

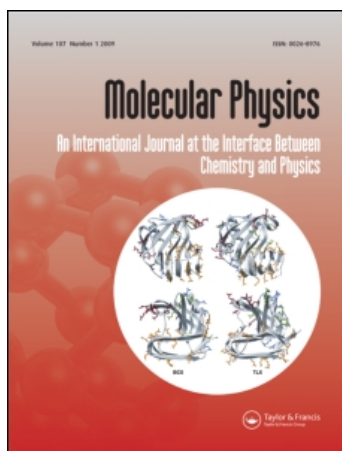
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Molecular Physics

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713395160>

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To cite this Article Vega, Carlos and Lago, Santiago(1991) 'Structural study of the angle-averaged soft Kihara potential for linear molecular models', *Molecular Physics*, 72: 1, 215 – 228

To link to this Article: DOI: 10.1080/00268979100100151

URL: <http://dx.doi.org/10.1080/00268979100100151>

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Structural study of the angle-averaged soft Kihara potential for linear molecular models. A test of perturbation theory

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(Received 24 May 1990; accepted 9 July 1990)

The angle-averaged potential corresponding to a Weeks–Chandler–Andersen division of an anisotropic Kihara potential is obtained for several molecular models. Monte Carlo (MC) simulations are performed and the structural results are compared with those coming from Percus–Yevick (PY) and from reference hypernetted chain (RHNC) equations. PY and RHNC give similar results at low densities, but for high densities and large anisotropies PY fails while RHNC gives excellent agreement with MC results. Monte Carlo simulations for soft repulsive rods are also carried out, and Z_0 , A_1 and A_2 are computed during the runs. A comparison of the simulated values with the theoretical ones as predicted by the perturbation scheme proposed by Fischer using PY and RHNC results for the background correlation function is also made.

1. Introduction

Repulsive forces have been shown to be responsible for the structure of simple liquids at high densities [1]. For non-polar molecular liquids there is also some evidence showing the predominant role played by the short-range forces in determining the structure. Several perturbations approaches have been developed on the basis of this. Fischer [2] devised a perturbation scheme, choosing the reference potential to contain all the repulsive forces, in the WCA spirit. This theory works well for linear molecules of moderate elongation and has been extended to mixtures [3] and nonlinear molecules [4]. The potential used by Fischer was the multicentre Lennard-Jones, although the theory was later applied to the GOCE [5] and Kihara [6] potentials. In Fischer's theory the structure of the reference fluid was approximated by a zeroth-order expansion of the background correlation function $y(r_{12}, \Omega_1, \Omega_2)$, around a RAM spherical potential $\phi(r)$. Of course, it is also possible to solve an integral equation [7–9] for the reference system, but then the theory becomes nearly as time consuming as simulation. The structure corresponding to the potential $\phi(r)$ is obtained by solving the Ornstein–Zernike (OZ) equation along with a closure relation. Percus–Yevick (PY) closure has always been chosen for this purpose, because it was thought to be adequate for soft repulsive potentials $\phi(r)$.

On the other hand, the reference hypernetted chain (RHNC) [10] equation has proved to be the most successful theory for spherical potentials. Moreover, the Labik–Malijevsky parametrization of the bridge function (the sum of all the so-called bridge diagrams) of hard spheres allows an easy application of this theory. However, this approach has mainly been applied to short-ranged repulsive spherical potentials [11, 12] but not to soft repulsive potentials with a longer repulsive range. The purpose of this paper is twofold. First, we shall show how PY closure fails in certain thermodynamic conditions for RAM $\phi(r)$ and should therefore not be used without caution.

In this case the RHNC equation proves to be reliable in yielding very good results for the structure of this $\phi(r)$ potential in all the studied conditions. Secondly, we shall show the effect of using the RHNC results for $\phi(r)$ instead of the traditional PY closure within the framework of Fischer's theory.

2. Theoretical background

In Fischer's perturbation theory [2] the full intermolecular potential is divided into a reference term and a perturbation term:

$$u(r_{12}, \Omega_1, \Omega_2) = u_0(r_{12}, \Omega_1, \Omega_2) + \lambda u_1(r_{12}, \Omega_1, \Omega_2), \quad (1)$$

where λ is a coupling parameter, r_{12} is the distance between the centres of mass of molecules 1 and 2, and Ω_i is the set of orientation coordinates of molecule i . The reference part of the potential combines all the repulsive forces in the system. Therefore the reference (u_0) and perturbation (u_1) parts are given by [13]

$$u_0(r_{12}, \Omega_1, \Omega_2) = \begin{cases} u(r_{12}, \Omega_1, \Omega_2) - u_{\min}(r_{12}, \Omega_1, \Omega_2) & \text{for } r_{12} < r_{\min}(\Omega_1, \Omega_2), \\ 0 & \text{for } r_{12} > r_{\min}(\Omega_1, \Omega_2), \end{cases} \quad (2)$$

$$u_1(r_{12}, \Omega_1, \Omega_2) = \begin{cases} u_{\min}(r_{12}, \Omega_1, \Omega_2) & \text{for } r_{12} < r_{\min}(\Omega_1, \Omega_2), \\ u(r_{12}, \Omega_1, \Omega_2) & \text{for } r_{12} > r_{\min}(\Omega_1, \Omega_2), \end{cases} \quad (3)$$

where r_{\min} is the distance between the centres of mass of the molecules at which a minimum occurs in the full potential for a given orientation. The value of the potential at r_{\min} is u_{\min} .

