# Perturbation theory for polyatomic fluids

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A Barker–Henderson like perturbation theory for polyatomic fluids is developed. The molecular interaction forces are assumed to be described by an interaction site model potential and the reference system is a fluid of hard interaction site model molecules.

The theory is used to study the equation of state of nitrogen, the theoretical results being compared with experimental data and with those coming from other theories. The agreement between theory and experiment is as good as that shown by Barker and Henderson theory for monoatomic systems.

## 1. INTRODUCTION

Since Zwanzig [1] published his pioneer work in 1954, several perturbation theories for simple fluids have been proposed. Two of them, that of Barker and Henderson (BH) [2] and that of Weeks, Chandler and Anderson (WCA) [3], proved to give good quantitative results even in the low temperature and high density region. In the last few years some of these theories have been extended to molecular fluids, the reference system being a hard sphere [4–7], a hard convex body [8] or a dumbell fluid [9–10]. Very recently Tildesley [11], using a blip-function technique, has reformulated the WCA theory for molecular systems with an interaction site model (ISM) potential for the intermolecular forces.

In this paper we consider the extension of the BH theory to molecular fluids with ISM intermolecular forces. Here, a system of HISM (hard interaction site model) molecules with hard core diameters depending on temperature but not on density, is used as a reference system. Such a model has been widely used with excellent results in describing structural properties of polyatomic liquids [12–13]. On the other hand, its thermodynamic properties can be satisfactorily computed from semiempirical equations of state recently developed [14–15] and its atomic correlation functions from the RISM theory [16]. Thus the HISM fluid appears as a reasonable good reference system for ISM molecular fluids.

A question arises as to the usefulness nowadays of a BH perturbation theory. Indeed, it is well known this theory is only a first approximation to the WCA theory. However, this theoretical superiority could be questionable in its practical applications. This would be so specially when the actual system under consideration is an ISM fluid in which the unperturbed correlation functions must be obtained from the very expensive computational solution of

RISM equations. While the hard core diameters in the BH approximation are density independent parameters and therefore easily obtained from the intermolecular potential functions, in the WCA case these quantities depend on both density and temperature, and must be evaluated as the numerical solution of a non-simple set of equations. Such circumstances lead to a substantial increase in computational time for the WCA theory with respect to the BH (especially when the properties to be evaluated are macroscopic quantities as equation of state, internal energy, heat capacities, etc.), a computational increase which not always is adequately compensated by an improvement in results [11].

The above considerations have encouraged us to investigate whether the BH theory, the most simple theory which leads to qualitative and quantitative satisfactory results, works also for ISM molecules. The computations are carried out only to first order. This limitation was imposed by our machine computational facilities, since second order corrections greatly increases the computational time.

However, with the exception perhaps of some particular situations, for example the neighbourhood of the critical region, first order results seem adequate to give a correct insight on the success of theory.

In § 2 we write down a first order perturbation expression for the Helmholtz free energy ; the atomic diameters in the reference system depend on temperature but not on density. In § 3, numerical results for the nitrogen fluid are pressented. Conclusions are summarized in § 4.

## 2. First order perturbation expansion for the Helmholtz free energy

The system is a fluid consisting of $N$ molecules in a volume $V$ at a temperature $T$, each molecule being imagined as composed by $m$ interaction sites or ' atoms '. The location of the $\lambda$-' atom ' of molecule $j$ is given by

$$\mathbf{r}_j{}^{(\lambda)} = \mathbf{R}_j + \mathbf{1}_j{}^{(\lambda)}, \tag{1}$$

where $\mathbf{R}_j$ stands for the centre of mass location of molecule $j$ and $\mathbf{1}_j{}^{(\lambda)}$ is the vector joining the centre of mass to the $\lambda$-' atom '. The intermolecular pair potential $\omega(\mathbf{1}, \mathbf{2})$ is assumed to be given by

$$\omega(\mathbf{1}, \mathbf{2}) = \sum u_{\lambda\mu}(r), \quad (\lambda, \mu = 1, 2, ..., m), \tag{2}$$

$u_{\lambda\mu}(r)$ being the intermolecular pair potential between atom $\lambda$ of molecule 1 and atom $\mu$ of molecule 2. Here 1 and 2 represent, respectively, the sets of all coordinates both of position and orientation, for molecules 1 and 2 ; and $r = |\mathbf{r}_1{}^{(\lambda)} - \mathbf{r}_2{}^{(\mu)}|$ is the distance between interaction centres. The system total potential is supposed to be pair additive.

