PAIR POTENTIAL IN LIQUIDS FROM THE EXACT BORN-GREEN EQUATION:

I. MODEL TESTING

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Born-Green Equation:

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Abstract

Pair potentials which are derived from the experimental pair correlation functions by either the Born-Green, the Percus-Yevick or the hypernetted chain equation have built-in inaccuracies because of the approximate nature of these equations. In this paper we show that the results can be improved upon by using the exact Born-Green equation properly. This method is checked by several Monte Carlo models and seems to work well.

I. Introduction

There are three approximate theories of the liquid state in frequent use.¹ Their common feature is that they attempt to relate the pair distribution function $g(r)$ to the inter-atomic pair potential $\phi(r)$. For convenience we list the theories and the relevant equations below:

Percus-Yevick (PY):

$$\phi_{PY}(r) = k_B T \ln \left\{ 1 - \frac{C(r)}{g(r)} \right\} \quad (1)$$

Hypernetted chain (HNC):

$$\phi_{HNC}(r) = k_B T \{ g(r) - c(r) - 1 - \ln g(r) \} \quad (2)$$

Born-Green with Superposition Approximation (BGSA):

$$\begin{aligned} \frac{d}{dr} \phi_{BGSA}(r) = & - \frac{k_B T}{g(r)} \frac{d}{dr} g(r) \\ & + \frac{\pi \rho}{r^2} \int_0^\infty g(t) \frac{d}{dt} \phi_{BGSA}(t) dt \int_{|r-t|}^{r+t} g(s) (s^2 - r^2 - t^2) s ds \end{aligned} \quad (3)$$

Here $c(r)$ represents the direct correlation function introduced by Ornstein and Zernike, i.e.,

$$h(r) = c(r) + \rho_0 \int c(|r - r'|) h(r') dr' \quad (4)$$

where $h(r) = g(r) - 1$ is the total correlation function, k_B Boltzmann's constant, ρ_0 the average number of atoms per unit volume; the quantities s, r, t are variables relating to the

three separations in a triplet of particles. Both $g(r)$ and $c(r)$ can be obtained from the observed structure factor $S(k)$ by appropriate Fourier transformation.

In 1963, Johnson and March² suggested that use should be made of these equations to obtain information about the nature of $\phi(r)$ for simple liquids like argon and sodium. Particular emphasis was focused on the BG theory in the form represented by the integro-differential equation (3) above. However, the accuracy of the experimental structure data was somewhat limited and for this reason the potentials obtained were not fully quantitative.

As more accurate structure factor data became available^{3,4} attention shifted to the somewhat simpler PY and HNC equations in which $g(r)$ and $c(r)$ were obtained directly from experiment. For metallic liquids, particularly lead, the PY and HNC potentials found by North et al.³ were not like those expected from the pseudopotential theory of metals, although they were-- in agreement with the findings of March and co-workers^{2,5}-- quite different from those obtained for liquid argon.⁴ Furthermore, North et al. showed that in spite of the great sensitivity of the final results to the low-angle form of $S(k)$, no reasonable choice of input data could lead to potentials which were in accord with theory. It was tentatively concluded that the PY and HNC equations were not applicable to liquid

metals. Subsequent investigations since then all used the BGSA equation.

In 1969, Gehlen and Enderby⁶ (GE) calculated the BGSA pair potential by solving the BGSA equation in momentum space. Their results for lead were similar to the results of North et al. from the PY and HNC equations. In 1971, Waseda and Suzuki^{7,8} (WS) solved the BGSA equation numerically for cesium and argon by a linearized simultaneous equation method and obtained oscillating potentials where predicted.⁹ The latter authors have analyzed many liquid metals¹⁰ since then and for everyone of them an oscillating pair potential was found. The differences between the GE results and the WS results is apparently due to the use of different input structure factor data.

The accuracy of the BGSA equation has been shown^{11,12} to be fair at low densities and poor at high densities. Thus we would expect the GE and WS results also to be fair at low densities and poor at high densities. The present paper presents a method which we believe could be used to improve on these results, (Sec. II). In section III we demonstrate the applicability of the method by a calculation on a model potential.

