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A STATE-DEPENDENT DIVISION SCHEME FOR THE POTENTIAL OF SIMPLE FLUIDS

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A new division scheme for the pair potential into long-range and short-range parts is presented, which takes account of the dependence on the density and makes possible the extraction of the bridge function $B(r)$ in the core region. The calculation of the correlation functions is carried out with the hybridized mean spherical approximation (HMSA). As attested by the comparison with the simulation results, HMSA used with this potential separation is suitable to produce accurate bridge function and pair correlation function for the Lennard–Jones fluid.

Keywords: Bridge function; Thermodynamic consistency

I. INTRODUCTION

There are many semianalytic methods in the study of the fluid structure for obtaining the molecular distribution functions. One of the most accurate is that of the self-consistent integral equations, which allows to calculate the pair correlation function, $g(r)$, and the indirect correlation function, $\gamma(r)$, by ensuring the equality between the virial and compressibility equations of state. In addition, every semianalytic method can be compared and tested against the methods of computer simulation, sometimes referred as exact and whose results serve as references, providing valuable information on the liquid state theory.

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Keeping in mind that $g(r)$ resulting from the integral equation theories is approximative, a thermodynamically structural solution for any pair potential $u(r)$ should be written under the appropriate and exact form

$$g(r) = \exp(-\beta u(r) + \gamma(r) + B(r)). \quad (1)$$

Actually, Eq. (1) defines the bridge function $B(r)$ that is required by the theory to provide the exact pair correlation function. From a theoretical point of view, $B(r)$ can be expanded in terms of diagrams as

$$B(r) = \sum_{n=4}^{\infty} \{\varepsilon_n(r)\}, \quad (2)$$

where $\{\varepsilon_n(r)\}$ represents a set of n points elementary diagrams [1]. However, only few low density clusters are known so that the expansion of $B(r)$ is not applicable in terms of clusters to the treatment of dense matter. Therefore, as attested in the literature, intensive studies of the possibilities to extract $B(r)$ from other different approaches have been carried out during the last fifteen years.

In studying the properties of $B(r)$ for various pair potentials, Rosenfeld and Ashcroft [2] arrived at the conclusion that the most important region in which the bridge function must be specified, in any theory, is the region of the first peak of $g(r)$. In their work, it has also been shown that the short-range part of $B(r)$ has a universal feature whose the form looks like the bridge function of the hard-sphere (HS) potential, whatever the pair potential under study. For that reason, the simulations performed in order to search for a detailed knowledge of $B(r)$ are mainly related to properties of the HS reference fluid. In contrast, Duh and Haymet [3] pointed out more recently that the bridge function is no longer recognized as universal.

Although the computer simulation yields a pair correlation function without any approximation to the many-body problem, the information is limited only within the half of the side length of the unit cell. This causes a difficulty in calculating the bridge function from simulation due to unavoidable truncation errors. Furthermore, the extraction of $B(r)$ from simulated pair correlation function requires complex algorithms, as well as the use of approximations at medium

and long distances. This difficulty has been, however, partly overcome by Llano-Restrepo and Chapman [4], who have calculated the direct correlation function, $c(r)$, and the cavity function, $y(r) = g(r)\exp[\beta u(r)]$, for the Lennard–Jones (LJ) pair potential by Monte Carlo simulation.

In this work the goal is to obtain consistently the bridge function in the core region in good agreement with MC calculations. Instead of providing a new integral equation, we want to show that it is possible to improve the results of the correlation functions, as well as the bridge function, when the separation of the pair potential $u(r)$ is optimized. The essence of the method is to recognize that the difference between the respective Mayer functions of the short-range and the long-range parts of the potential becomes quite smooth around the principal peak of $g(r)$. We substantiate this in the next sections by carrying out numerical tests for the Lennard–Jones pair potential.

II. INTEGRAL EQUATION THEORY AND POTENTIAL SEPARATION

In the framework of the integral equation (IE) method, a particular efficient class of closures is due to Rogers and Young [5], which involves a mixing function chosen to ensure the thermodynamic consistency between the virial and compressibility equations of state. Their integral equation is an interpolation between the hyper-netted chain (HNC) and Percus–Yevik (PY) approximations. To improve this method, Zerah and Hansen [6] used a closure, called hybridized-mean-spherical approximation (HMSA), that interpolates between the HNC and soft-core mean spherical approximation (SMSA) *via* a continuous mixing function. The latter IE presents several advantages. Firstly, it is adapted to the treatment of the attractive potential tail. Secondly, it provides self-consistent results between those of HNC, which corresponds to $B(r) = 0$, and those of SMSA that overestimates the bridge function of simulation over a wide range of distances.