The residual part of the Helmholtz free energy A can be expanded in terms of the parameter λ to give

$$A = A_0 + A_1 + A_2 + \dots, \quad (6)$$

where A_0 is the residual Helmholtz energy of the reference system and

$$A_1 = \frac{1}{2} N n \int u_1(r_{12}, \Omega_1, \Omega_2) g_0(r_{12}, \Omega_1, \Omega_2) dr_{12} d\Omega_1 d\Omega_2$$

$$= \langle U_1 \rangle_0, \quad (7)$$

$$A_2 = -(2kT)^{-1} (\langle U_1^2 \rangle_0 - \langle U_1 \rangle_0^2), \quad (8)$$

with

$$U_1 = \sum_{i < j} u_1(i, j) \quad (9)$$

where N is the number of particles, n the number density, k the Boltzmann constant, T the absolute temperature and $g_0(r_{12}, \Omega_1, \Omega_2)$ the pair correlation function of the reference systems, and the angular brackets with subscript 0 indicate canonical averages over the reference system.

In Fischer's theory the λ expansion is truncated at first order, and therefore knowledge of A_0 and g_0 is needed.

$g_0(r_{12}, \Omega_1, \Omega_2)$ is approximated by

$$g_0(r_{12}, \Omega_1, \Omega_2) = \exp \left[- \frac{u_0(r_{12}, \Omega_1, \Omega_2)}{kT} \right] \gamma(r_{12}), \quad (10)$$

where $\gamma(r_{12})$ is the background correlation function of a spherical system at the same density and temperature as the actual system and interacting through a spherical

potential given by $\phi(r)$:

$$\exp \left[-\frac{\phi(r_{12})}{kT} \right] = \left\langle \exp \left[-\frac{u_0(r_{12}, \Omega_1, \Omega_2)}{kT} \right] \right\rangle_g, \quad (11)$$

where the subscript g indicates the geometrical average. $y(r)$ is obtained by solving the OZ equation for a spherical potential:

$$S(r_{12}) = n \int c(r_{13}) [c(r_{23}) + S(r_{23})] dr_{13}, \quad (12)$$

$$S(r_{12}) = h(r_{12}) - c(r_{12}), \quad (13)$$

$$h(r_{12}) = g(r_{12}) - 1, \quad (14)$$

where $c(r_{12})$ is the direct correlation function. An appropriate closure relation must be chosen to solve the OZ equation. Previously [2, 3, 4, 6] PY has always been used. Here we shall use the PY as well as the RHNC closures given by

$$(PY) \quad c(r_{12}) = \left\{ \exp \left[-\frac{\phi(r_{12})}{kT} \right] - 1 \right\} [S(r_{12}) + 1], \quad (15)$$

$$(RHNC) \quad c(r_{12}) = \exp \left[-\frac{\phi(r_{12})}{kT} + S(r_{12}) - B(r_{12}) \right] - 1 - S(r_{12}), \quad (16)$$

where $B(r_{12})$ is the bridge function of a reference system which will be in this work that of hard spheres.

A_0 for the reference potential is found as the Helmholtz free energy of a hard system A_H whose diameter is obtained by setting equal to zero the first-order term of the blip expansion [14]:

$$\int \left[\exp \left(-\frac{u_0}{kT} \right) - \exp \left(-\frac{u_H}{kT} \right) \right] y_0(r_{12}, \Omega_1, \Omega_2) dr_{12} d\Omega_1 d\Omega_2 = 0. \quad (17)$$

As long as y_0 is unknown, it is approximated by [2]:

$$y_0(r_{12}, \Omega_1, \Omega_2) = y(r_{12}). \quad (18)$$

A_H is obtained by integrating one of the equations of state available for hard convex bodies [15]. Since one of the goals of this work is to show the influence on the thermodynamic properties of using different closure relations for obtaining $y(r)$, it is convenient to know the exact values of A_1 and A_0 (or its differential counterpart Z_0) for every state. This can be achieved by simulating the reference system. Z_0 can be evaluated during the run and, eventually, A_0 can be obtained by integrating

$$\frac{A_0^{\text{res}}}{NkT} = \int \frac{(Z_0 - 1)}{n} dn \quad (19)$$

from zero to the desired density. A_1 can be obtained from (7) as the average of the perturbation potential energy on the reference system, and A_2 from its fluctuations according to (8). For site-site potentials the value u_{mn} depends on the relative orientation of the molecules, and this makes the simulation of the reference system rather involved. In fact, no simulation has been carried out for the reference system given by (2) and (3) in the multicentre model potential, as far as we are aware. However, if the value of the potential minimum is independent of the relative

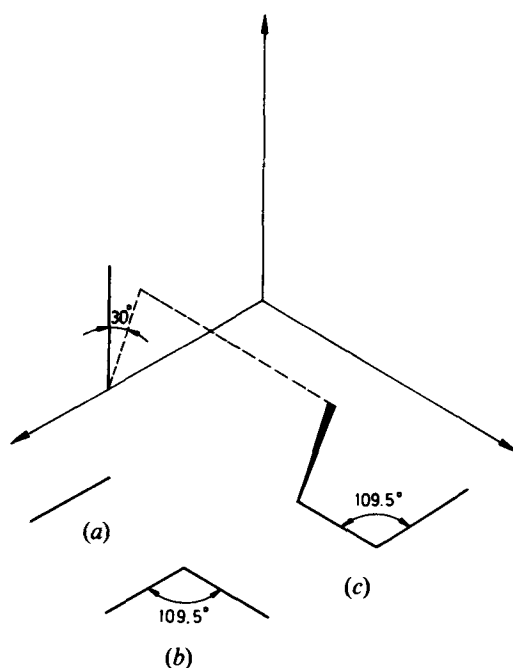


Figure 1. Molecular cores used in this paper for the Kihara potential: (a) linear; (b) angular propane-like; (c) *gauche*⁺ butane-like.

orientation then the simulation of the reference potential becomes much simpler and some examples can be found in the literature [5, 16, 17]. In this work we shall choose the Kihara potential [18]:

$$u = 4\epsilon \left[\left(\frac{\sigma}{\rho} \right)^{12} - \left(\frac{\sigma}{\rho} \right)^6 \right], \quad (20)$$

where ρ is the shortest distance between the molecular cores describing the molecular geometry and ϵ and σ are the potential parameters. The molecular core does not necessarily have to be convex, although this is the most common choice. In the next section we shall describe the method used for the evaluation of $y(r)$ as well as the details of the MC simulations for both the spherical potential $\phi(r)$ and the reference potential u_0 .

