

# MC test of perturbation theories based on site-site potentials

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The extension of the Barker-Henderson (BH) theory to diatomic potentials is examined by comparison of the predicted thermodynamic properties with "exact" MC results. Two choices of the potential separation have been considered; corresponding to the BH scheme and that of Weeks-Chandler-Andersen (WCA). Attention has been paid to the effect of the usual approximations to the exact properties of the hard reference system (equation of state and pair correlation functions) and to the convergence rate of the expansion. Conclusions can also be drawn for the extension of the WCA-blip function theory to these systems. It is shown that the behavior of the perturbation expansions exhibits the same features observed in atomic fluids. Nevertheless, the presence of the molecular anisotropy leads to a rather different assessment of the relative usefulness of each theory. Incidentally, small inaccuracies of the well-known Boublik and Nezbeda equation for the compressibility factor of dumbbells have been discovered at very high densities (outside the range previously reported).

## I. INTRODUCTION

Barker-Henderson (BH) and Weeks-Chandler-Andersen (WCA) theories<sup>1,2</sup> are the most powerful means to obtain the properties of atomic liquids. In both cases the properties of the hard spheres—the simplest reference system—are needed. For molecular liquids modeled by site-site potentials there are a number of possibilities in the division of the total potential into attractive and repulsive parts. Two kinds of expansions can be made according to the frame in which the potential is considered. If the division is made for the full molecular potential we find an orientational dependence of the reference system. This can be overcome by an appropriate averaging. The so-called Reference Average Mayer (RAM) theory of Smith and Nezbeda sphericalizes the pair potential interaction.<sup>3</sup> It is also possible to relate the orientational dependent reference system with a hard system made up of fused spheres via the "blip" function expansion. This procedure leads in the case of a diatomic potential to the well-known dumbbell particles as a reference system.<sup>4</sup> The evaluation of thermodynamic properties seems to be too expensive in both theories. As a matter of fact, no realistic models have been investigated with the RAM theory. Excellent results have been reported by making use of the expansion of Ref. 4 but it is also very time consuming since the hard fused spheres system must be obtained after an averaging over the angle-dependent potential. Moreover, the pair correlation function cannot be easily related to that of a known system and further approximations are needed.

Expansions over each of the site-site potentials of

the pair interaction lead in a simple way to a reference system with the same symmetry. Thus the hard fused spheres appear in a natural way as a reference system. The problem of a molecular system then reduces to a simple addition of site-site contributions. Besides that, these expansions have been proved to produce very good predictions for the thermodynamic properties.<sup>5</sup> For structural properties they are inadequate—unless further approximations<sup>6</sup> are introduced—because of the partial information contained in the atom-atom correlation functions. Thus, the expansions based on the division of the site-site interaction appear essentially designed for the evaluation of the thermodynamic quantities with a minimum cost of computer time. Our aim in this paper is to investigate in detail the predictions of this kind of theory. As long as the thermodynamic properties are unaffected by multipolar interactions, so that almost equivalent nonpolar site-site potentials may be constructed, these theories are of great interest since they may work for most of the systems made up of small molecules.

Both the BH<sup>7</sup> and WCA<sup>8</sup> procedures have been extended to interaction site potentials. Although the superiority of the WCA in atomic fluids was clearly demonstrated by Verlet and Weiss,<sup>9</sup> reported BH first order results showed for diatomics<sup>10</sup> the same accuracy as WCA did. It is our purpose to establish the reasons for this. Monte Carlo simulations have been carried out for the reference systems coming from the extended BH theory with two different choices of the potential splitting. One is the original BH scheme while the other one is that of the original WCA theory. Hereafter they will be referred

to as BH and WCA, respectively, but we recall that such reference systems are obtained within the BH expansion. We outline a brief summary of the theory in Sec. II.

The effect of the usual approximations to the properties of the reference system on the zeroth, first, and second order terms of the free energy expansion will be tested against "exact" MC results (Sec. III). Unfortunately, no direct simulations have been reported for the free energy of a diatomic system in which the anisotropic effects are of importance (the simulations by Quirke and Jacucci<sup>11</sup> have been done for a model of nitrogen whose interactions are nearly spherical). Thus—and because of the intrinsic interest of the derived properties—the various approximations will be also tested against Molecular Dynamics results for the pressures and internal energies (Sec. IV) of a model chlorine<sup>12</sup> along an isotherm and an isochore representative of the liquid phase. Given the similarity between the reference systems of our WCA and the proper site-site WCA theory of Tildesley<sup>8</sup> conclusions can also be drawn for the latter expansion. A discussion of the implications of this study is made in Sec. V.

## II. THEORETICAL BACKGROUND

In this paper we deal with molecular systems modeled by site-site potentials. The expansion is of general application to these systems but we are now mainly interested in homonuclear diatomic molecules. The pair interaction  $u(\mathbf{1}, \mathbf{2})$  depending on the molecular orientations is defined by the sum of the four interactions  $u_{\lambda\mu}(r_{\lambda\mu})$  between two sites in each molecule which depend only on the distance between the "atoms" of molecules 1 and 2. The essential feature of the perturbation theories working in the site frame is that the division of the potential into a reference and a perturbative parts is made on  $u_{\lambda\mu}(r_{\lambda\mu})$  instead of  $u(\mathbf{1}, \mathbf{2})$ ,

$$u_{\lambda\mu}(r_{\lambda\mu}) = u_{\lambda\mu}^r(r_{\lambda\mu}) + u_{\lambda\mu}^p(r_{\lambda\mu}). \quad (2.1)$$