Associated with each interaction $u_{\lambda\mu}(r)$ we define a generalized potential $v_{\lambda\mu}(r)$ by the expression

$$\exp\left[-\beta v_{\lambda\mu}(r)\right] = \left\{ 1 - H\left(d_{\lambda\mu} + \frac{r - d_{\lambda\mu}}{\alpha_{\lambda\mu}} - 1\right) \right\}$$

$$\times \exp\left[-\beta u_{\lambda\mu}\left(d_{\lambda\mu} + \frac{r - d_{\lambda\mu}}{\alpha_{\lambda\mu}}\right)\right] + H\left(d_{\lambda\mu} + \frac{r - d_{\lambda\mu}}{\alpha_{\lambda\mu}} - \sigma_{\lambda\mu}\right)$$

$$+ H(r - \sigma_{\lambda\mu}) \left\{ \exp\left(-\beta\gamma_{\lambda\mu}u_{\lambda\mu}(r)\right) - 1 \right\} \tag{3}$$

where $\beta = 1/kT$, $k$ is the Boltzmann constant, $\sigma_{\lambda\mu}$ the value at which $u_{\lambda\mu}(\sigma_{\lambda\mu}) = 0$ and $H(x)$ the step function defined by

$$H(x) = 0, \quad x < 0, \qquad H(x) = 1, \quad x > 0.$$

Finally, $\alpha_{\lambda\mu}$ and $\gamma_{\lambda\mu}$ are the perturbation parameters modifying the original interatomic potentials. If $\alpha = \gamma = 1$ the generalized potential reduces to the original one. If $\alpha = \gamma = 0$ for any $\alpha$, $\mu$, then $v_{\lambda\mu}(r)$ becomes a HISM potential, and the system a fluid of fused hard spheres with diameter $d_{\gamma\gamma}$ ($\gamma = 1, \ldots, m$).

Following Barker and Henderson [2] we expand the Helmholtz free energy $A$ in a Taylor double series around the $2m^2$-dimensional point $\alpha_{\lambda\mu} = \gamma_{\lambda\mu} = 0$, thus using the HISM system as reference. This yields

$$A = A_0 + \sum \frac{\partial A}{\partial \alpha_{\lambda\mu}}\bigg|_0 + \sum \frac{\partial A}{\partial \gamma_{\lambda\mu}}\bigg|_0 + \text{higher order terms,} \tag{5}$$

where $A_0$ is the Helmholtz free energy of the reference system and the subscript 0 indicates that the derivatives are evaluated at zero values of the perturbation parameters. The derivatives in (5) are related to the configurational partition function.

$$Q_N = \int \ldots \int \exp[-\beta U_N]\, d1\, d2 \ldots dN \tag{6}$$

by

$$\frac{\partial A}{\partial \xi} = -kT \frac{\partial \ln Q_N}{\partial \xi} \quad (\xi = \alpha_{\lambda\mu}, \gamma_{\lambda\mu}), \tag{7}$$

so that from (6)

$$\frac{\partial A}{\partial \xi} = -\tfrac{1}{2}kT \int\int \exp[\beta v_{\lambda\mu}(r)] \frac{\partial}{\partial \xi}\{\exp[-\beta v_{\lambda\mu}(r)]\} \frac{N(N-1)}{Q_N}\int \ldots \int$$

$$\times \exp(-\beta U_N) \cdot \delta(\mathbf{r}_1^{(\lambda)} - \mathbf{r}') \cdot \delta(\mathbf{r}_2^{(\mu)} - \mathbf{r}'') \cdot d1 \ldots d\mathbf{N}\}$$

$$\times d\mathbf{r}' \cdot d\mathbf{r}'' = -\tfrac{1}{2}kT\rho^2 \int\int \frac{\partial}{\partial \xi}\{\exp[-\beta v_{\lambda\mu}(r)]\}$$

$$\times \exp[\beta v_{\lambda\mu}(r)]g_{\lambda\mu}(r)\, d\mathbf{r}'\, d\mathbf{r}''. \tag{8}$$

Here $g_{\lambda\mu}(r)$ is the atomic pair correlation function for a system with interatomic interactions $v_{\lambda\mu}(r)$, $\delta(\mathbf{r})$ is the Dirac delta and $\rho = N/V$ the number density.