3. Computational details

The potential $\phi(r_{12})$ of (11) was obtained for the reference system defined in (2)–(5) specialized to the Kihara potential defined by (20). We have chosen three different kinds of core, which are plotted in figure 1. These are (i) a linear rod, (ii) an angular propane-like model and (iii) a *gauche*⁺ butane model. The linear model was studied for three values of the reduced length $L^* = L/\sigma$, where L is the length of the rod: $L^* = 0.15, 0.6$ and 1.0 . In the propane or butane model $L^* = b/\sigma$ was kept equal to 0.4123 and 0.427 respectively, where b is the carbon–carbon distance. Efficient algorithms for evaluating the shortest distance between rods have been described elsewhere [19, 20]. The geometrical average of (11) was obtained using Conroy's method [21] with 4822 orientations for each value of r_{12} . This method has proved to be accurate for nonlinear molecules [4].

We solved the integral equation for $\phi(r)$ using the Labik–Malijevsky method [22] with $N = 512$ and $\Delta r_{12} = 0.0125\sigma$. The bridge function of hard spheres that is needed in the RHNC approximation was taken from the Labik–Malijevsky parametrization [23, 24]. The diameter of the reference hard sphere in the RHNC approximation, d_{HS} , was obtained according to Lado [25]:

$$\int [g(r) - g^{\text{HS}}(r, d_{\text{HS}})] \frac{dB^{\text{HS}}(r)}{dd_{\text{HS}}} dr = 0. \quad (21)$$

Equation (21) was solved numerically using an iterative procedure with several values of d_{HS} . These trial values were taken to coincide with the grid in r space [26].

We carried out two different kind of simulation. First, we performed MC simulations with the spherical potential $\phi(r)$, (11), as obtained from the reference system of linear, propane and *gauche*⁺ butane models interacting through the Kihara potential. We used 216 spherical particles in a cubic box with periodic boundary conditions. Typically we performed 200 000 moves for equilibration, and averages were obtained after 600 000 additional moves. The acceptance ratio was always kept around 50%.

The second type of simulations were MC simulations of the anisotropic reference potential (2)–(5) of linear rods (see figure 1), interacting through the Kihara potential. We used 216 particles and 420 000 configurations for equilibration and 500 000 configurations for obtaining the averages. A_1 and A_2 were obtained by evaluating all the contributions as far as the half of the box length. When comparisons between theory and simulation are made for A_1 , we integrated (7) only up to half of the box length in order to avoid ambiguities.

4. Results and discussion

The RAM potential as given by (11) is temperature-dependent. Nevertheless, when applied to a reference anisotropic repulsive system, the temperature dependence is weak and it is the molecular shape that mainly determines the shape of the potential. In figure 2 we plot the Boltzmann factor defined by (11) for three linear models. For these models the value at which the Boltzmann factor starts to differ from zero does not depend strongly on the reduced length of the molecules. However, the value at which the RAM potential $\phi(r)$ vanishes does depend on the reduced length, and is given by $2^{1/6}\sigma + L$ for linear molecules. Therefore $\phi(r)$ obviously becomes softer as L^* increases. However, before presenting our main conclusion, let us give the relation between the Boltzmann factor of any pair potential and the second virial coefficient B_2 :

$$f(r_{12}, \Omega_1, \Omega_2) = \exp \left[- \frac{u(r_{12}, \Omega_1, \Omega_2)}{kT} \right] - 1, \quad (22)$$

$$B_2 = - \frac{1}{2} \int \langle f \rangle_{\text{g}} d\mathbf{r}_{12}. \quad (23)$$

From (11), (22) and (23), we can see that B_2 is the same for the reference anisotropic potential u_0 and for the spherical potential $\phi(r)$. Figure 2 along with (11), (22) and (23) illustrate our second conclusion—namely, that B_2 for the reference anisotropic system is an increasing function of the reduced length at a given temperature.

This conclusion can be understood better if one considers that the linear anisotropic reference system has similar properties to a hard spherocylinder (a cylinder with two