We are concerned with two choices of potential separation. The BH scheme is one in which

$$\begin{aligned} u_{\lambda\mu}^r(r) &= u_{\lambda\mu}(r), & r < \sigma, \\ &= 0, & r > \sigma, \end{aligned} \quad (2.2a)$$

$$\begin{aligned} u_{\lambda\mu}^p(r) &= 0, & r < \sigma, \\ &= u_{\lambda\mu}(r), & r > \sigma, \end{aligned} \quad (2.2b)$$

where  $\sigma$  is such that  $u_{\lambda\mu}(\sigma) = 0$ . To avoid unnecessary complexity in the notation we have removed the subscripts on the site-site distances. The WCA division reads as follows:

$$\begin{aligned} u_{\lambda\mu}^r(r) &= u_{\lambda\mu}(r) + \epsilon, & r < r_{\min}, \\ &= 0, & r > r_{\min}, \end{aligned} \quad (2.3a)$$

$$\begin{aligned} u_{\lambda\mu}^p(r) &= -\epsilon, & r < r_{\min}, \\ &= u_{\lambda\mu}(r), & r > r_{\min}, \end{aligned} \quad (2.3b)$$

$\epsilon$  being the value of  $u_{\lambda\mu}(r)$  at the minimum,  $u_{\lambda\mu}(r_{\min}) = -\epsilon$  and  $u_{\lambda\mu}'(r_{\min}) = 0$ . A  $\lambda$  expansion of the Helmholtz free energy

$$A = A_r + A_1 + A_2 + \text{higher order terms} \quad (2.4)$$

gives for  $A_1$  the expression

$$A_1 = \sum_{\lambda} \sum_{\mu} 2\pi N\rho \int_0^{\infty} u_{\lambda\mu}^p(r) g_{\lambda\mu}^r(r) r^2 dr. \quad (2.5)$$

The next step is to relate the properties of the reference system with those of a hard diatomic (HD) system, i.e., dumbbell particles. In the BH procedure an appropriate definition of the diameters of the hard body cancels the first order term of the expansion for  $A_r$ . Furthermore,  $g_{\lambda\mu}^r(r)$  is also replaced by the pair correlation function  $g_{\lambda\mu}^{\text{HD}}$ . Thus, in the BH theory,

$$A_r \simeq A_{\text{HD}} \quad (2.6a)$$

BH theory.

$$g_{\lambda\mu}^r(r) \simeq g_{\lambda\mu}^{\text{HD}} \quad (2.6b)$$

We now display the explicit relations for the BH diameters in both potential separations (2.2) and (2.3):

$$d_{\lambda\mu} = \int_0^{\sigma} [1 - \exp\{-\beta u_{\lambda\mu}^r(r)\}] dr \quad \text{BH splitting}, \quad (2.7a)$$

$$d_{\lambda\mu} = \int_0^{r_{\min}} [1 - \exp\{-\beta u_{\lambda\mu}^r(r)\}] dr \quad \text{WCA splitting}. \quad (2.7b)$$

As our study is mainly concerned with the BH procedure we will distinguish the results coming from Eqs. (2.7a) and (2.7b) by the potential division involved, i.e., BH and WCA, respectively. The proper site-site WCA theory approximates

$$A_r \simeq A_{\text{HD}} \quad (2.8a)$$

WCA theory,

$$y_{\lambda\mu}^r(r) = y_{\lambda\mu}^{\text{HD}}(r) \quad (2.8b)$$

$y_{\lambda\mu}(r)$  being the background correlation functions. The diameters are the solutions of the blip-function equation

$$\begin{aligned} \int_0^{\infty} [\exp\{-\beta u_{\lambda\mu}^r(r)\} \\ - \exp\{-\beta u_{\lambda\mu}^{\text{HD}}(r)\}] y_{\lambda\mu}^{\text{HD}}(r) r^2 dr = 0. \end{aligned} \quad (2.9)$$

Actually, the expression (2.7) is a zeroth order result<sup>9</sup> for the expansion of the diameters given by Eq. (2.9) and the values are very close together (see Table I of Ref. 8 and Table I of this paper). Then several parts of our study of the site-site BH theory will be also useful for the extended WCA procedure.

The second order term in the expansion has been obtained via Monte Carlo simulation and with the aid of the simple extension to site-site potentials of the Kirkwood superposition approximation (SSA). The suitable expression for the simulation is

$$\begin{aligned} A_2^*/T^* &= -\frac{1}{2N} \cdot \frac{1}{T^{*2}} \sum_{\lambda} \sum_{\mu} \sum_i \sum_j \{ \langle N_i^{\lambda\mu} N_j^{\lambda\mu} \rangle_{\text{HD}} \\ &\quad - \langle N_i^{\lambda\mu} \rangle_{\text{HD}} \langle N_j^{\lambda\mu} \rangle_{\text{HD}} \} u^{*p}(r_i) u^{*p}(r_j), \end{aligned} \quad (2.10)$$

where  $N_K^{\lambda\mu}$  denotes the number of pairs of atoms  $\lambda, \mu$  whose distance lie between  $r_K + \Delta r/2$  and  $r_K - \Delta r/2$ . The

TABLE I. Simulation results for a diatomic LJ with  $l_2^* = 0.608$  (see the text).

