

Determination of the Structure and Thermodynamics of Square Well Potential From the Tail of the Direct Correlation Function.

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Following Stell, one can determine the pair correlation function $h(r)$ of the hard sphere fluid for all distance r by specifying only the tail of the direct correlation function $c(r)$ at separation greater than the hard core diameter σ . More recently, Katsov and Weeks extended Stell ideas to describe the structure of continuous fluids containing repulsive and attractive parts like Lennard-Jones and Yukawa fluids. In this paper, we extend these ideas to determine the structure and thermodynamics of square well potential from the tail of the direct correlation function. This potential is used essentially to model complex systems like polymers and colloids. We use the Martinov-Sarkisov bridge functions in the closure relation. An efficient numerical algorithm is used based on Labick procedure. We give results for the structure and thermodynamics at different values of the width of the square well potential, and at different thermodynamical states.

Keywords: square well potential, structure, thermodynamics, and correlation functions.

I- Introduction

Since thirty years ago, the square well potential has been considered as the simplest extension of hard sphere potential, containing simultaneously interactions, which derive from repulsive and attractive forces and can be further considered as model describing more realistic and physical systems. Recently, it has been used both in simulation and theoretical studies in order to model n-alkanes and also in simulation of other complexes system like colloids which are present in biophysics, food science, the cosmetic industry as well as medical applications [1-8].

Since Ornstein and Zernik had derived in 1914 their famous equation which relates the total correlation functions $h(r) = g(r) - 1$ to the direct correlation function $c(r)$, where $g(r)$ is the radial distribution function [9], authors don't stop to search new closures for this equation; for example, the Percus-Yevick equation (PY), the Hyper-netted-chain equation (HNC), the Mean spherical Approximation (MSA), and other closures which depend on one or more variational parameters like the Roger-Young closure (RY)[10]. This great number of closures is often based on graphical or functional methods [9].

However, despite all those efforts no closure is capable, to now days, to reproduce the structure of all physical systems whatever the nature of the potential which model them. This is probably due to the fact that the standards closures are obtained from non controlled approximations introduced essentially for mathematical commodity [9].

Following Stell [11], one can determine the pair correlation function $h(r)$ of the hard sphere fluid for all distance r by specifying only the tail of the direct correlation function $c(r)$ at separation greater than the hard core diameter σ . In the core of the hard sphere, $c(r)$ can be determined by solving the Ornstein-Zernik OZ equation under the limit condition $h(r) = -1$ for $r < \sigma$. More recently, Katsov and Weeks[12] extended Stell ideas to describe the structure of continuous fluids containing repulsive and attractive parts. In this work we exploit Stell, Katsov and Weeks ideas to study one of the most important potential used to model colloids and linear polymers which is the square well potential.

The article is organised like this: in section II, we give a brief summary of the theory, in section III, we present our results with other data, and we close by a conclusion including the impotents remarks that we have obtained.

II. A SUMMARY OF THE THEORY

The fluid is composed of N particles in a volume V at the temperature T . The square-well pair potential is given by

$$u(r) = \begin{cases} \infty, & 0 < r < \sigma \\ -\varepsilon, & \sigma \leq r \leq \sigma + \lambda \\ 0 & \sigma + \lambda < r \end{cases} \quad (1)$$

where σ is the hard-core diameter of the atoms or particles. The depth of the attractive well is specified by $\varepsilon > 0$. If $\varepsilon < 0$, $u(r)$ represents a

hard-core potential with a repulsive shoulder of height $|\varepsilon|$ attached ; our analyses will encompass the case $\varepsilon > 0$ and $\lambda \geq 1$. The specified parameter λ is related to ε by $\varepsilon = \lambda / (\lambda + \sigma)$. There are three controlled parameter for the system, the temperature T , the packing fraction $\phi = \pi \rho \sigma^3 / 6$ and the relative with ε of the attractive well with respect to the total range of interaction. $\rho = N/V$ is the number particle density.

The method used in this work to study the structure and thermodynamics of a homogeneous and isotropic fluids are based on the (OZ) equation which links the total and the direct correlation functions $h(r)$ and $c(r)$ by :

$$h(r) = c(r) - \rho \int c(|r-r'|) h(r') dr' \quad (2)$$

This equation contains more than one unknown, to solve it we need a second closure relation. The general relation, which links the structural functions $h(r)$ and $c(r)$ to the pair potential of interaction $u(r)$ is given by the following equation [9,11]

$$g(r) = e^{-\beta u(r) + g(r) - 1 - c(r) - B(r)} \quad (3)$$

where $B(r)$ are the bridge functions. Varieties of bridge functions, based on mathematical considerations are proposed, for instance,

$$B^{PY}(r) = \ln[1 + \gamma(r)] - \gamma(r) \quad (4a)$$

$$B^{HNC}(r) = 0 \quad (4b)$$

$$B^{MS}(r) = [1 + 2\gamma(r)]^{1/2} - \gamma(r) - 1 \quad (4c)$$

$$B^{RY}(r) = \ln \left[1 + \frac{\exp\{[1 - \exp(a r)]\gamma(r)\} - 1}{1 - \exp(a r)} \right] \quad (4d)$$

where the quantity $\gamma(r) = h(r) - c(r)$ is know as the indirect correlation function, the labels PY, HNC, MS and RY denoted the Percus- Yevick, the hyper-netted chain, the Martinov-Sarkisov, and Roger- Young closure respectively, and the adjustable parameter $a = 1.87$ [11].