Previous studies [7–9] have shown that the HMSA integral equation provides a good description of a great many properties of liquids

in using effective pair potentials as interatomic potentials. In these works, the potential $u(r)$ is split at the position of its minimum r_m – according to the prescription of Weeks *et al.* [10], giving a short-range part, $u^{SR}(r)$, and a long-range part, $u^{LR}(r)$. With this general separation, the HMSA integral equation reads

$$g(r) = h(r) + 1 = \exp[-\beta u^{SR}(r)] \times \left[1 + \frac{\exp\{f(r)[\gamma(r) - \beta u^{LR}(r)]\} - 1}{f(r)} \right], \quad (3)$$

and has to be solved simultaneously with the Ornstein–Zernike equation

$$\gamma(r) = h(r) - c(r) = \rho \int h(r')c(|r - r'|)dr'. \quad (4)$$

The function $f(r)$ is the mixing function intended to obtain the thermodynamic consistency. Once $\gamma(r)$ and $f(r)$ are known, one can then generate the bridge function $B(r)$ owing to the relationship

$$B(r) = \beta u^{LR}(r) - \gamma(r) + \ln \left[1 + \frac{\exp\{f(r)[\gamma(r) - \beta u^{LR}(r)]\}}{f(r)} \right]. \quad (5)$$

As we can see, the bridge function is zero when $f(r)$ equals unity, reducing the integral equation to that of the HNC closure, whereas it corresponds to the SMSA when $f(r)$ comes near zero. These integral equations are very tractable, but in special circumstances – high densities and low temperatures – they lead to a severe inconsistency between the virial and compressibility equations of state, *i.e.*, $\rho k_B T \chi_T \neq S(0)$, where $S(0)$ is the long-wavelength limit of the structure factor. Furthermore, it is noticeable that $B(r)$ depends explicitly on the long-range part $u^{LR}(r)$ of the pair potential. Surprisingly, in using the WCA division scheme of potential, HMSA provides bridge function and cavity function in the core region (especially at zero separation) not in good agreement with MC calculations over a wide range of densities and temperatures [11]. This feature points out that consistent thermodynamic properties do not imply necessary the exactness of the correlation functions $g(r)$, $\gamma(r)$ and $y(r)$. Generally, the main

disagreements between the results of various theories, and their mutual disagreement with MC results, are a consequence of the respective assumptions made on $B(r)$ in this region.

Since our investigation focus on the bridge function, we want to show that it is possible to obtain consistently $B(r)$ in good agreement with MC calculations, without new integral equation, if the separation of the pair potential $u(r)$ is optimized. This new division scheme is developed in the mind that it has to be state-dependent following the idea emphasized by Kang and Ree [12], Du and Haymet [13] and Lee *et al.* [14]. For our purpose, we consider the HMSA with the LJ pair potential that reads

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] = u^{SR}(r) + u^{LR}(r), \quad (6)$$

where σ is the size of the potential core and ϵ the depth of the attractive part located at r_m . From Eq. (5) we see that $B(r)$ is very sensitive to the long-range part of the potential, therefore we assume that an optimization of it could be the key in obtaining a good agreement for $B(r)$ in the core region. Optimization means, according to us, the determination of state-dependent short-range part, $u^{SR^*}(r)$, and long-range part, $u^{LR^*}(r)$, in order to ensure the equality $u(r) = u^{SR^*}(r) + u^{LR^*}(r)$. To achieve this, we propose a partition the LJ potential as follows (Fig. 1)

$$u^{LR^*}(r) = \begin{cases} p\epsilon & r \leq r_1 \\ a_1 + a_2 r + a_3 r^2 + a_4 r^3 & r_1 < r \leq r_2, \\ u(r) & r > r_2 \end{cases} \quad (7)$$

with $u^{SR^*}(r) = u(r) - u^{LR^*}(r)$. The range of distances is divided into three parts delimited by r_1 and r_2 . Also, the present separation of the pair potential reduces to the WCA scheme when $p = 1$ and $r_1 = r_2 = r_m$. Then, the coefficients a_1 , a_2 , a_3 and a_4 of the polynomial function are determined in order to keep safe the continuity and the first derivative of the potential at the positions $r = r_1$ and $r = r_2$ as well. The analytical solution of the set of equations provides the values of the a_i parameters *versus* r_1 , r_2 , $p\epsilon$, $u(r_2)$ and $u'(r_2)$ as