$\rho_\sigma^*$	$T^*$	$d$	$l_2^*$	$\rho_d^*$	$(\beta p/\rho)_{HD}$	$A_1^*/T^*$	No. conf. $\times 10^{-6}$	$A_2^*/T^*$	No. conf. $\times 10^{-6}$
BH									
0.550	1.5	3.2332	0.6305	0.4931	13.04	-9.178	2.50		
0.541	1.5	3.2332	0.6305	0.4850	12.25	-9.037	1.80	-0.374	3.30
0.520	1.5	3.2332	0.6305	0.4662	10.88	-8.686	1.50		
0.512	1.5	3.2332	0.6305	0.4590	10.56	-8.547	1.00	-0.331	2.30
0.495	1.5	3.2332	0.6305	0.4438	9.56	-8.249	1.10		
0.485	1.5	3.2332	0.6305	0.4348	9.07	-8.072	1.00		
0.470	1.5	3.2332	0.6305	0.4214	8.31	-7.797	0.75		
0.4546	1.5	3.2332	0.6305	0.4076	7.68	-7.524	1.50	-0.282	1.10
0.4546	1.2	3.2500	0.6273	0.4140	8.02	-9.455	1.30		
0.4546	1.3	3.2442	0.6284	0.4118	7.80	-8.712	1.30		
0.4546	1.4	3.2386	0.6295	0.4096	7.75	-8.067	1.00		
0.4546	1.5	3.2332	0.6305	0.4076	7.68	-7.524	1.50	-0.282	1.10
0.4546	1.65	3.2254	0.6321	0.4046	7.61	-6.824	1.20		
0.4546	1.8	3.2180	0.6335	0.4019	7.45	-6.238	1.40	-0.189	3.00
0.4546	1.95	3.2109	0.6349	0.3992	7.38	-5.750	1.50		
0.4546	2.1	3.2042	0.6362	0.3967	7.33	-5.326	1.50		
0.4546	2.25	3.1977	0.6375	0.3943	7.19	-4.959	1.30		
WCA									
0.550	1.5	3.3534	0.6079	0.5502	17.45	-10.639	1.60		
0.541	1.5	3.3534	0.6079	0.5412	16.71	-10.424	1.90		
0.520	1.5	3.3534	0.6079	0.5202	14.51	-9.921	1.50		
0.512	1.5	3.3534	0.6079	0.5122	13.69	-9.729	1.40		
0.495	1.5	3.3534	0.6079	0.4952	12.45	-9.323	1.50		
0.485	1.5	3.3534	0.6079	0.4852	11.64	-9.089	1.40		
0.470	1.5	3.3534	0.6079	0.4702	10.62	-8.735	1.50		
0.4546	1.5	3.3534	0.6079	0.4548	9.76	-8.366	3.00		
0.4546	1.2	3.3825	0.6027	0.4667	10.39	-10.473	1.00		
0.4546	1.3	3.3722	0.6045	0.4625	10.04	-9.665	1.00		
0.4546	1.4	3.3625	0.6063	0.4585	10.00	-8.968	1.00		
0.4546	1.5	3.3534	0.6079	0.4548	9.76	-8.366	3.00		
0.4546	1.65	3.3405	0.6103	0.4495	9.45	-7.604	0.80		
0.4546	1.8	3.3286	0.6125	0.4447	9.23	-6.969	1.00		
0.4546	1.95	3.3174	0.6145	0.4403	8.96	-6.427	0.90		
0.4546	2.1	3.3070	0.6165	0.4361	...	-5.965	1.00		
0.4546	2.25	3.2971	0.6183	0.4322	8.71	-5.568	1.00		

asterisks indicate reduced quantities which for thermodynamic quantities are obtained in the usual way, i.e., with  $\epsilon$  for energies and  $\sigma$  for lengths. As the reference system also has an obvious parameter to reduce distances (the diameters of the hard body), a subscript will point out to what parameter the quantity is referred (for instance,  $\rho_\sigma^*$  and  $\rho_d^*$  means the reduced density of the actual and reference system using  $\sigma$  and  $d$  as length parameters, respectively). Finally, the extension of the SSA put into the second order term gives

$$A_2/NkT = \sum_{\lambda} \sum_{\mu} \left\{ -\frac{1}{4} \rho J_1 - \frac{1}{2} \rho^2 J_2 - \frac{1}{8} \rho^3 (2J_3 + 3J_4) \right\},$$

$$J_1 = 4\pi \int_0^{\infty} g_{\lambda\mu}^{HD}(r) \{u_{\lambda\mu}^R(r)\}^2 r^2 dr,$$

$$J_2 = 4\pi \int_0^{\infty} g_{\lambda\mu}^{HD}(r) u_{\lambda\mu}^R(r) \gamma(r) r^2 dr,$$

$$J_3 = 4\pi \int_0^{\infty} \{\gamma(r)\}^2 r^2 dr,$$

$$J_4 = 4\pi \int_0^{\infty} \{g_{\lambda\mu}^{HD}(r) - 1\} \{\gamma(r)\}^2 r^2 dr,$$

$$\gamma(r) = \frac{2\pi}{r} \int_0^{\infty} g_{\lambda\mu}^{HD}(s) u_{\lambda\mu}^R(s) ds \int_{|r-s|}^{r+s} \{g_{\lambda\mu}^{HD}(t) - 1\} t dt, \quad (2.11)$$

where we have used further approximations suggested by Smith *et al.*<sup>20</sup>

### III. THE SIMULATION OF THE REFERENCE SYSTEM

We have carried out a conventional Monte Carlo simulation<sup>13</sup> of the properties of the hard reference system in order to elucidate without ambiguities the accuracy of the perturbation expansion. The properties of a model chlorine ( $l_2^* = 0.608$ ) will be evaluated through the perturbation expansion along a representative isotherm  $T^* = 1.5$  and isochores  $\rho_\sigma^* = 0.4546$  corresponding to the liquid phase.<sup>12</sup>

Our sample consists of 256 hard dumbbells with diameter given by Eqs. (2.7a) and (2.7b), which will be used to define the reduced quantities of the reference system  $\rho_\sigma^*$  and  $l_2^*$ . Note that the dependence of the

diameters on temperature implies that the reduced lengths  $l_d^*$  are different for different  $T^*$  because the site-site distance  $l$  is the same for the reference and the actual potentials. As the diameters roughly differ by a 3% depending on the convention used for the potential splitting, two series with rather different parameters have to be simulated. For the same state point of the nonperturbed system,  $\rho_d^*$  is about a 10% higher for the WCA-like splitting. Conversely, reduced lengths are 3% lower. The state points, the actual model, and the corresponding simulated quantities of the reference system are displayed in Table I.