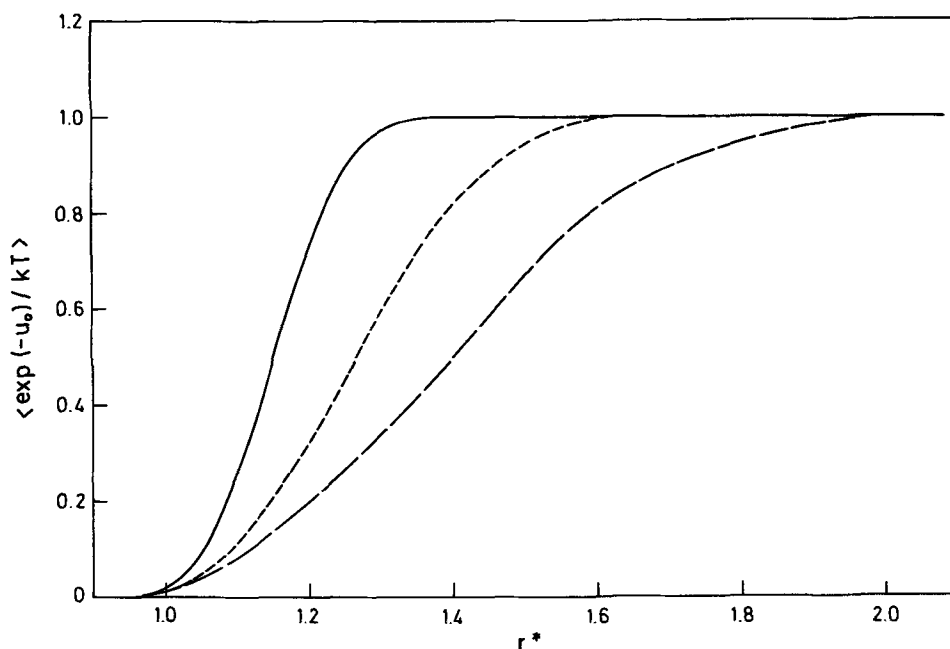


Figure 2. Boltzmann factor of the spherical RAM potential $\phi(r_{12})$ as obtained for linear molecules using the reference Kihara potential (2), (3) at $T^* = 1.0$ and $L^* = 0.3$ (—), 0.6 (---) and 1.0 (—·—).

spherical caps). B_2^H for hard convex bodies is a function only of the non-sphericity parameter α and is given by [15]

$$B_2^H = (1 + 3\alpha)V_m, \quad (24)$$

where V_m is the molecular volume. For hard spherocylinders α is given by

$$\alpha = \frac{(L^* + 2)(L^* + 1)}{3L^* + 2}, \quad (25)$$

$$L^* = L/d, \quad (26)$$

where d is the hard-body diameter. Usually L^* will take very similar values to L if the Barker-Henderson prescription for calculating d is used. From (24)–(26), it follows that B_2^H for hard spherocylinders increases with the reduced length L^* . For hard spherocylinders the distance between the centres of mass at which the unweighted average of the Boltzmann factor vanishes is σ for any value of L^* . Moreover, the first value at which this Boltzmann factor is unity is given by $(1 + L^*)\sigma$. Therefore the range of the spherical potential $\phi(r)$, (11), obtained for hard spherocylinders increases with L^* . This also means that $\phi(r)$ becomes a softer repulsive potential as L^* increases or correspondingly (because of (25)) as α increases. It is therefore reasonable to suppose that B_2 for soft repulsive rods will also be an increasing function of L^* and that $\phi(r)$ will become softer as L^* increases. This can be seen in figure 2.

On the basis of the results obtained for linear cores, we suggest that for anisotropic repulsive potentials (soft or hard) B_2 increases with α and that the spherical RAM $\phi(r)$ becomes softer as α increases (i.e. for hard spheres $\alpha = 1$ and the Boltzmann factor

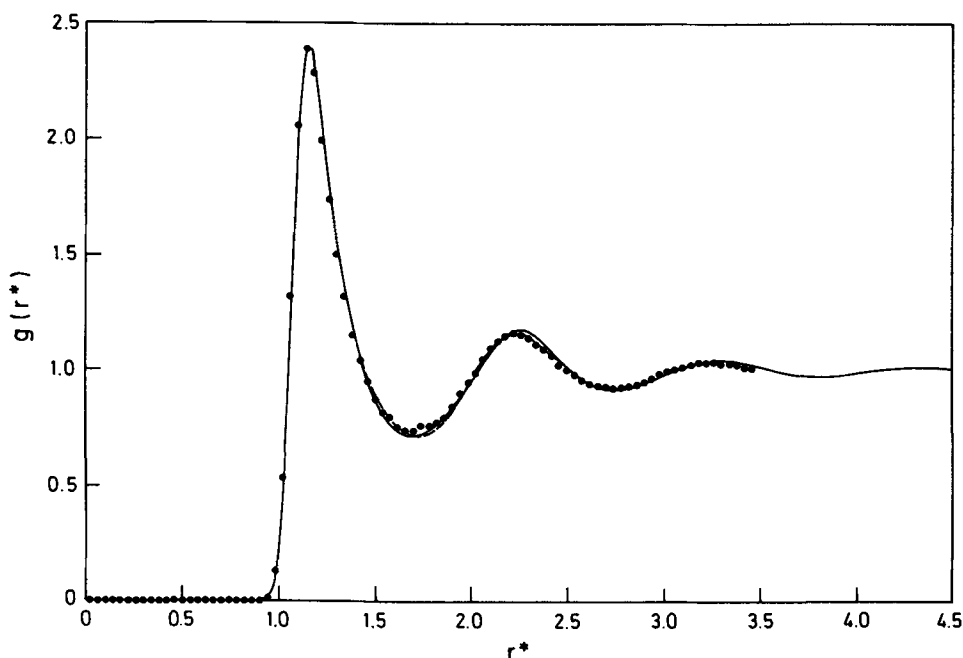


Figure 3. Pair correlation function of a spherical RAM potential $\phi(r_{12})$ for a linear model with $L^* = 0.15$ interacting through the reference Kihara potential (2) and (3) as obtained from MC simulations (●) and from PY (—) and RHNC (---) approximations at $T^* = 1.0$ and $\eta = 0.4$.

becomes a Heaviside step function). In the hard case α can be obtained from geometrical considerations, and for the soft repulsive potential α is obtained from the equivalent hard body.

We carried out MC simulations of some of the spherical RAM potentials corresponding to the Boltzmann factor plotted in figure 2, and solved the OZ integral equation for $\phi(r)$, using the RHNC and PY closure relations. For every model we have simulated two values of the packing fractions defined as

$$\eta = nV(\sigma), \quad (27)$$

where $V(\sigma)$ is the volume of a spherocylinder of diameter σ and length L .