Making $\alpha_{\lambda\mu}$ and $\gamma_{\lambda\mu}$ equal to zero in (8) and following standard procedures one obtains

$$\frac{\partial A}{\partial \alpha_{\lambda\mu}}\bigg|_0 = -2\pi NkT\rho g_{\lambda\mu}{}^0(d_{\lambda\mu})\, d_{\lambda\mu}{}^2 \left[ d_{\lambda\mu} - \int_0^{\sigma_{\lambda\mu}} \{1 - \exp[-\beta u_{\lambda\mu}(z)]\} \right] dz, \tag{9}$$

$$\frac{\partial A}{\partial \gamma_{\lambda\mu}}\bigg|_0 = 2\pi N\rho \int_{\sigma_{\lambda\mu}}^{\infty} u_{\lambda\mu}(r)g_{\lambda\mu}{}^0(r)r^2\, dr, \tag{10}$$

where the $g_{\lambda\mu}{}^0(r)$ are the atomic pair correlation functions for the reference

system, which, as mentioned above, is a fluid of HISM molecules. Further, we chose $d_{\lambda\mu}$ so that [2],

$$d_{\lambda\mu} = \int_0^{\sigma_{\lambda\mu}} \{1 - \exp\left[-\beta u_{\lambda\mu}(z)\right]\} \, dz. \tag{11}$$

With this choice the right-hand side in (9) vanishes. Then, introducing (10) into (5), one obtains for $A$,

$$A = A_0 + 2\pi N\rho \sum_{\lambda,\,\mu} \int_{\sigma_{\lambda\mu}}^{\infty} u_{\lambda\mu}(r) g_{\lambda\mu}{}^0(r) r^2 \, dr + \text{higher order terms.} \tag{12}$$

Formally this expression is similar to that of Barker and Henderson. Moreover, for $m = 1$, it yields exactly those authors' relationships. Therefore our theory includes theirs as a particular case. Consequently, the study of a polyatomic molecular system can be reduced to that of simple interactions among the 'atoms' forming the molecules. Note that the temperature effect is taken into account through the atomic diameters of the HISM molecules. These do not depend, as in other theories [3], on the density, and thus considerable computational time is saved. This is an important fact if one recognizes that the atom–atom radial correlation functions must be calculated from the RISM equations which are intrinsically more involved than the calculation of the radial correlation function for hard spheres.

## 3. EQUATION OF STATE FOR LIQUID NITROGEN

In this section we use the perturbation theory just outlined to investigate the $N_2$ equation of state in its whole density range. The molecules are depicted as rigid diatomics having two interaction sites separated by a distance $L$. The site–site interactions are assumed to be represented by a Lennard-Jones potential

$$u(r) = 4\epsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \tag{13}$$

with the Cheung and Powles parameters [17] $\epsilon/k = 37\cdot3$ K, $\sigma = 3\cdot287$ Å and $L = 1\cdot09$ Å.

The reference system is a fluid which consists of $N$ homonuclear rigid diatomics (dumbells) made up of two fused hard spheres with a hard core diameter $d$ given by (11). Unfortunately, up to now, no rigorous theory is available for such a system. However, within the last few years successful approximations have been proposed both for the atomic pair correlation functions and for the equation of state.

Of the various analytical approximations recently developed for the equation of state of non-spherical hard particles two of them could be successfully applied to our reference system. They are Boublik's equation [20] for hard convex bodies (HCB) and Nezbeda's equation [14] for dumbells (DB). The former was initially proposed for convex bodies but can also be applied to dumbells. This is so due to the similarity between these and spherocylinders whose behaviour is best described by the HCB equation of state. Comparison of calculated values for dumbells obtained from these two equations with pseudoexperimental data have shown quite a good agreement in the case of Boublik's HCB equation
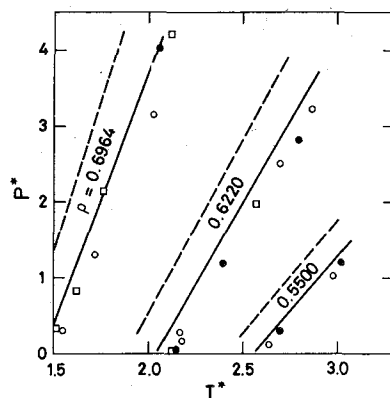
Figure 1. Reduced pressure as a function of reduced temperature at densities $\rho\sigma_{xx}^3 = 0.5500$, $0.6220$ and $0.6964$. The full (———) and dash (- - - -) lines are theoretical results obtained, respectively, with the equations of state of Boublik and Nezbeda for the unperturbed system. The black circles (●) are experimental values and (○), (□) represent molecular dynamic data of Cheung and Powles and Barojas *et al.* respectively.