The starting configuration corresponds in each of the series to the point at higher density. The particles are oriented with the molecular axis parallel to the direction of the  $Z$  axis and the centers placed at the positions of a face centered cubic lattice. Half a million configurations are generated to equilibrate the system. The displacements in Cartesian coordinates of the centers and the orientations of the molecular axes are monitored by two independent parameters fitted to get a rate of acceptance close to 0.35. Moreover, the parameters are chosen in such a way that the acceptance is approximately the same for each kind of move—either translational or rotational—when the other is held constant. When equilibrium is reached the parameters are fixed for the calculations. The final configuration in the calculation step is used to generate the starting one of the next state point at a lower density by expanding the box and the positions of the dumbbells. When one point differs from the next one only in the temperature of the nonperturbed system, both the box length and the reduced lengths of the dumbbells must be slightly modified. It is to be noticed that in each of the series all the simulations referring to the isochore  $\rho_d^* = 0.4546$  correspond to a very restricted surface on the space phase of the reference system (see Table I).

The compressibility factor and the leading terms in the expansion of  $A/NkT$  are directly provided by the simulation. We describe immediately the main features of the simulation of these quantities whose results are displayed in Table I.

### A. Compressibility factor

We evaluated the compressibility factor of the dumbbells by a linear extrapolation at the contact point of the corresponding averages every 256 steps over three consecutive shells of thickness  $0.03d$ . It is a rather low value which obviously avoids a possible nonlinear behavior in the extrapolation. In contrast, the statistics would be poor for short runs. The earlier results corresponded to the reference system in the BH original scheme for the isotherm  $T^* = 1.5$  of the model chlorine with  $\rho_d^*$  varying from 0.550 to 0.4546. They may be taken as a test of the MC program and the values are very close to that predicted by the Boublik and Nezbeda (BN) equation.<sup>14</sup> This is not fulfilled when the WCA splitting is used. In such case, small departures from BN equation were discovered. We remark that Eq. (2.7a) leads to a reduced density of the dumbbells system which is a 10% higher

than that obtained with the diameter defined by Eq. (2.7b). Thus, in the former case we get unusual values of  $\rho_d^*$  corresponding to densities for which, to our knowledge, no results have been previously reported. Figure 1 shows the difference between simulation and analytical predictions. Interestingly enough, the statistical error in the simulations might explain the difference up to  $\rho_d^* \approx 0.50$  which is the higher density reported by Freasier<sup>15</sup> and Tildesley *et al.*<sup>16</sup> for almost the same reduced length.

The statistical error of our values may be evaluated by examining the simulations when the nonperturbed model has a constant density. As pointed out below, they can be considered as partial averages of a roughly unique and very long run of about 12 million configurations. In Fig. 2 departures of our simulated compressibility factors from those obtained with BN equations are represented. The temperature of the nonperturbed system is chosen as an independent variable because neither  $\rho_d^*$  nor  $l_d^*$  are constant. The standard deviation is  $\sigma_{N-1} = 0.04$  for the BH-like splitting while it rises to 0.06 in the WCA scheme. Besides that, the average difference is negligible in the former case ( $-0.005$ ) and very little in the latter one ( $-0.04$ ). Thus, the statistics are slightly poor at high densities but the error cannot explain the differences shown in Fig. 1. Nevertheless, such differences—which reach a maximum of about 3%—are only noticeable in the context of a perturbation expansion where very accurate values for the properties of the reference system are needed.

### B. First order contributions to $A/NkT$

First order contributions to the free energy have been calculated by evaluating the pair site-site distribution function at intervals of  $0.01d$  from the contact distance. For contributions beyond  $2.5\sigma$ , no structure in the fluid

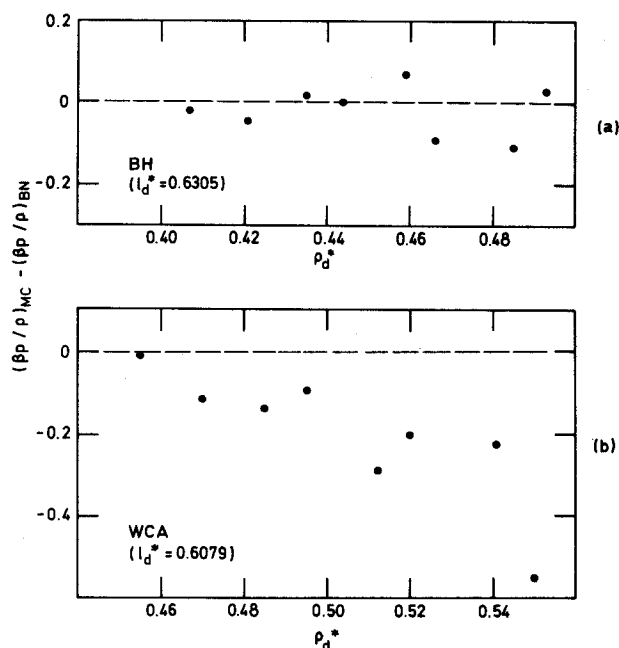


FIG. 1. Departures of the simulated compressibility factors from the BN equation. The temperature of the actual system is  $T^* = 1.5$ . (a) Diameters of the dumbbells corresponding to a BH choice [Eq. (2.7a)] and (b) WCA division [Eq. (2.7b)].