Results are shown in figures 3–5. PY works properly when compared with simulations at low densities for the three studied reduced lengths. At high densities, PY reproduces the MC data for $L^* = 0.15$, but fails for the other two lengths. RHNC compares well with MC results in all cases. The discrepancies between PY and RHNC at high densities can be summarized by saying that PY overestimates the height of the first peak of $g(r)$ and shifts it to the right. Moreover, PY oscillates slightly out of phase with respect to the simulations.

We have also investigated propane and *gauche*⁺ butane simple models. Figure 6 compares the Boltzmann factor of modelled propane with that of a linear model with the same potential range at the same reduced temperature. As they are very different, it is clear that $\phi(r)$ for an angular model has a different shape to $\phi(r)$ for a linear one, even if the range of the potential is the same. In fact, $\phi(r)$ for an angular model is considerably harsher than $\phi(r)$ for a linear model. We also carried out MC simulations and solved the integral equation for the RAM potential of propane and *gauche*⁺

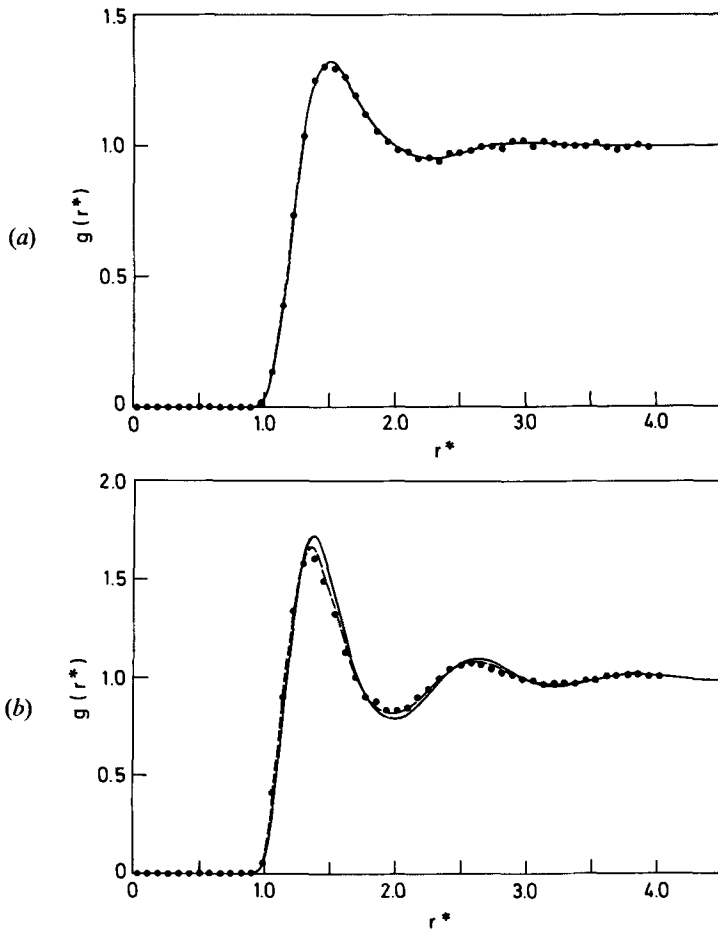


Figure 4. As figure 3, but for $L^* = 0.6$ and $T^* = 1.0$: (a) $\eta = 0.2$; (b) $\eta = 0.4$.

butane (see figure 1). The results are shown in figures 7 and 8. Again, PY fails at high densities, where RHNC still works very well. Furthermore, the discrepancies between PY with MC results exhibit the same features as in the linear case.

Thus it seems that the use of PY in previous work [2, 3, 4, 6] cannot be justified for elongated linear models or for angular ones like propane, especially at high densities. This is an important point because it is at high densities where the perturbation scheme must be applied and RHNC works very well in all the studied cases.

In applying RHNC, the diameter of the equivalent hard sphere is obtained from (22). We have observed that the equivalent hard-sphere diameter d_{HS} increases for a given state with the range of the potential (i.e. with L^*). d_{HS} decreases with temperature and with density for a given L^* .

We shall now see the effect of introducing the accurate $y^{RHNC}(r)$ instead of $y^{PY}(r)$ in the perturbation theory through (7), (10) and (17). In order to calculate the properties of the reference system, we have used the Nezbeda equation of state [27], which has proved to yield very good agreement with MC results for hard spherocylinders of different elongations:

$$\frac{p}{\rho kT} = \frac{1 + (3\alpha - 2)\eta + (\alpha^2 + \alpha - 1)\eta^2 - \alpha(5\alpha - 4)\eta^3}{(1 - \eta)^3}. \quad (28)$$

