple liquids interacting with the Lennard-Jones potential<sup>1,2</sup>. Later, the belief in monotonous density profiles prevailed. It was found that the oscillatory character of the density profiles is an artefact of insufficient averaging<sup>3</sup> in the computer simulation procedures while the integral equation approach was shown to be extremely sensitive with respect to the choice of the input quantities, such as pair potential, pair correlation functions and so on<sup>4</sup>. The experiment cannot provide a definite answer, either. The X-ray scattering on the liquid surface can give an estimate of the range in which the liquid-vapour transition is accomplished but not the exact form of the density profile.

In this work, we present the results of a calculation where the equations for the single particle and for two particle correlation functions were solved simultaneously as a system of a pair of coupled equations. The equations are taken from the Born-Green-Yvon-Bogolyubov hierarchy of equations.

In the next section, we develop the formalism which turns the BGYB equations to a form suitable for numerical treatment. In the last section, the results are given and it is stated that the results obtained for the pair correlation function are significant while the numerical procedure fails to reproduce a significant result for the density profile. This means that it will be necessary to make some further efforts to solve this problem.

## 2. THE SYSTEM OF EQUATIONS AND THE NUMERICAL SOLUTION

The first and the second members of the hierarchy of BGYB equations are usually solved separately. The solution of the second member for the homogeneous bulk liquid gives the pair correlation function. If the information about the single particle distribution function is needed, one should solve the first member of the hierarchy. However, this equation needs the pair correlation function as input. In the inhomogeneous region, where the inhomogeneity is introduced along one direction, the pair correlation function is a function of three variables. A flat liquid-vapour interface represents such a system. A common practice to model the pair correlation function for such a case is to mix the liquid bulk and vapour pair correlation functions. There is no unique way of doing this and it was found<sup>4</sup> that the results depend strongly upon the details of this procedure. To get more consistent results one can try to solve the equations for the density profile and the pair correlation function simultaneously. The two equations read as follows

$$\nabla \ln \varrho(\vec{r}) = - \frac{1}{kT} \int \nabla V(|\vec{r}-\vec{t}|) g(\vec{r}, \vec{t}) \varrho(\vec{t}) d\vec{t} \quad (1)$$

$$\begin{aligned} \nabla \ln \varrho(\vec{r}) + \nabla \ln g(\vec{r}, \vec{s}) = & - \frac{1}{kT} \nabla V(|\vec{r}-\vec{s}|) - \frac{1}{kT} \\ & \int \nabla V(|\vec{r}-\vec{t}|) g(\vec{r}, \vec{s}) g(\vec{s}, \vec{t}) \varrho(\vec{t}) d\vec{t} \end{aligned} \quad (2)$$

The density profile is marked by  $\rho(\vec{r})$  and the pair correlation function by  $g(\vec{r}_1, \vec{r}_2)$ . The superposition approximation was taken into account on the right side of (2) by expressing the three particle correlation function by the triple product of the two particle correlation functions. In the case of a flat liquid-vapour interface, the density profile is a function of one variable only  $\rho(\vec{r}) = \rho(z)$  while the pair correlation function depends upon three variables: the distance of the two particles, position of the gravity centre of the two particles with respect to the Kirkwood-Buff dividing surface<sup>5</sup> and the orientation of the pair with respect to the dividing surface. In our calculation we shall neglect the orientational dependence so that the pair correlation function will be the function of two variables only

$$g(\vec{r}_1, \vec{r}_2) = g(r, z^*) \quad (3)$$

with  $z^*$  being the gravity centre coordinate of the two particles.