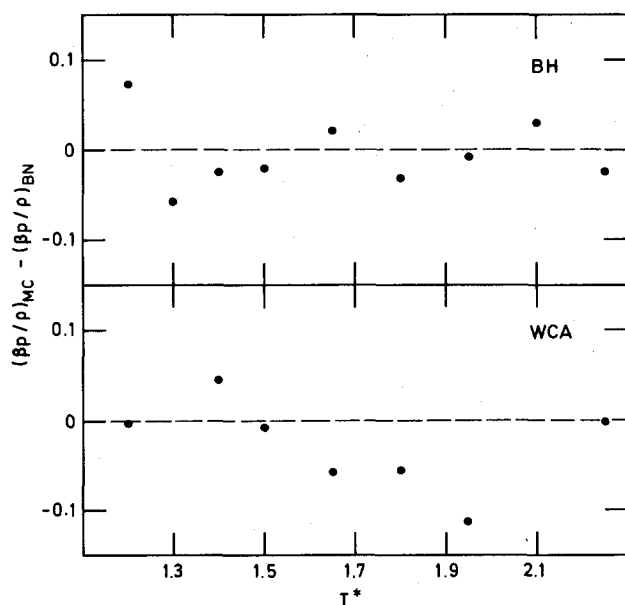


FIG. 2. Same as Fig. 1 when the density of the soft system is constant ( $\rho_s^* = 0.4546$ ).

is assumed. The number of configurations generated in each run depends on the density of the hard system and for most of the state points is between 1.0 and 1.5 million. A fit of the Monte Carlo results for  $A_1^*/T^*$  against  $1/T^*$  or  $\rho_s^*$  shows that the error is always less than 0.003.

The comparison of the pseudoexperimental data with those coming from the use of the RISM equation<sup>17</sup> for the distribution function is given in Fig. 3. The RISM results appear as sufficiently accurate—the maximum difference is 0.1—but far outside from the statistical error. The discrepancies are larger for the WCA choice except at the higher densities where the approximation introduces similar errors in both potential separations. More important is the dependence of the error on  $\rho_s^*$  and  $T^*$  because of the great sensitivity of the derived properties—energy and pressure—to small changes in  $A/NkT$ . So we anticipate that the main feature of the RISM results will be the dependence of the discrepancies along the isochore in the case of the BH division since they lead to nonnegligible errors in the predicted pressures.

### C. Second order term

Equation (2.10) is the suitable form of the second order term for MC simulation purposes. There are four covariances to be evaluated, although they are all equivalent in the case of a homonuclear diatomic. But now, oppositely to the evaluation of  $A_1/NkT$ , it is not possible to perform the overall contribution laying aside the individual site-site contributions. Because of the high packing the move of the particles is strongly restricted. As a consequence, the distance between any two atoms in different molecules—especially when they are close together—changes very slowly. A good sampling of all the fluctuations around the mean number of atomic distances lying in each pair of shells [see Eq. (2.10)] requires a very long run. Since the atoms are equivalent, the mutual exchange of the sites in a molecule produces a new configuration which is indistinguishable from the

previous one but where the atomic distances are different. We have checked that this trick—applied randomly every averaging step—both enhances the convergence of the covariances and leads to a value which agrees with that obtained in usual and longer runs.

When convergence is achieved the four atom-atom contributions always differ considerably even though the four covariances are similar at each of the distances. We believe this to be due to the cancellation occurred in the sum over the distances.<sup>18</sup> Maximum ratios between the highest and lowest site-site contributions are about 2 for the BH separation and up to 8 for the WCA case. This fact throws some doubt upon the accuracy of our results in the BH separation and renders unacceptable the predictions in the WCA division which must be discarded.

An approximate evaluation of the second order term makes use of the site-site Kirkwood superposition approximation (SSA). Despite the formidable aspect of the relation (2.11), a considerable amount of computer time is saved by the tabulation of the inner integral.<sup>19,20</sup> Even so the second order term becomes about 20 times more expensive than the first order one. Comparison with the Monte Carlo results for the BH separation shows good agreement which somewhat reinforces the validity of the simulation (Fig. 4).

Advantage can be taken of the similarity of the corresponding hard reference systems at different (but not too much) temperatures. Indeed, the compressibility factors already displayed this feature (see column 6 in Table I). At a constant density, the fluctuations in the total potential energy will be essentially determined by the effect of the temperature. We have used the fluctuations

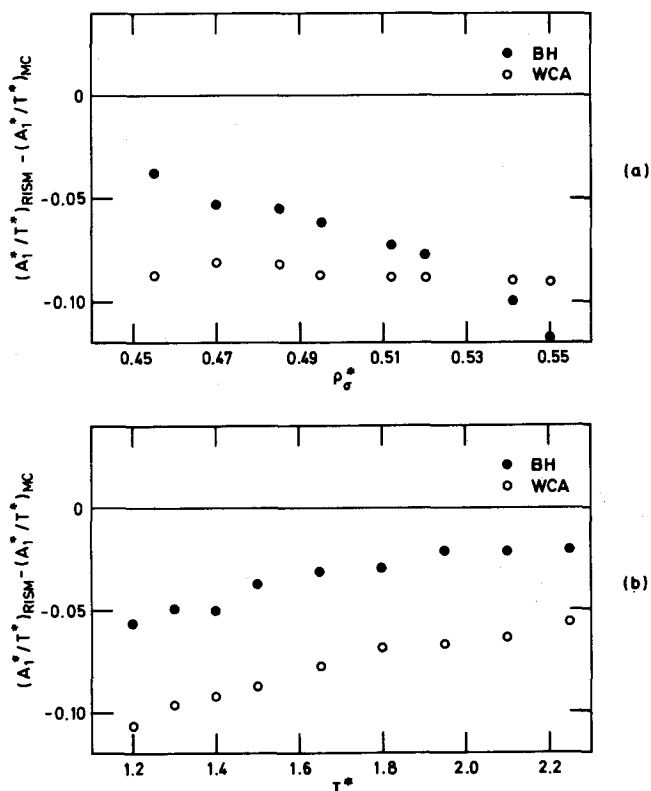


FIG. 3. Errors induced in  $A_1/NkT$  by the RISM approximation to the pair correlation function.