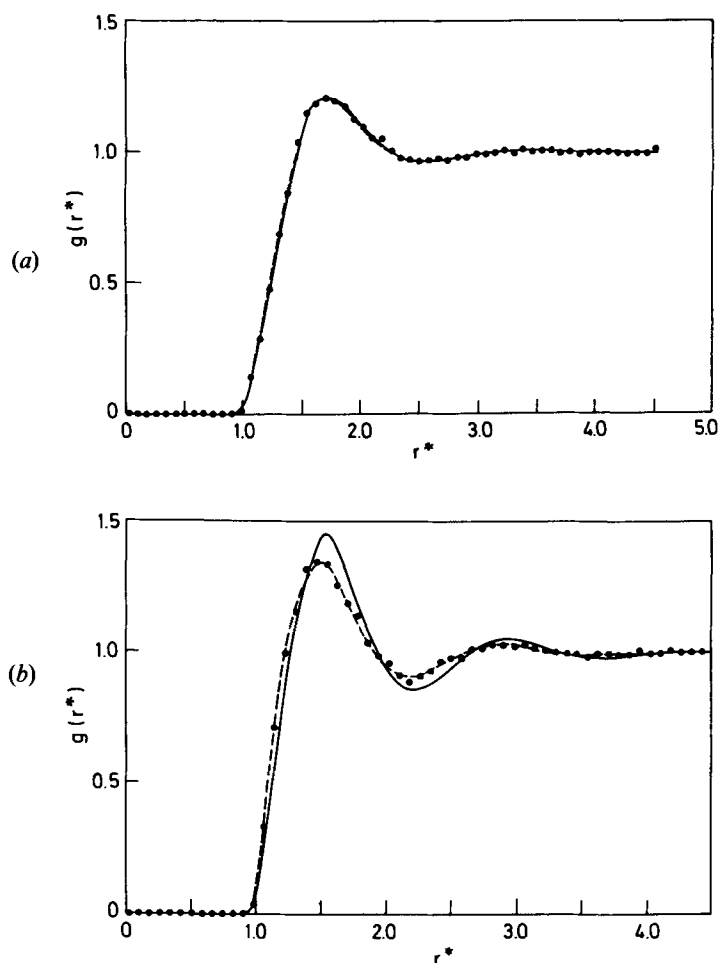


Figure 5. As figure 3, but for $L^* = 1.0$ and $T^* = 1.0$: (a) $\eta = 0.2$; (b) $\eta = 0.4$.

Table 1 shows the effect on the properties of the reference system. The agreement with the MC results is improved when $y^{\text{RHNC}}(r)$ is used instead of $y^{\text{PY}}(r)$. For $L^* = 0.29$ the RHNC results agree with the MC results within the simulation error for all the densities studied, but the PY results do not. For high anisotropies, $L^* = 1$, RHNC results are closer than PY to the simulation data, but they also disagree with MC results at high densities. Deviations at $L^* = 1$ for the predicted and computed compressibility factors cannot be explained just by the fact that we are using an approximate hard-body equation of state. The maximum deviation of the compressibility factor, as given by (24), from the simulation results observed for hard spherocylinders with $L^* = L/d = 1$ at $\eta < 0.5$ amounts to 0.1. Therefore at $\eta < 0.5$ the discrepancies between theoretical and simulated results in table 1 for $L^* = 1$ and $\eta = 0.4$ must arise from neglect of the orientational dependence in $y_0(r_{12}, \Omega_1, \Omega_2)$. RHNC values of the hard-body diameter as obtained from (17) are always smaller than PY ones, which brings the theoretical results closer to the experimental ones. We believe that for $L^* = 1$ and $\eta = 0.4$ only the introduction of an orientational dependence in the background correlation function will yield a smaller hard-body diameter and improve the agreement with MC results. Approximation of

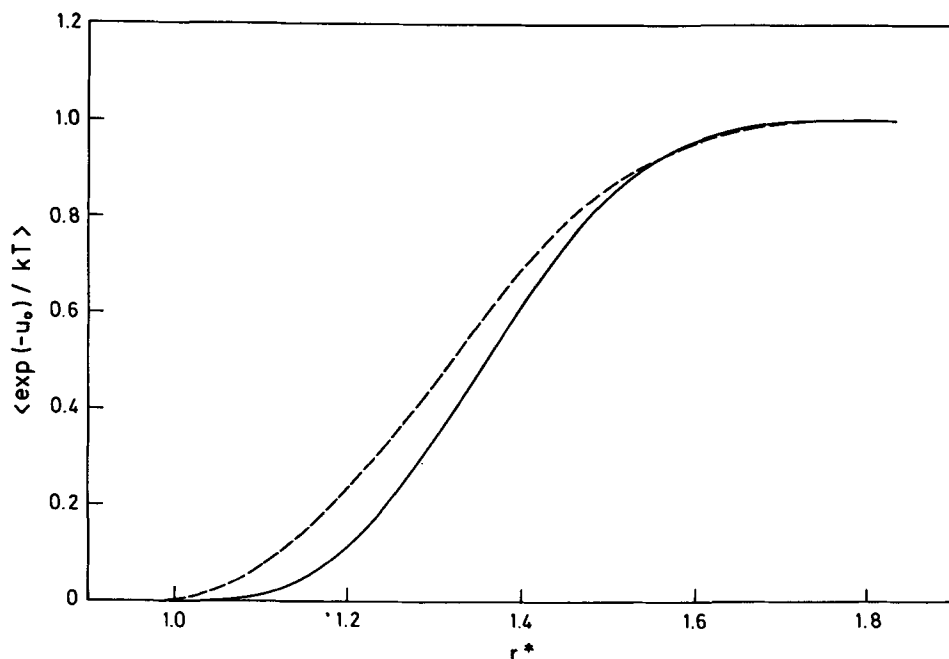


Figure 6. Boltzmann factor of the spherical RAM potential $\phi(r_{12})$ as obtained for a propane-like model ($L^* = 0.412$) using the reference Kihara potential (2), (3) at $T^* = 0.5875$ (—) and for a linear model with the same range of the potential ($L^* = 0.7$) at the same temperature (----).

(10) gives too high values of the hard-body diameter and produces too high values of Z_0 and A_0 at high densities.

The influence on the A_1 term for spherocylinders is shown in table 2, along with simulation results for A_1 and A_2 obtained following (7) and (8) and evaluated during the MC runs of the reference system. The use of $y^{\text{RHNC}}(r)$ instead of $y^{\text{PY}}(r)$ does not improve the agreement with simulations at high densities. Moreover, the results are not very sensitive to the choice of $y(r)$. This is striking because $y^{\text{RHNC}}(r)$ and $y^{\text{PY}}(r)$ are really very different (see figures 3–5). Figure 9 shows the integrand as a function of r_{12} for $y^{\text{RHNC}}(r)$ and $y^{\text{PY}}(r)$. Clearly, some cancellation of errors occurs. The higher peak of $g^{\text{PY}}(r)$ is compensated by the fact that $g^{\text{RHNC}}(r)$ starts to differ from zero for lower r . The conclusion is that the final value of the integral A_1 , (7), is very close in both cases. However, the theoretical values of A_1 are always too high when compared with simulations. These discrepancies must again arise from the approximation in (10). Stronger orientational dependence in $y_0(r_{12}, \Omega_1, \Omega_2)$ is needed in order to improve the agreement between theory and experiment.