II. The exact Born-Green equation

The exact Born-Green equation, where one uses the triplet correlation function $g^{(3)}$ instead of the SA of Kirkwood, can be written for pairwise interactions as

$$\frac{\partial}{\partial \underline{r}_1} \phi(r_{12}) = - \frac{k_B T}{g(r_{12})} \frac{\partial}{\partial \underline{r}_1} g(r_{12}) - \rho_0 \int \frac{g^{(3)}(\underline{r}_1, \underline{r}_2, \underline{r}_3)}{g(r_{12})} \frac{\partial}{\partial \underline{r}_1} \phi(r_{13}) d\underline{r}_3 \quad (5)$$

Since the triplet function depends only on the relative distances between particles 1, 2 and 3, we can also put the equation in the following form

$$\begin{aligned} \frac{d}{dr} \phi(r) = & - \frac{k_B T}{g(r)} \frac{dg(r)}{dr} \\ & + \frac{\pi \rho_0}{r^2 g(r)} \int_0^\infty \frac{d\phi(t)}{dt} dt \int_{|r-t|}^{r+t} g^{(3)}(r, s, t) (s^2 - r^2 - t^2) s ds \end{aligned} \quad (6)$$

where r, s , and t represent the three relative distances r_{12} , r_{23} and r_{13} , respectively. The right hand side of (6) can be looked upon as an operator K operating on $g(r)$, $\frac{d\phi}{dr}$, and $g^{(3)}(r, s, t)$, such that

$$\begin{aligned} \frac{d}{dr} \phi(r) = & K(g(r), g^{(3)}(r, s, t), \frac{d\phi(r)}{dr}) \\ = & - \frac{k_B T}{g(r)} \frac{dg(r)}{dr} + \frac{\pi \rho_0}{r^2 g(r)} \int_0^\infty \frac{d\phi}{dt} dt \int_{|r-t|}^{r+t} g^{(3)}(r, s, t) (s^2 - r^2 - t^2) s ds \end{aligned} \quad (7)$$

Suppose $g_A(r)$ is the exact pair correlation from experimental data, and $\phi_A(r)$ is the exact pair potential we are looking for, then they, together with the exact triplet correlation function $g_A^{(3)}$ which can be obtained from $\phi_A(r)$ by computer,¹³ must satisfy the exact BG equation identically, i.e.,

$$\frac{d}{dr}\phi_A(r) = K(g_A, g_A^{(3)}, \frac{d}{dr}\phi_A) \quad (8)$$

Now let us denote by $\phi_B(r)$ the solution of the corresponding BGSA approximate equation, and by g_B and $g_B^{(3)}$ the corresponding pair and triplet functions which would satisfy the exact BG equation; that is,

$$\frac{d}{dr}\phi_B(r) = K(g_B, g_B^{(3)}, \frac{d}{dr}\phi_B) \quad (9)$$

If the two functions $g_A(r)$ and $g_B(r)$ are indistinguishable from one another, then the potential $\phi_B(r)$ is the correct pair potential we are looking for, thus if

$$g_B(r) = g_A(r)$$

we shall have:

$$\phi_B(r) = \phi_A(r), \quad g_B^{(3)} = g_A^{(3)}$$

and

$$\frac{d\phi_B(r)}{dr} = K(g_A, g_B^{(3)}, \frac{d}{dr}\phi_B(r)) \quad (10)$$

But since the BGSA equation is approximate in nature, we would generally expect the LHS and the RHS of equation (10) to have

different values. In such case, suppose we denote by $\phi'_B(r)$ the solution of equation (10), i.e.

$$\frac{d}{dr} \phi'_B(r) = K(g_A, g_B^{(3)}, \frac{d}{dr} \phi'_B(r)), \quad (11)$$

then, by comparing equations (8), (9), and (11), we would expect $\phi'_B(r)$ to lie between the exact potential $\phi_A(r)$ and the BGSA potential $\phi_B(r)$. In other words, we expect to have

$$\int |\phi'_B(r) - \phi_A(r)|^2 dr < \int |\phi_B(r) - \phi_A(r)|^2 dr \quad (12)$$

and thus $\phi'_B(r)$ represents the first improvement upon the BGSA solution $\phi_B(r)$. That the solution of (11) does exist and that it does satisfy (12) will be demonstrated in the next section with a model calculation.

III. Model test

From previous work we have the means to see whether in a "model" experiment it is possible to improve the potential as just proposed. In our earlier paper¹³ we presented three sets of triplet correlation functions which were calculated by Monte Carlo method with the same Lennard-Jones potential at the reduced density $\rho^* = 0.45$, and reduced temperatures $T^* = 1.552, 1.194$ and 0.776 , respectively. Since the LJ potential is characterized only by the parameters σ and ϵ we can think of these triplet functions as corresponding to the

same reduced temperature $T^* = 1.552$, but with different depths ϵ , 1.3ϵ , and 2.0ϵ , respectively. As our first test we pretend that the exact potential $\phi_A(r)$ to be the LJ potential with depth ϵ , and assume that we might have obtained from a BGSA computation a $\phi_B(r)$ which is also LJ potential but with depth 1.3ϵ . We should emphasise here that we have deliberately chosen such a potential which differs from $\phi_A(r)$ much more than the usual BGSA solution, in order to illustrate the validity of our method.