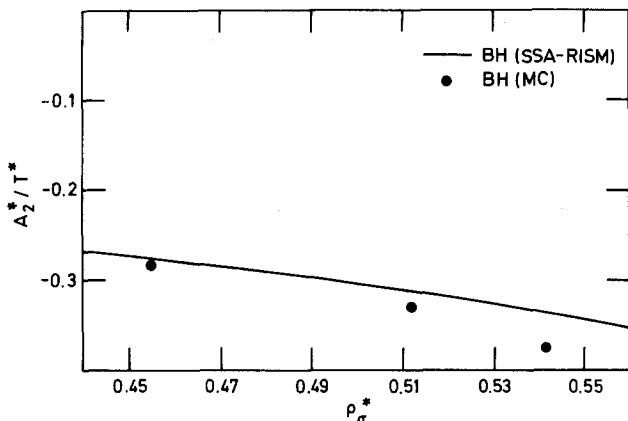


FIG. 4. Second order contribution to the free energy at  $T^* = 1.5$ .

at  $T^* = 1.5$  to predict the second order term at different temperatures. The results—displayed in Table II—show a good agreement with the trend exhibited by the SSA predictions and, what is more important, agree very well with a simulated point at  $T^* = 1.8$ . Thus, the simulation of one state point would be sufficient to obtain the contributions at the same density and fairly different temperatures (if the covariances at  $T^* = 1.8$  are used then the prediction for  $T^* = 1.2$  is  $-0.425$  close to the value  $-0.441$  obtained with the fluctuations at  $T^* = 1.5$ ). This allows us to propose the following relationship:

$$A_2^*/T_2^* = (A_2^*/T_1^*) \cdot (T_1^*/T_2^*)^2. \quad (3.1)$$

It is easy to realize that the same holds for the SSA predictions. Indeed, a similar expression may be written for  $A_1/NkT$ . It leads to a relative error of the same order but, as long as such a term is quite high, absolute errors render the approximation unsuitable.

#### IV. DERIVED PROPERTIES

Pressure and internal energy are the quantities of major interest in our work. The configurational part of these quantities has been evaluated by fitting the Helmholtz free energy to a third order polynomial in  $\rho_\sigma^*$  and  $1/T^*$ , respectively, and then differentiating the corresponding basic relations

$$p^* = \rho_\sigma^{*2} T^* \left( \frac{\partial A^*/T^*}{\partial \rho_\sigma^*} \right)_{T^*}, \quad (4.1)$$

$$U^* = \left( \frac{\partial A^*/T^*}{\partial 1/T^*} \right)_{\rho_\sigma^*}. \quad (4.2)$$

TABLE II. Temperature dependence of  $A_2^*/T^*$  (BH).  $\rho_\sigma^* = 0.4546$ . Second column shows the values obtained when the covariances of the HD systems are approximated by those at  $T^* = 1.5$  (see the text).

$T^*$	MC	Covariances at $T^* = 1.5$	SSA
1.2		-0.441	-0.429
1.3		-0.375	-0.367
1.4		-0.324	-0.317
1.5	-0.282	-0.282	-0.278
1.65		-0.233	-0.232
1.8	-0.189	-0.196	-0.196
1.95		-0.167	-0.168
2.1		-0.144	-0.146

#### A. Pressure

Predicted pressures along the isotherm  $T^* = 1.5$  of the model chlorine from the different approaches are represented in Figs. 5—BH separation—and 6 (WCA) together with Molecular Dynamics data. The first remark to be made is the influence of using RISM distribution function instead of the exact ones, which causes a non-negligible error. Besides that, the dependence of the errors in the  $g_{\lambda\mu}^{HD}$ 's upon the reduced density and elongation of the hard particles makes the departures rather erratic. Hence the different magnitudes of the discrepancies: In the BH choice (BH1-RISM), the differences with respect to BH1-MC are important while they are negligible for the WCA separation. Keeping in mind that our WCA diameters are very close to that of the proper WCA atom-atom theory given by Tildesley,<sup>8</sup> we conclude that the latter will be also unaffected by errors in the  $g_{\lambda\mu}^{HD}$ 's at least in the conditions studied. But the main feature of this investigation is the extreme sensitivity of the derived properties to small errors in  $A/NkT$ . Note—see Fig. 3—that for both divisions of the potential the errors introduced by the RISM approximation are of the same order—or even greater but almost constant for the WCA—and that what causes the final discrepancies is the slight dependence on density of the errors in BH1-RISM. There, a major difference of about 1.3% in  $A/NkT$ , becomes a minimum error of about 20% in  $p^*$ : The error is magnified, at least, by a factor of 15!