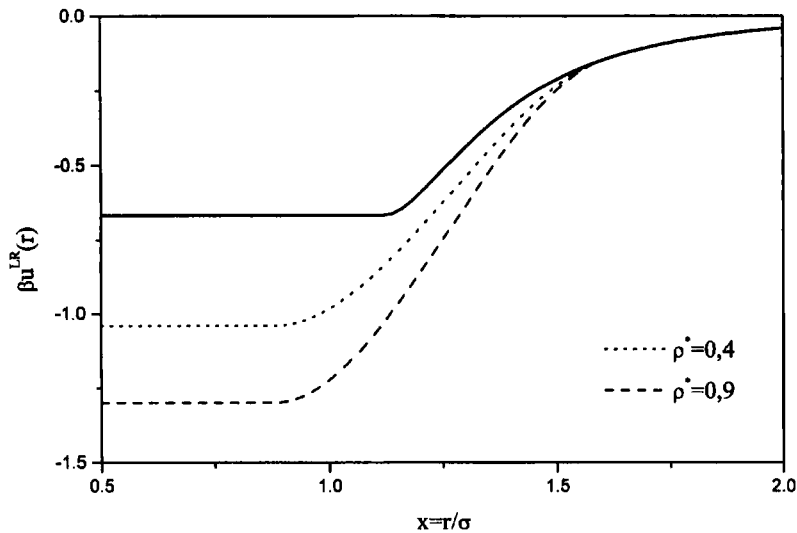


FIGURE 1 Long-range part $u^{LR}(r)$ of the LJ potential, at $T^* = 1.5$ for two densities. The thick line corresponds to the WCA scheme.

follows

$$\begin{aligned}
 a_1 &= \frac{r_1^3 u(r_2) - r_2 r_1^3 u'(r_2) - 3r_2 r_1^2 u(r_2) + r_1^2 r_2^2 u'(r_2) + 3p\epsilon r_1 r_2^2 - p\epsilon r_2^3}{(r_1 - r_2)^3}, \\
 a_2 &= -\frac{r_1(-r_1^2 u'(r_2) - r_1 r_2 u'(r_2) + 6p\epsilon r_2 - 6u(r_2) + 2r_2^2 u'(r_2))}{(r_1 - r_2)^3}, \\
 a_3 &= \frac{-2r_1^2 u'(r_2) + 3p\epsilon r_1 - 3r_1 u(r_2) + r_2 r_1 u'(r_2) + 3p\epsilon r_2 - 3r_2 u(r_2) + r_2^2 u'(r_2)}{(r_1 - r_2)^3}, \\
 a_4 &= -\frac{-r_1 u'(r_2) - 2u(r_2) + r_2 u'(r_2) + 2p\epsilon}{(r_1 - r_2)^3}.
 \end{aligned} \tag{8}$$

Specifically, the model is relied on three parameters r_1 , r_2 and p . The region between r_1 and r_2 is that of the main peak of $g(r)$, the crucial region in which $B(r)$ has to be specified according to Rosenfeld and Ashcroft [2]. The parameter r_1 corresponds to the distance at which $g(r)$ becomes non zero, and r_2 to the first minimum of $g(r)$, roughly

estimated by $r_2 = r_m + 2(r_m - r_1)$. Strictly, for the LJ potential, these values are $r_1 = 0.88\sigma$ and $r_2 = 1.6\sigma$, whatever the temperature and the density [15]. Thus, the state dependence separation of the potential takes place *via* the parameter p , which is responsible for the depth of the long-range part $u^{LR*}(r)$ of the potential. At this stage of our study, we require that the zero separation value of the bridge function, $B(0)$, calculated with HMSA coincides with that of MC [4], in order to choose the value of p .