The OZ equation coupled to one of the approached form of equation 3 is called Integral. The problem which encounters the standards IETs is due to the fact that they don't verify the thermodynamic consistency for all thermodynamical states, i.e. those relations have a limited field of validity since their bridge functions are selected for mathematical consideration. For example, the PY IET gives a good result only for systems characterized by a dominant repulsive interactions and fail when an attractive part is present. Contrary to the PY , the HNC gives good success only for systems modelled by long range potential like Yukawa potential.

In this work we try to use the advantage of some of these IET simultaneously, for this we proceed as follows.

When $\varepsilon = 0$, i.e. in the absence of the attractive part, the square well potential become a Hard Spheres potential $u_{SW}(r) = u_{HS}(r)$ where

$$u_{HS}(r) = \begin{cases} \infty & r \leq \sigma \\ 0 & r > \sigma \end{cases} \quad (5)$$

On the other hand, it is well know that the HS fluid structure can be determined with a great exactitude using the PY integral equation. The principal of our idea is very simple, it consist to:

1- calculate the structure of an initial hard spheres fluid of diameter σ using PY closure.

2- create a square well potential of a width λ with a positives values relatively greater than 1. In this initial state, the introduced attractive part mustn't have an important effect with respect to the repulsive one that is why we must choose an initial SW fluid in the infinite dilution with $\varepsilon \approx 0$. In order to exploit the asymptotic behaviour of the HS structural functions , we split the interparticle distance r in two parts: outside the hard core diameter for $r > \sigma$, we calculate the bridge function for the SW initial system using that given in reference [14] which is applicable in the case of small attraction given by

$$B_{SW} = \ln g_{HS}(r) - g_{HS}(r) + c_{HS}(r) + 1 \text{ for } r > \sigma \quad (6)$$

and inside the hard core diameter where he repulsion is important for $r < \sigma$ we used the PY bridge functions.

3- Once the bridge functions are known for all r we exploit these series to calculate the structure by solving the system formed by the OZ equation and the Sarkisov-Martinov closure [14].

4- We calculate the structure of a new SW potential, of width $\lambda_N = \lambda_O + \Delta\lambda$, from the asymptotic behaviour of correlation functions of an old SW potential characterised by λ_A , we inject the asymptotic structural functions of the old SW potential in equation (6), i.e.,

$$B_{SW}^N = \ln g_{SW}^O(r) - g_{SW}^O(r) + c_{SW}^O(r) + 1 \text{ for } r > \sigma \quad (6)$$

where the label O and N denote respectively old and new, and we repeat the operation 3. The numerical resolution is based on Labick algorithm[15] and the modification proposed by Lomba [16] on Broyles cycles. We have described the numerical procedure in our previous work [17].

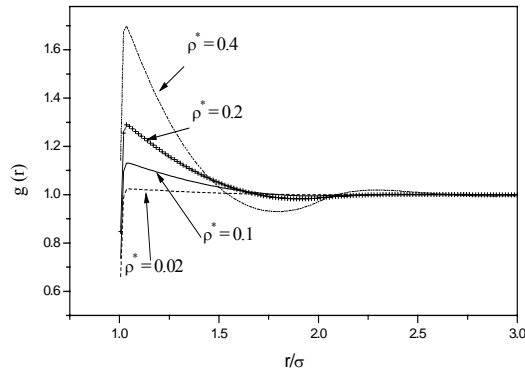


Fig.1. Radial distribution function of some initial HS potentials for different thermodynamic stats generated by the PY integral equation.

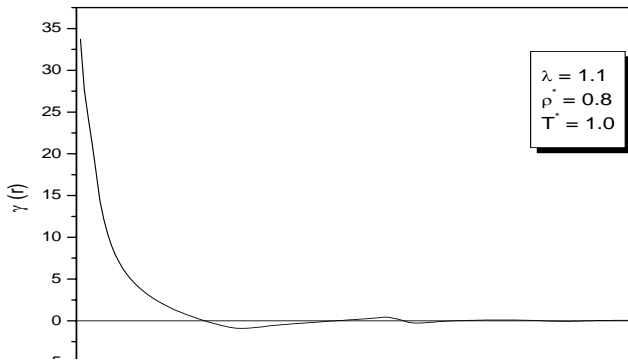


Fig 2. indirect correlation function $h(r) - c(r)$ for a SW potential at reduce temperature $T^* = 1.0$ and reduce density $\rho^* = 0.8$. The potential width is $\lambda = 1.1$