[15]. However, the results are less satisfactory for Nezbeda's DB-equation, for which the deviation from simulation experiments might be as high as 15 per cent for the highest density and non-sphericity. Furthermore, when both equations are used as the unperturbed part in our perturbation theory (see below), the best results again are those obtained with the HCB equation

$$p/\rho kT = [1 + (3\alpha - 2)y + (3\alpha^2 - 3\alpha + 1)y^2 - \alpha^2 y^3]/(1 - y)^3, \tag{14}$$

which will be used in all our calculations except those in figure 1 where the Nezbeda approximation has also been considered. In (14) $y$ is the packing fraction and for dumbells

$$\alpha = (1 + L^*) \cdot (2 + L^*)/(2 + 3L^* - L^{*3}), \quad L^* = L/d. \tag{15}$$

For homonuclear diatomics all of the atomic correlation functions, $g_{\lambda\mu}^0$, are the same ; we call them $g_{xx}^0(r)$. These were obtained from Chandler and Andersen's RISM equations [16]. We have solved numerically these equations following the computational method proposed by Lowden and Chandler [12]. The integral in

$$h_{\lambda\mu}(r) = (2\pi)^{-3} \int \hat{h}_{\lambda\mu}(k)\exp(-i\mathbf{kr}) \, d\mathbf{k} \tag{16}$$

where $\hat{h}_{\lambda\mu}(k)$ is the Fourier transform of the total correlation function $h_{\lambda\mu}(r)$, has been evaluated by Filon's method [21]. To improve its convergence a 'window' function [22], $\omega_f(k) = \sin(\pi k/k_{max})/(\pi k/k_{max})$, has been used. Here $k_{max}$ is the integration upper cut-off. The integration interval was $\Delta k \simeq 0.1$ Å$^{-1}$ with $k_{max} \simeq 40$ Å$^{-1}$.

For a fluid of homonuclear diatomic molecules equation (12) becomes

$$A = A_0 + 8\pi N\rho \int_{\sigma_{xx}}^{\infty} u_{xx}(r)g_{xx}{}^0(r)r^2\, dr + \text{higher order terms} \qquad (17)$$

from which we get for the pressure the first order equation

$$p = p_0 + 8\pi\rho^2 \left[ \int_{\sigma_{xx}}^{\infty} u_{xx}(r)g_{xx}{}^0(r)r^2\, dr + \rho \int_{\sigma_{xx}}^{\infty} u_{xx}(r)[\partial g_{xx}{}^0(r)/\partial\rho]r^2\, dr \right], \qquad (18)$$

where $p_0$ is the reference system pressure. By using RISM equations we have put $\partial g_{xx}{}^0/\partial\rho$ in terms of the derivatives $\partial a_i/\partial\rho$ ($i = 1, \ldots, 4$), $a_1, \ldots, a_4$ being the coefficients in the expansion

$$c(r) = \sum_i a_i[(r/d) - 1]^{i-1}, \quad r < d \qquad (19)$$

for the atomic direct correlation function. The quantities $\partial a_i/\partial\rho$ were obtained from the coupled sets of algebraic equations

$$\left. \begin{array}{l} \partial I_{\mathrm{RISM}}/\partial a_i = 0, \\[2mm] \dfrac{\partial}{\partial\rho}\,[\partial I_{\mathrm{RISM}}/\partial a_i] = 0, \end{array} \right\} \quad (i = 1, \ldots, 4), \qquad (20)$$

where the first set consists of the derivatives written in the form of equation (10) in reference [23] and the second contains the density derivatives of the first set.

Integration of (18) was carried out numerically at intervals of $\Delta r = 0\cdot 0125$ and was cut off at $r = 3\cdot 50\,\sigma$. Contribution from higher distances were evaluated assuming $g_{xx}{}^0(r) = 1$ and $dg_{xx}{}^0(r)/d\rho = 0$.
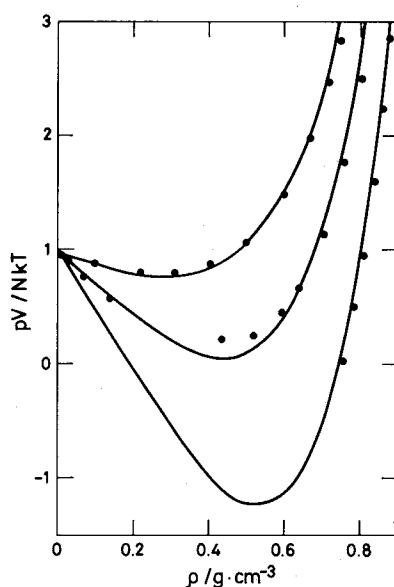


Figure 2.   Compressibility factor versus density.   The lines are the isotherms of 88, 126 and 190 K, and the points are experimental data.