Neglect of the angular anisotropy of the pair correlation function is a rather crude approximation, but it is necessary in order to keep the numerical procedure within the reach of the present generation of computers. Having defined the arguments of our unknowns  $\rho$  and  $g$ , equations (1) and (2) can be partly integrated to give:

$$\ln(\varrho(z)/\varrho_V) = \frac{2\pi}{kT} \int_z^\infty dz_1 \int_0^\infty dz_2 (z_2 - z_1) \varrho(z_2) \Psi(z_1, z_2) \quad (4)$$

$$\Psi(z_1, z_2) = \int_{|z_2 - z_1|}^{\infty} V'(r) g(r, z^*) dr \quad (5)$$

$$\ln g(r, z_2) = - \frac{V(|z_2 - \tilde{z}|)}{kT} - \frac{2\pi}{kT} \int_z^{\infty} dz_1 \int_0^{\infty} dr_{13} r_{13}^2 V'(r_{13})$$

$$\int_{-1}^1 v dv g(r_{13}, z_{13}^*) [g(r_{23}, z_{23}) - 1] \rho(z_3); v = \cos \angle(\vec{z}, r_{13}) \quad (6)$$

Equations (4) and (6) follow directly from (1) and (2). Equation (6) results from subtracting (1) from (2). The meaning of the variables appearing in (4), (5) and (6) is depicted in Figure 1.

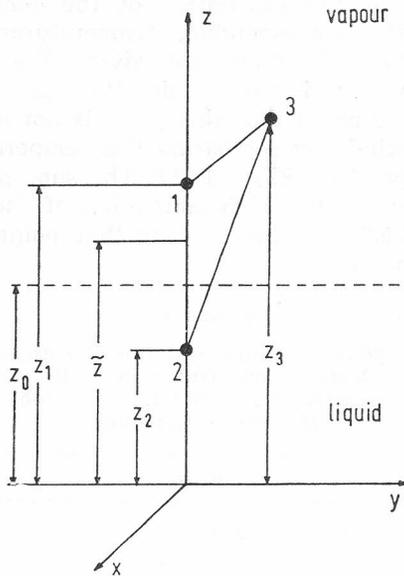


Figure 1. Meanings of symbols appearing in equations (4) to (6).

Equations (4) and (6) were solved for the Lennard-Jones 6, 12 pair potential. The density profile  $\rho(z)$  was tabulated in discrete points spaced equidistantly within  $0.04 \sigma$ . Also, the pair correlation function was calculated on a square lattice with  $\Delta r = \Delta z = 0.04 \sigma$ . The integrals were calculated by means of the trapez rule. Since equations (4) and (6) represent a system of coupled nonlinear equations, we used the iterational procedure which starts with an initial guess and afterwards the output of  $i$ -th step is inserted into the r. h. s. of the equations in the  $i + 1$ -th step.

### 3. RESULTS AND DISCUSSION

Liquid and vapour can coexist at any temperature in the interval between the triple point temperature and the critical temperature. For the Lennard-Jones system the two temperatures are determined by various methods, such as molecular dynamics calculations<sup>6</sup> and by the calculations

based on the integral equations approach<sup>7</sup>. Their approximate values are  $kT_{tp} = 0.72 \epsilon$  and  $kT_c = 1.35 \epsilon$ .

Experimental measurements on noble gases are also in rough agreement with the abovementioned values. The calculation should be performed for some temperature from the central part of the interval between the triple point and critical point. Close to the triple point one usually encounters difficulties due to the existence of the solution for the pair correlation function. On the other hand, the surrounding of the critical point is characteristic of the long ranged correlations which cannot be treated numerically within equation (6). The study of the vicinity of the critical point is a difficult problem even for the homogeneous case where the pair correlation function is a function of one variable. Table I shows some possible points which can be chosen for the calculation of the density profile and pair correlation function. The corresponding temperatures, densities of liquid phase and vapour phase densities are given. We chose the point at  $kT = 1.30 \epsilon$  where liquid and vapour densities are  $0.43 \sigma^{-3}$  and  $0.17 \sigma^{-3}$ , respectively. It should be noted that this point is not as close to the critical point as one would conclude by comparing this temperature with the abovementioned critical temperature  $kT_c = 1.35 \epsilon$ . The superposition approximation of BGYB equations gives a too high estimation of the critical temperature (approximately  $kT_c = 1.637 \epsilon$ ),<sup>8</sup> which means that point  $kT_c = 1.3 \epsilon$  is rather far from the critical point.