At low densities the perturbation scheme does not converge with only the two first terms (A_0 and A_1). This is shown in table 2, where high values of A_2 at low densities are presented. At high densities, the term A_2 is only 1% of A_1 . This fast convergence of the perturbation series was previously suggested [16] by the resemblance between the structure of the reference system and the system interacting through the full potential.

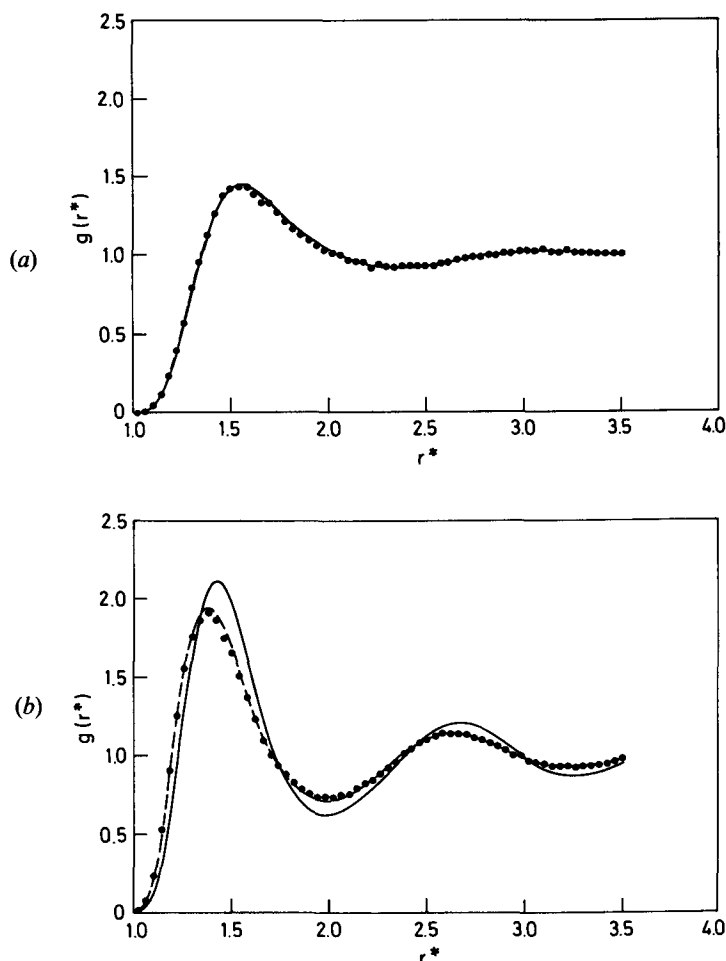


Figure 7. As figure 3, but for a propane-like model ($L^* = 0.4123$) at $T^* = 0.5875$: (a) $n\sigma^3 = 0.2$; (b) $n\sigma^3 = 0.41$.

5. Conclusions

PY closure relation of the OZ equation fails at high densities for soft repulsive spherical potentials when the range of the potential is large. When the range is small, it always works properly. RHNC with Labík–Malijevsky parametrization works very well in all the cases studied, and therefore should replace the PY relation if one is interested in the liquid structure.

The theory reproduces Z_0 and A_1 correctly at low densities, which is easily explained by the fact that the background correlation function loses its orientational dependence at zero density, and so the quality of the approximation (10) improves. Z_0 , A_0 and A_1 as given by Fischer's theory take too high values at high densities, and this deviation is not very dependent on whether $y^{\text{RHNC}}(r)$ or simpler approximations such as $y^{\text{PY}}(r)$ are used. We believe that the theory fails because it neglects the orientational dependence of the function $y_0(r_{12}, \Omega_1, \Omega_2)$, and efforts should be made to remedy this. Some improvements have already been suggested [28, 29], but they are very difficult to implement numerically.