Numerical calculations were planned so that the accuracy of the theory could be established by comparison with (*a*) model simulation data, (*b*) experiment, and (*c*) other theoretical approximations. The results are given on figures 1 to 5.

A comparison at different reduced densities, $\rho^* = \rho \sigma_{xx}^3 = 0.5500$, 0.6220 and 0.6964, is made on figure 1, between our theoretical results and the molecular
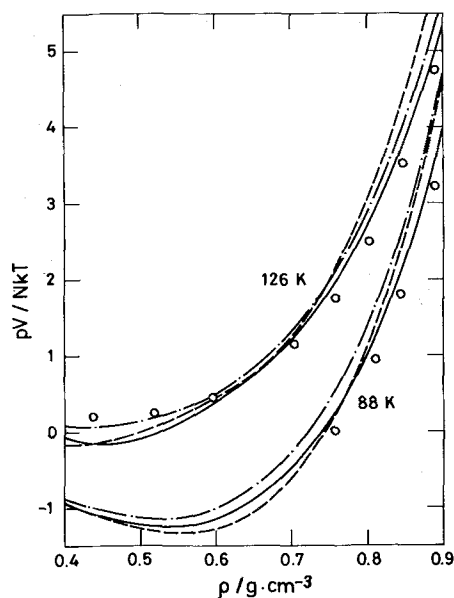


Figure 3. This figure compares the compressibility factor of $N_2$ obtained in the present work (————) and those given by the perturbation theories of Boublik for spherocylinders (- - - - -) and Barker and Henderson with a Lennard-Jones potential for molecular interactions (—·—·). The circles are experimental data.
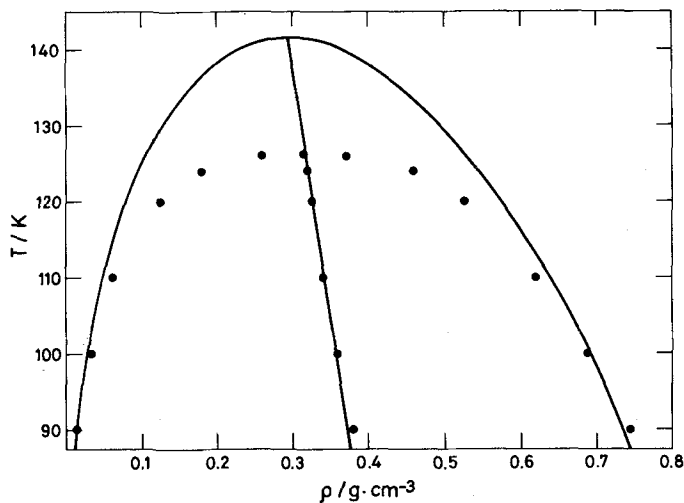


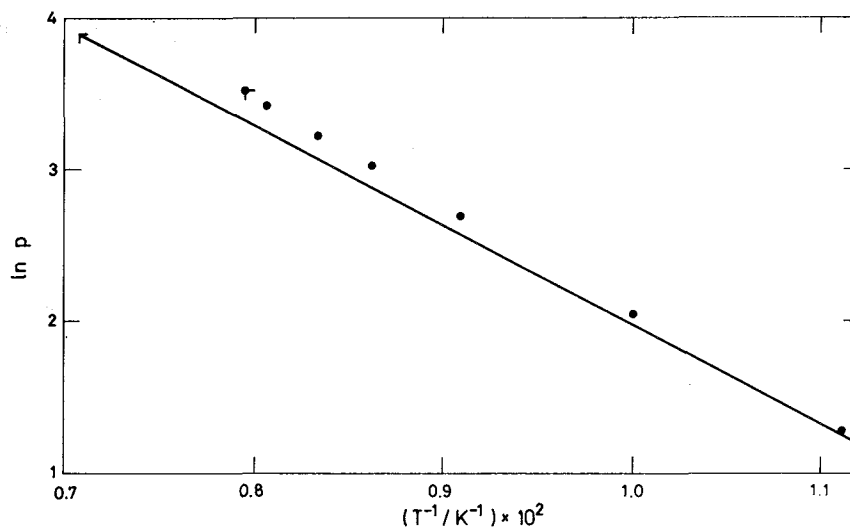Figure 4. Liquid–vapour equilibrium curve. The points are experimental values.