The similar slope of the SSA and MC calculations for  $A_2/NkT$  in the BH scheme allows us to add the approximate correction to our exact first order values producing the results labeled as BH2-MC in Fig. 5. The agreement with MD pressures is very good so we can conclude that—analogously to the situation for spherical potentials—two terms are sufficient to produce a satisfac-

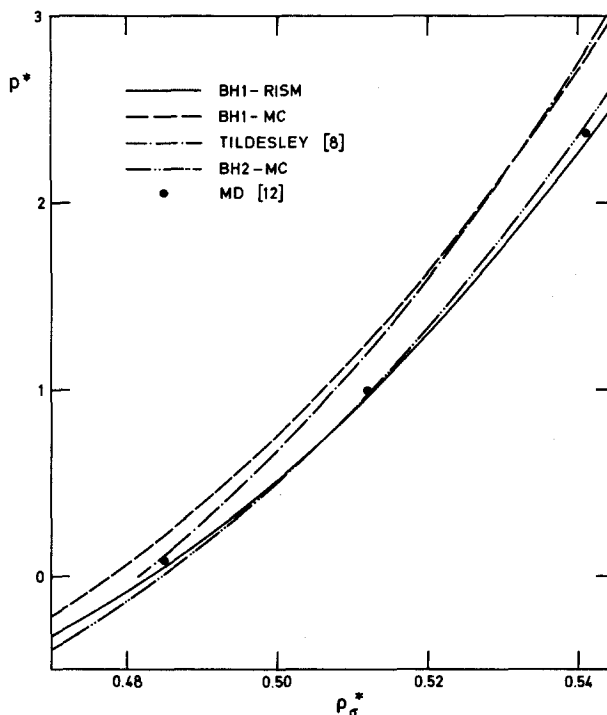


FIG. 5. Pressures for the BH separation along the isotherm  $T^* = 1.5$ .

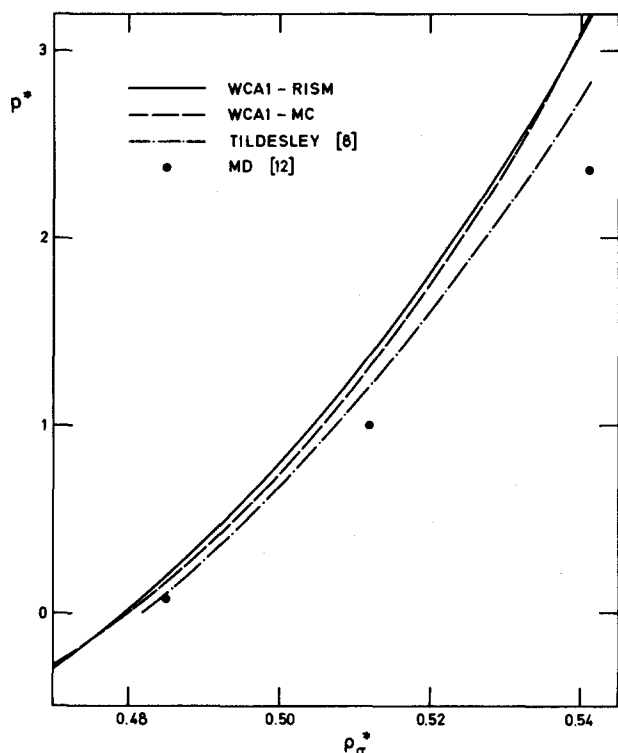


FIG. 6. Same as Fig. 5 but for the WCA division.

tory convergence of perturbation expansion. There is another similarity not previously expected. The errors coming from the use of the RISM approximation (a Percus–Yevick-like approximation for anisotropic potentials) are of the same order and different sign than those coming from neglecting the second order term. This explains the close agreement with MD of our first order reported pressures for diatomic systems with elongations going from 0.33 for liquid  $N_2$ <sup>7</sup> to 0.79 for a diatomic potential for liquid  $CO_2$ .<sup>21</sup> Interestingly enough, this behavior has also been pointed out for spherical systems<sup>18</sup> when the PY closure is used. Then the cancellation occurs for all the systems and conditions so far studied and seems to be inherent to the nature of both approximations.

As mentioned above WCA1-RISM predictions for pressure (Fig. 6) are indistinguishable from WCA1-MC. Moreover, the contribution of the terms coming from the substitution of the reference system by a hard dumbbell model may be roughly estimated as the difference with respect to Tildesley results [the author showed the validity of the approximation involved by Eq. (2.8)]. They appear to make a little contribution when one realizes that they are approximately a half of the departures of such blip-function theory predictions with respect to MD data. One may ask for the reasons which make such a difference—up to four times<sup>22</sup> the error reported in the MD simulation—in an expected first order theory. The answer lies in the use of the BN equation for the compressibility factor of the hard dumbbells system. Small deficiencies of the analytical equation at very high densities have been already shown in Sec. III and they account for the differences between Tildesley and MD pressures well within the statistical uncertainty of the simulations. With this correction only the first order is needed to get

accurate results in the blip-function site–site theory thus fulfilling previous expectations based on the experience on monoatomic liquids.<sup>9</sup>

## B. Internal energy

The evaluation of the configurational part of the internal energy requires the knowledge of the Helmholtz free energy of the hard dumbbells system. We use the analytical integration of the BN equation [Eq. (20) of Ref. 8]. The more characteristic feature of the curves obtained for the BH separation (Fig. 7) is the importance of second order term. Moreover, now the RISM approximation introduces no substantial modifications in the predicted energies so the cancellation produced for pressure does not occur here. In this way first order exact energies are clearly insufficient. The addition of the second order term leads to better results but they are still in disagreement with Molecular Dynamics data. The inaccuracies introduced by the SSA approximation are likely responsible for a part of these differences. But we would suggest another possibility consisting in the processing which allows the estimation of the zeroth order contributions from the compressibility factors of the hard dumbbells system which is far from negligible in the BH scheme. Conversely, the WCA division of the potential leads to a small contribution from the hard reference system and no errors will be induced by the numerical differentiation of the BN equation for  $A_{HD}/NkT$ . Besides that, the internal energy in the WCA separation (we recall that it has been combined with a BH-like theory) is very close (Fig. 8) to that of the blip-function theory (applied to the same potential separation) revealing again the small effect of substituting the actual soft reference system by that made up of fused spheres obtained with a BH expansion. Again Tildesley's values agree with MD data within the small errors introduced by the RISM approximation and by the numerical differentiation of  $A/NkT$  which seems to be responsible for a rather strange slope. Thus, the good agreement with MD of the approximated first order