TABLE I

*Coexistent Liquid and Vapour Densities and the Corresponding Temperatures for the Lennard-Jones Fluid. Densities are Given in Units  $\sigma^{-3}$  and the Temperatures in  $\epsilon/k$ , Where  $\sigma$  and  $\epsilon$  are Parameters of the Lennard-Jones Potential and  $k$  is the Boltzmann Constant*

$T$	$\rho_V$	$\rho_L$
0.8	0.005	0.77
0.9	0.02	0.715
1	0.03	0.66
1.1	0.05	0.60
1.2	0.095	0.523
1.3	0.17	0.43
1.35	0.30	0.30

The calculation proceeded as follows. The numerical procedure of solution of eq. (6) was tested to check whether the limiting behaviour of  $g(r, z_2)$  agrees with the liquid and vapour bulk pair correlation function calculated by the numerical procedure for the homogeneous bulk system. We found that both limits were satisfactorily reproduced. The calculation was then started with the initial guess for the pair correlation function in the form of the vapour pair correlation function, while the density profile was expressed by an analytical function<sup>9</sup>:

$$\rho(z) = \rho_V + \frac{1}{2} (\rho_L - \rho_V) \{ \tanh [(z - z_0) a] + 1 \} \quad (10)$$

Parameter  $\alpha^{-1}$  determines the depth of the liquid-vapour interface and was set equal to  $\alpha^{-1} = 2\sigma$ . Coordinate  $z_0$  defines the dividing surface. With the input as defined above equation (6) was first subjected to the iterative procedure. The density profile was held fixed in the form of (10) while 15 iterational steps were performed. The resulting two dimensional array representing the pair correlation function in the inhomogeneous region is shown in Figure 2. We can see that the transition between the two limiting

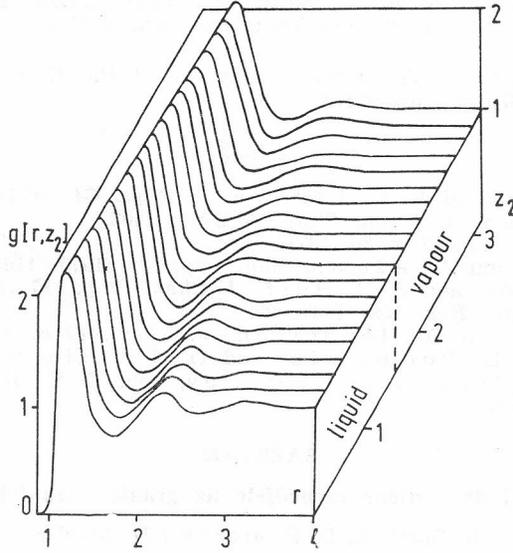


Figure 2. The pair correlation function of the liquid-vapour interface.

pair correlation functions belonging to the liquid and vapour bulk phase is gradual and monotonous. Of course, this result cannot be treated as the final result since the iterations should be continued in order to get a convergent result also for the density profile by running the iterative procedure on equation (5). This was found to be a more difficult task than one can imagine. We found that the iterative procedure based on eq. (1) converges very poorly. Detailed examination of equation (4) shows that the numerical procedure fails to reproduce the correct difference between the two bulk densities. This property destabilizes the iterational procedure so that the iterations proceed towards an apparently stable density profile which is depicted in Figure 3. When the iterational procedure was subjected to a more stringent criterium it was established that if the iterations are continued the density profile drifts further and may finally diverge. Thus, we can conclude that some further work will be necessary to get significant results. However, according to the positive experience obtained by studying models of the crystal-liquid interface with the integral equation theories we can expect that also the liquid-vapour interface should be manageable using this approach.

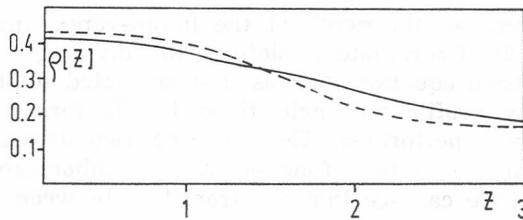


Figure 3. Density profile of an apparently converged solution. Dashed line depicts the input function in the form of (10).

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#### SAŽETAK

##### Jednočestične i dvočestične raspodjele na granici faza tekuće-plinovito.

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Proučavana je granica faza tekuće-plinovito za jednostavne fluide, modelirane Lennard-Jonesovim potencijalom, s pomoću prva dva člana hijerarhije Born-Green-Yvon-Bogolyubova.