Figure 5.   Theoretical (———) and experimental ( ● ) vapour pressure as a function of $1/T$.
The angles denote the critical points.

dynamics (MD) data from Cheung and Powles [17], and Barojas *et al.* [18]. The Boublik HCB and Nezbeda DB equation of state mentioned above are used here for the unperturbed state. It is apparent that agreement between theoretical and pseudoexperimental data is good if one uses the HCB equation of Boublik. A less satisfactory agreement exists with Nezbeda's DB approximation. In this case the departures from the machine calculations are rather large, in particular at high densities.

The compressibility factor at temperatures of 88, 126 and 190 K is plotted on figure 2 as a function of density ; the experimental data are the smoothed values of Jacobsen and Stewart [24]. The agreement is excellent at high densities. Slight deviations are noticeable at low densities and they become appreciable, as expected, in the critical region. In figure 3 a comparison is made between the results we obtain for 88 and 126 K in the region comprising medium and high densities with those from Barker and Henderson's first order perturbation (BH1) theory and from Boublik's theory for rod-like molecules [8]. Since the non-sphericity of the nitrogen molecule is not very pronounced it is to be expected that the results will be of comparable accuracy for both theories. This expectations is fulfilled at intermediate densities when differences between the various theories are small. This is not the case at high densities where our theory provides results more in agreement with the experimental ones than do either the BH1 theory or Boublik's. This suggests that divergences in these theories at low density might be due to considering only a first order perturbation, disregarding higher order contributions. At high densities atom–atom potentials appears to be a better description for the intermolecular forces than spherical potentials are.

Calculated values for the critical quantities seem to confirm this picture. The table contains our results and those from BH1 theory and BH2 theory (Barker–Henderson second order perturbation theory). As it is seen, theories using only one perturbation term give similar results. On the other hand, the

Critical constants.

|  | Exptl. | BH2 | BH1 | This work |
|---|---|---|---|---|
| T/K | 126·2 | 134 | 139·6 | 141·6 |
| p/bar | 34·0 | 44 | 52·2 | 49·7 |
| p/g.cm⁻³ | 0·314 | 0·295 | 0·295 | 0·295 |

differences between values obtained from BH1 and BH2 and the agreement of the latter with pseudoexperimental data (see table 1 of [2]) show that in order to study the critical region the second term of the expansion is needed.

The densities and pressures of the liquid–gas curve were calculated by solving numerically the simultaneous equations

$$p_1 = p_g,$$
$$(A + pV)_l = (A + pV)_g. \qquad (21)$$

Figures 4 and 5 show the densities of the coexisting phases and the dependence of the vapour pressure with temperature. Our theory gives a good account of the coexistence line and vapour pressures at low temperatures but gives low estimates for the equilibrium pressure at temperatures near the critical point. Consequently it is clear why the theoretical critical temperature and pressure are high whereas the critical density is acceptable.

## 4. Conclusions

Application of our theory to a quasispherical molecule has brought to the fore some of its good and not so good points. On the one hand a comparison with MD results brands our theory as satisfactory and reassures us that for high densities—conditions under which simulation data were obtained—our development and its application are valid and useful. On the other hand, departures from the expected values observed in the critical region could be explained in terms of the first and second order perturbation in the original Barker and Henderson theory. Consequently one may safely state that our theory applied to polyatomic systems leads to results as good as Barker–Henderson theory does for monoatomics. This is reinforced by the probable fact that atom–atom potentials would give a better force description for quasispherical interacting molecules than a spherically symmetry potential. Results obtained by MD on molecules having a strong quadrupole moment such as $Br_2$ [19] are very satisfactory and therefore we expect the same from our theory. Finally we would like to point out that, in spite of the approximations involved, the pair correlation function obtained from the RISM equations does not seem to introduce appreciable errors in the theory. Likely the reason for it is that the lower limit $\sigma_{xx}$ of the integration over $g_{xx}{}^0(r)$ remains outside the contact region in which the results of the RISM equations are poorer. These contributions are included in the equation of state for the dumbell molecules, where Boublik's equation is a good approximation.

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