III. RESULTS OF CALCULATIONS

So, in our procedure of calculation, p is considered as a simple adjustable parameter. Besides, for the iterative process implemented in the HMSA, it is sufficient to adopt $f(r)$ as a constant $f_0 \in [0; 1]$ over the entire r -range, as proposed by Bretonnet and Jakse [16]. Practically, the algorithm starts with an initial value of $p (= 1)$ and with the HMSA, which guarantees the thermodynamic consistency and provides a first result for the parameter f_0 and the correlation functions $g(r)$ and $B(r)$. In the next iteration cycle, the previous value of p is replaced by the new one and at the end of that iteration cycle, a new set of quantities f_0 , $g(r)$ and $B(r)$ is produced. The four quantities p , f_0 , $g(r)$ and $B(r)$ vary at each step of the procedure, which is repeated until obtaining equality between the calculated bridge function at zero separation and the MC one.

This process is very poorly time consuming, because the number of iterations that ensures the thermodynamic self-consistency is very low. Our calculations have been performed with the classical method of Gillan [17], improved by Labik *et al.* [18], but no mention will be made here on the efficiency of the method, which combines the traditional scheme and the Newton–Raphson technique for solving nonlinear integral equations. It is sufficient to bear in mind that the fast Fourier algorithm is used and a reasonable compromise between computing time and numerical precision is obtained with the step size of 0.02 and a grid of 1024 points.

As an example, we treat the typical LJ potential revisited by the optimization of the potential separation that is proposed in Eq. (7). All units are expressed in terms of the LJ parameters, *i.e.*, reduced

temperature $T^* = k_B T / \varepsilon$ and reduced density $\rho^* = \rho \sigma^3$. The thermodynamic states correspond to conditions where simulation data are available, namely $T^* = 1.5$, $\rho^* = 0.4, 0.6, 0.7, 0.8$ and 0.9 . Calculations are carried out using the state-dependent division scheme (SDDS) as well as the classical WCA separation for the sake of comparison. As expected, the thermodynamic consistency is reached for all states under study.

As it can be seen from Table I, when the density is increasing, the mixing parameter f_0 is decreasing in all the cases studied: f_0 obtained with SDDS is slightly higher than that obtained with WCA separation, but at high densities (0.7 to 0.9), it varies monotonously for SDDS and remains constant (~ 0.2) for the WCA separation.

More interesting is the fact that the parameter p is found to increase with density and to be more than 1 for each thermodynamic state under study. At high density (0.6–0.9), the depth of the long-range part of the potential, $u^{LR^*}(r)$, is almost twice the value ε . This feature points out, *a posteriori*, that a state dependence has to be included in the division scheme of the effective pair potential. It has been shown in a previous work [11], that HMSA used with WCA separation led to overestimated values of $B(0)$. In the present calculation, we anticipate that $B(0)$ can be reduced only if the parameter p is greater than unity. This proves clearly that the bridge function at zero separation is extremely sensitive to the imposed depth of the long-range part $u^{LR^*}(r)$ involved in the SDDS.

In order to have an accurate indication of the variation in the bridge function with density, the exact relations [19] between the indirect correlation function, the cavity function and the bridge function, at zero separation, are useful, namely

$$B(0) = \ln y(0) - \gamma(0), \quad (9)$$

TABLE I Mixing parameter f_0 and parameter p for WCA and SDDS division schemes at $T^* = 1.5$, for five densities

$T^* = 1.5$ ρ^*	f_0		p	
	SDDS	WCA	SDDS	WCA
0.4	0.750	0.615	1.500	1.000
0.6	0.535	0.265	1.850	1.000
0.7	0.455	0.205	1.905	1.000
0.8	0.400	0.200	1.930	1.000
0.9	0.370	0.200	1.950	1.000

where $\ln y(0)$ corresponds to the excess chemical potential – equal to $\beta\mu$ in the case of HS fluid-, and

$$\gamma(0) = \left(\beta \frac{\partial P}{\partial \rho} - 1 \right) + \rho \int g(r)c(r)dr. \quad (10)$$