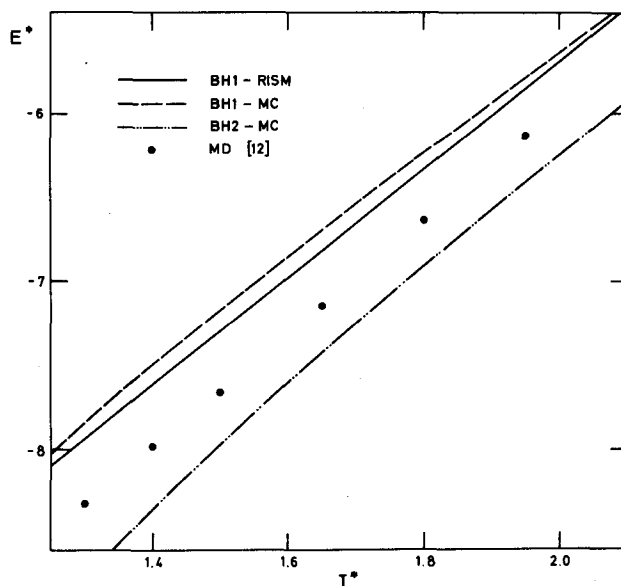


FIG. 7. Internal energies (BH splitting) along the isochore  $\rho^* = 0.4546$ .

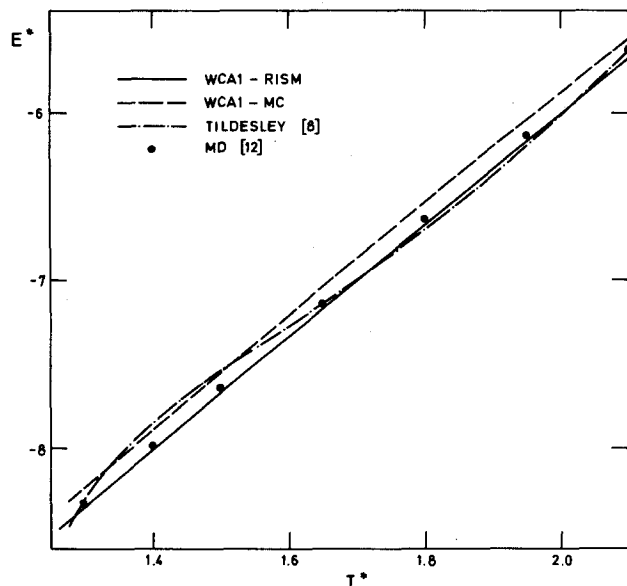


FIG. 8. Same as Fig. 7 but for the WCA separation.

results for the WCA splitting is now intrinsic and not due to a cancellation of errors.

## V. DISCUSSION

The extension of the well-known BH and WCA theories to interaction site potentials exhibits—at least for diatomics—the same features already shown by Verlet and Weiss<sup>9</sup> in spherical systems. Although the convergence rate has not been explicitly evaluated, the excellent agreement of the corrected BH2 and the blip-function schemes confirm that higher order terms are negligible. Thus, BH and WCA separations lead to essentially second and first order expansions, respectively. The BH procedure applied to a WCA separation differ from the blip function in the definition of the hard system substituting the soft repulsive potential of the  $\lambda$  expansion and in the approximations to the correlation functions (blip function uses the background correlation function  $y_{\lambda\mu}^{\text{HD}}$  instead of  $g_{\lambda\mu}^{\text{HD}}$ ). These criteria cause a little loss of convergence but also a considerable saving in computer time (in fact, ten evaluations of the pair correlation functions are needed to obtain accurately the blip-function diameters). This need was overcome for spherical systems by an appropriate fitting. But for diatomics it is difficult to do the analog since the molecular anisotropy introduces a new reduced parameter—the elongation—to define the equivalence of the corresponding states. Thus—provided that the properties of the hard reference system are available—the combined BH-WCA procedure may be a cheaper alternative to the expensive WCA theory without significant loss of accuracy. A similar statement for the site-site pair correlation functions is made in the paper by Gubbins *et al.* on monoatomics.<sup>23</sup>

The simplicity of an exact evaluation of the properties of the hard system is also affected by the molecular anisotropy and somewhat new differences in the assessment of the perturbation expansions are introduced. WCA separation always leads to a hard system close to the metastable region. This paper has pointed out that

the inaccuracies in the properties of the hard system may render meaningless the difference between the BH and WCA procedure when applied to the WCA division. Oppositely, the BH separation implies a lower density in the reference system and the available equations of state are accurate enough. Thus, the lack of accuracy for the hard fused spheres system may disturb the initial appraisal of these theories. These questions may become dramatic if one thinks in more complicated systems (e.g., tetrahedral molecules). There, we may try to benefit from the fortunate cancellation produced in the BH expansion between second order contributions and the errors induced by a PY-like approximation for the pair distribution functions. Anyway, the absence of a universal hard reference system removes a part of the goals of the perturbation theories for highly anisotropic liquids unless accurate equations of state are proposed for hard fused spheres of any geometry.

## ACKNOWLEDGMENTS

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