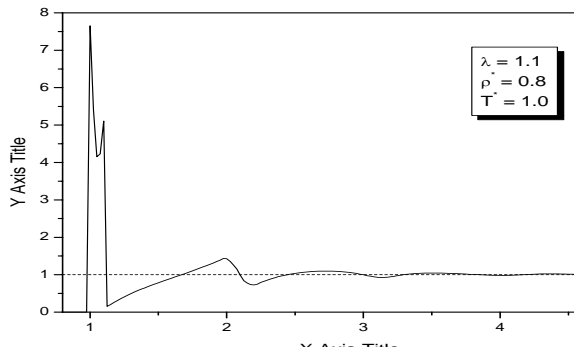


Fig.3. Pair Distribution function of $h(r) - 1$ for a SW potential at reduce temperature $T^* = 1.0$ and reduce density $\rho^* = 0.8$. The potential width is $\lambda = 1.1$

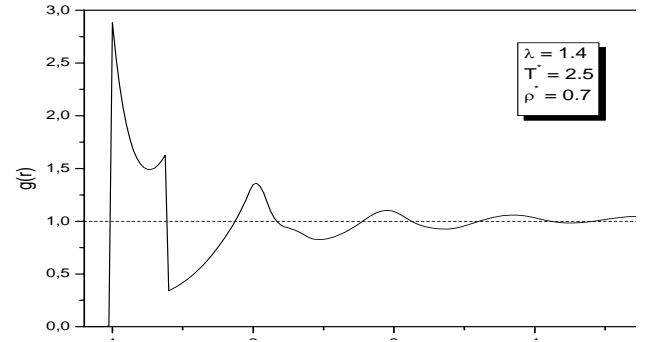


Fig.4. Pair Distribution function of $h(r) - 1$ for a SW potential at reduce temperature $T^* = 2.5$ and reduce density $\rho^* = 0.7$. The potential width is $\lambda = 1.4$

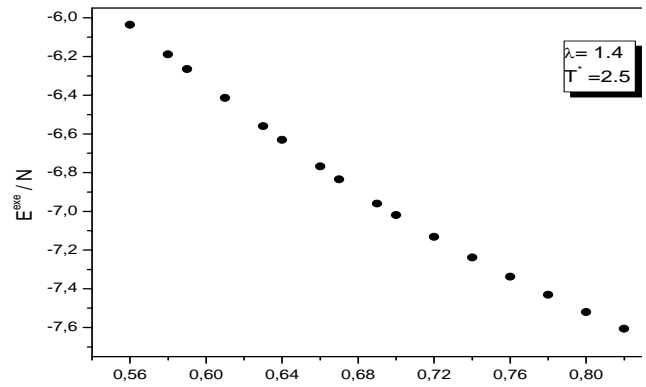


Fig 4. Internal excess energy per particle as a function of density for the isotherm $T^* = 2.5$ and for the with potential $\lambda = 1.4$

III. RESULTS

We have studied the structure of the square well potential using a new method based on Stell, Katsov and Weeks ideas. The reduced density is $\rho^* = \rho \sigma^3$ and the reduced temperature is $T^* = T/k_B \varepsilon$ is the unit of the energy. On Figure 1 we give the structure of some initial hard spheres potential fluid for different thermodynamic states computed by the PY integral theory. In figure 2 we plot the indirect correlation function for the initial state $\lambda = 1.1$. This initial state allows to generate successive stat of increasing λ , the convergence is extremely rapid on a PC computer. Figure 3 gives

the Radial distribution function of square well potential of a width $\lambda=1.4$ for different thermodynamic states generated by the proposed method.

A number of thermodynamic properties of the square well potential can be computed from the radial distribution function in particular the excess internal energy and the constant volume heat capacity per particle which are given directly as integrals over the pair distribution function:

$$\frac{E_{\text{exe}}}{N} = 2\pi\rho \int_V u(r)g(r)r^2 dr, \quad (7)$$

$$\frac{C_v}{Nk_B} = \frac{2\pi\rho}{k_B} \int_0^\infty \left(\frac{\partial g(r)}{\partial T} \right)_V u(r) r^2 dr \quad (8)$$

Figure 4 give the excess internal energy for $\lambda=1.4$ for the isotherms $T^*=2.5$ as a function of reduced density. The convergence is extremely rapid by slowly varying the energy state.

IV CONCLUSIONS

In this work we have computed the structure and thermodynamics properties of a fluid modelled by the square well potential. This type of potential describes more realistic and important systems such as colloids and polymers solution. The method used is based on the coupling of the advantages of the integral equation theories and Stell, Katsov and Weeks ideas of exploiting the information given by the asymptotic behaviour of the direct correlation function.

The range of r is separated into a hard core region and an outside attractive part of the potential. In the hard core region the PY IET is used. Outside the core the data is generated using the preceding bridge functions. We have exploited the tail of the correlation functions to obtain the structure and the excess internal energy per particle of square well potential of different widths at different thermodynamic states.

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