The pair function for the potential $\phi_A(r)$ and the $g^{(3)}$ for the potential $\phi_B(r)$ were substituted into (11), and the s-integral was first evaluated as a function of r and t and recorded as a two-dimensional matrix. The t integral was replaced by a summation over a fine t -grid. The input for $\frac{d\phi}{dt}$ for the first iteration was taken to be $\frac{d\phi_B}{dt}$, the RHS was then evaluated and the result used as the next input until the output and the input are the same. The solution $\frac{d\phi_B'}{dr}$ was obtained this way in less than ten iterations and is shown in Fig. 1 as black dots. On the same graph we also show the derivative of the 'exact' potential $\phi_A(r)$ as a full line and the derivative of the 'incorrect' potential $\phi_B(r)$ as a broken line. The function $\frac{d\phi_B'}{dr}$ was numerically integrated and was shown in Fig. 2 together with ϕ_A and ϕ_B . In Table 1 we list

two other cases tested by our method. It is obvious from Fig. 2, 4 and 6 that the output potential $\phi'_B(r)$ always lies closer to the exact potential ϕ_A than the input potential ϕ_B . Thus one can get closer and closer to the real pair potential by applying this method repeatedly, if one knows the pair correlation function exactly.

IV. Discussion

In reference 11 and 12, it was shown that the numerical accuracy of equation (8) is poor for r values less than σ or greater than 2σ . Thus one should not try to apply this method to those regions of r . Fortunately, the potential in those regions can be found accurately by thermal and high energy molecular beam collision experiments respectively.¹ One should use those methods to fix the short and long range part of the potential and use our method for the bowl part of the potential.

Secondly, we should point out that in all three of our tests we used a deeper input potential than the exact one. This is because when the input potential is shallower than the exact one, equation (11) is very sensitive to the initial input and the iteration method diverges. In such cases the first term on the RHS of (11) has very large negative values

for small r , this soon spreads to the other terms via the integral when the equation is iterated. However, this equation can be solved by other methods such as the one used by Waseda et al.⁸ We will report the results in a later paper. We also feel that the inaccuracy of our results at small r values is mainly due to the difficulty of differentiating the pair correlation function at small r , e.g. the first term on the RHS of (11). We are studying the short range behavior of the pair correlation function and looking for a reliable way to obtain better information about $g(r)$ in this region. This will probably improve the results for small r . For better results at large r , one probably needs a triplet function with longer range. (The range of our $g^{(3)}$ is 2.33σ). All of these improvements are necessary before we can actually use this method extensively to improve the BGSA results because, in fact, the BGSA generated potentials are probably not far from the real potential over much of the range of r .

Thirdly, the output of this method is the derivative of the potential, and when it is integrated we can choose the integration constant freely. In our model calculation this is chosen arbitrarily, since our purpose was to show the qualitative nature of the method; we might use this constant as

a parameter to obtain a best fit for the pair correlation function, i.e. to minimize the quantity

$$\int |g_B'(r) - g_A(r)|^2 dr$$

where $g_B'(r)$ is the pair function for the output potential $\phi_B'(r)$ via computer.

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Table 1. The three Monte Carlo models used to test our method.

ϕ_A is the potential taken as the 'exact' potential,
 ϕ_B is the input potential choosed and ϕ'_B is shown in
the figure listed under the last column.

	ϕ_A	ϕ_B	ϕ'_B Shown in Figure
Test 1	ϕ_{LJ}	1.3 ϕ_{LJ}	1,2
Test 2	1.3 ϕ_{LJ}	2.0 ϕ_{LJ}	3,4
Test 3	ϕ_{LJ}	2.0 ϕ_{LJ}	5,6

Figure Captions

- Fig. 1: Iteration result $\frac{d\phi_B}{dr}$ (black dots) as compared to the 'exact' potential (ϕ_{LJ} , full line) and the input potential ($1.3 \phi_{LJ}$, broken line).
- Fig. 2: Three curves of Fig. 1 integrated with respect to r .
- Fig. 3: Same as Fig. 1, except full line now represents $2 \phi_{LJ}$ and broken line is $1.3 \phi_{LJ}$.
- Fig. 4: Three curves of Fig. 3 integrated with respect to r .
- Fig. 5: Same as Fig. 1, except full line now represents $2 \phi_{LJ}$ and broken line is ϕ_{LJ} .
- Fig. 6: Three curves of Fig. 5 integrated with respect to r .

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6