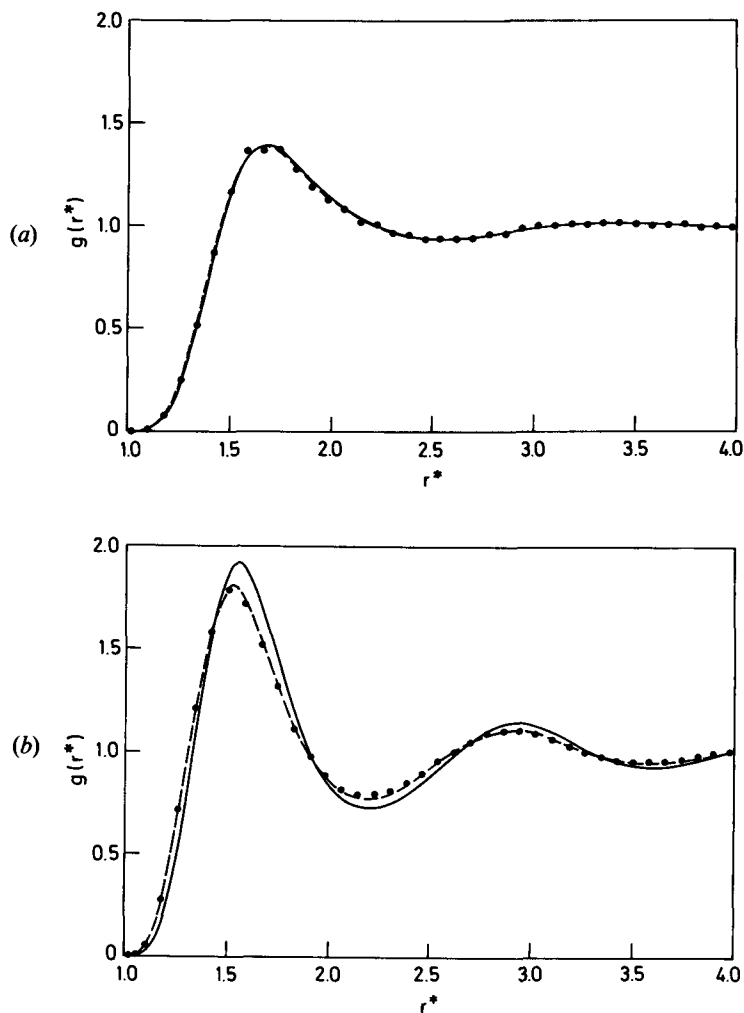


Figure 8. As figure 3, but for a *gauche*⁺ butane-like model ($L^* = 0.427$) at $T^* = 1.0$: (a) $n\sigma^3 = 0.15$; (b) $n\sigma^3 = 0.3$.

Table 1. Compressibility factors Z and blip diameters d of soft repulsive spherocylinders as obtained from simulation and from RHNC and PY approximations.

L^*	T^*	η	Z_0^{MC}	Z_0^{RHNC}	Z_0^{PY}	d^{RHNC}	d^{PY}
0.29	1.075	0.2	2.53 ± 0.03	2.53	2.53	1.01386	1.01391
0.29	1.075	0.3	4.29 ± 0.04	4.24	4.27	1.01317	1.01333
0.29	1.075	0.4	7.48 ± 0.05	7.50	7.60	1.01200	1.01259
1	1	0.2	2.73 ± 0.03	2.77	2.77	1.01640	1.01646
1	1	0.3	4.79 ± 0.04	4.81	4.83	1.01579	1.01606
1	1	0.4	8.54 ± 0.06	8.72	8.79	1.01502	1.01561

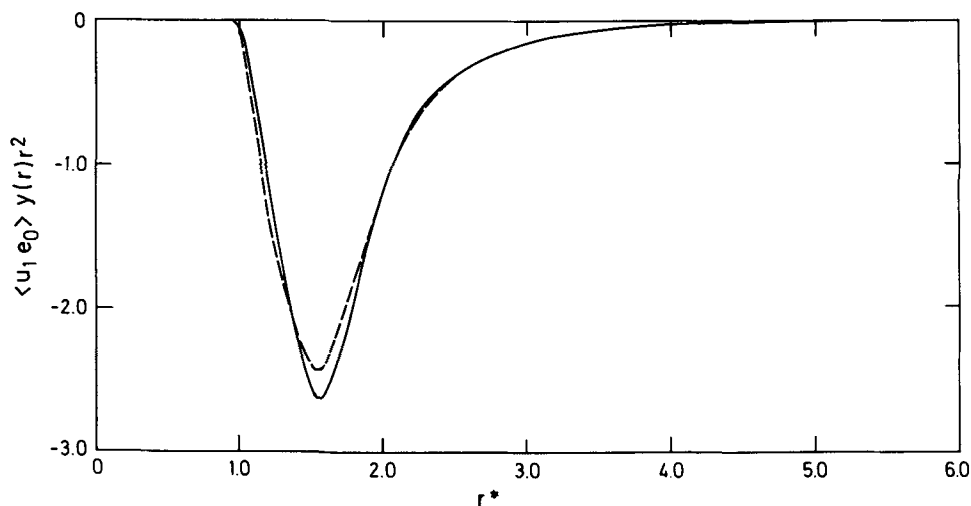


Figure 9. Integrand in (7) as obtained when using $y^{\text{RHNC}}(r_{12})$ (---) and $y^{\text{PY}}(r_{12})$ (—) for a linear model with $L^* = 1.0$, $T^* = 1.0$ and $\eta = 0.4$. e_0 is the Boltzmann factor of the reference potential.

Table 2. First and second perturbation terms for soft spherocylinders. Notation as in table 1.

L^*	T^*	η	A_1^{MC}/NkT	A_1^{RHNC}/NkT	A_1^{PY}/NkT	A_2/NkT
0.29	1.075	0.2	-2.08 ± 0.01	-2.07	-2.07	-0.087
0.29	1.075	0.3	-3.37 ± 0.01	-3.34	-3.34	-0.046
0.29	1.075	0.4	-4.74 ± 0.005	-4.68	-4.69	-0.023
1	1	0.2	-1.96 ± 0.01	-1.92	-1.91	-0.083
1	1	0.3	-3.27 ± 0.01	-3.07	-3.05	-0.070
1	1	0.4	-4.68 ± 0.01	-4.23	-4.23	-0.043

For the linear Kihara models studied, deviations of theoretical Z_0 , A_0 and A_1 from the simulated values show the same features as those found for the Gaussian (GOCE) potential [5]. In both potential models the potential well depth values do not depend on the relative orientation. This suggests that Fischer's theory, when applied to a potential with a non-orientational dependence of the well depth, overpredicts A_0 and A_1 and therefore the pressure of the full potential model.

We have shown that WCA potential division makes the perturbation series converge very rapidly. Nevertheless, an improvement of the approximation given by (10) is necessary.

This work was supported by the Project PB88-0143 of the Direccion General de Investigacion Cientifica y Tecnica. C.V. acknowledges a grant from the Plan de Formacion de Personal Investigador.

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