The integral never exceeds 3% of $\gamma(0)$ and, for the HS fluid, the determination of $B(0)$ leads to

$$B(0) \approx -\frac{15\eta^2 - 2\eta^3 + 3\eta^4}{(1 - \eta)^4}, \quad (11)$$

where $\eta = (\pi/6)\rho D^3$ is the packing fraction of the HS fluid of D diameter. The second set of exact relations is for the derivative with respect to r , which reads for the HS fluid,

$$D \left(\frac{\partial B(r)}{\partial r} \right)_{r=0} = 6\eta y(D)[y(D) - 1] \quad (12)$$

Then, $-B(r)$ is expected (i) to be a non negative oscillating function under contact ($r = \sigma$), (ii) to present a damped decay just before reaching the zero value and (iii) to approach $r = 0$ with a near zero slope contrary to what happens for the HS fluid.

As we are interested in the consequences of the SDDS on the bridge function over the entire range of the core region, we compare in Figure 2 our results of $B(r)$ with those of the simulation. The benchmark to be used to test the SDDS is the MC simulation performed by Llano-Restrepo and Chapman [4] that, to our knowledge, is the only complete study of the bridge function for the LJ fluid by simulation. Showing the bridge functions in the core for all five thermodynamic states, we observe that the curves follow the MC simulation one extremely well from zero separation to contact. Incidentally, we also have compared our results to the well-known parameterized function of Groot *et al.* [20] for the HS fluid, after the rule to match the HS diameter is adopted [11]. The results are not reported on the figure for clarity, but the agreement is very good except for $B(0)$ since the HS bridge function approaches $r = 0$ almost linearly. In addition, when we compare the bridge functions calculated using the SDDS and the WCA division scheme, it appears that the

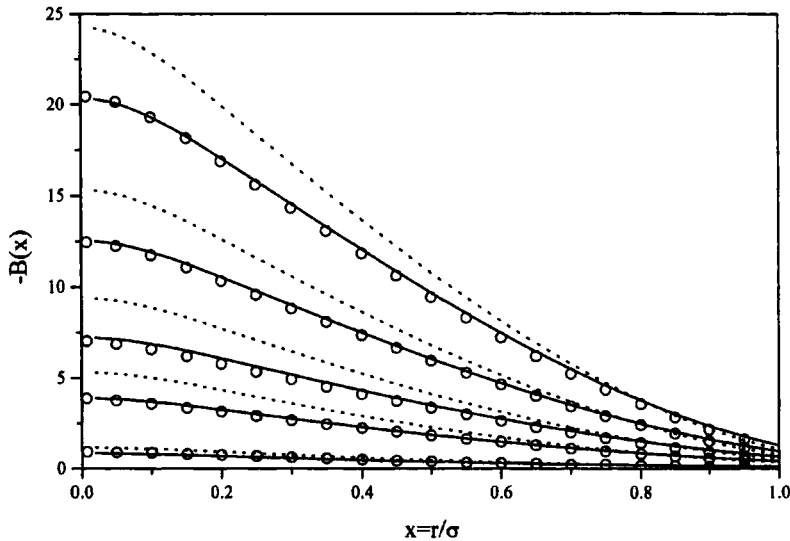


FIGURE 2 Bridge function $B(r)$ at $T^* = 1.5$, for five densities, calculated with the HMSA integral equation by using the WCA division scheme (dot line) and SDDS (solid line), compared to Monte-Carlo (open circles).

difference starts to be distinguishable beyond the density $\rho^* = 0.4$. The relative difference is 2% at $\rho^* = 0.4$, but reaches 19% at $\rho^* = 0.9$, indicating that the SDDS is less influent at low densities.

IV. CONCLUSION

In this work, a new division scheme of the potential is proposed for simple fluids that makes it possible to extract consistently the bridge function in the core region. In this scheme, the depth of the attractive part of the potential is fixed *via* a suitable parameter adjusted on MC values of the bridge functions at zero separation. Numerical tests have been carried out for a pure LJ fluid in several states along the isotherm $T^* = 1.5$. The bridge function has been successfully compared with those of the useful MC simulation. The main feature pointed out in this paper is that the bridge function has been shown to be extremely sensitive to the imposed depth of the attractive potential involved in the division scheme. This justifies, *a posteriori*,

that a state dependence has to be included in the potential separation. In a near future, we intend to mix the thermodynamic consistency condition with that division scheme of the potential in order to eliminate the dependence of the parameter p .

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