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Thermophysical Properties of Fluids: From Realistic to Simple Models and Their Applications[1]

I. Nezbeda[2–4] and L. Vlček[2]

Recent systematic and extensive computer simulations on realistic models of polar and associating fluids have shown that the long-range interactions have only marginal effect on the properties of these fluids. This finding leads to short-range models upon which a perturbation theory may be developed. An attempt to develop a methodology to construct such models (called primitive models) directly from the parent realistic models without resorting to (or reducing at least to minimum) *ad hoc* adjustments is presented and exemplified by constructing models of methanol, water, and carbon dioxide. It is shown that the structural properties of the primitive model fluids obtained by means of purely theoretical considerations compare well with those of their realistic counterparts.

KEY WORDS: associating fluids; perturbation expansion; primitive models; RAM theory; structure of fluids.

1. INTRODUCTION

Simple theoretical models of matter have contributed a good deal to the advancement of our understanding of nature and to the development of elaborate theories, with the ultimate goal of quantitative understanding of the properties of real fluids. Simple models result usually from intuitive speculations and typical examples are, e.g., the model of hard spheres

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[2] E. Hála Laboratory of Thermodynamics, Institute of Chemical Process Fundamentals, Academy of Sciences, 165 02 Prague 6, Czech Republic.

[3] Physics Department, J. E. Purkyně University, 496 00 Ústí n. Lab, Czech Republic

[4] To whom correspondence should be addressed. E-mail: IvoNez@ICPF.CAS.CZ

used already by van der Waals near the end of the 19th century, or the simple models mimicking association introduced in the beginning of the 1980s [1–3]. Although the role and usefulness of these models cannot be questioned, their serious disadvantage is that they defy further systematic refinement.

In the statistical mechanics of fluids one can arrive at simple models by a series of well defined approximations to the originally complex formulation of the problem. These approximations are based on the known effect of various parts of the given total Hamiltonian on the properties of fluids, e.g., the well known fact that the structure of nonpolar fluids is determined primarily by the short-range repulsive part of the intermolecular interaction. Recent findings on the effect of the long-range forces on the properties of polar and associating fluids [4–7] have made it legitimate to write various properties of these fluids in a perturbed form with the leading reference term given by a suitably chosen short-range reference (SRR) [8, 9]. To implement this scheme, the properties of the SRR fluid must be available in an analytic form and this is the point where simple models enter the scheme; it is convenient (and likely the only feasible way) to estimate the properties of the SRR fluid by mapping them onto the properties of an appropriate simple model (called primitive model); cf. a similar scheme for simple fluids: Lennard–Jones fluid → soft repulsive SRR fluid → hard-sphere fluid. To demonstrate feasibility of this approach we may mention the recently derived molecular-based equation of state for water [10].

To extend the above approach to associating and strong polar fluids and to put it on a sound footing, simple models (referred to as ‘primitive’ models, PM, in the same spirit as primitive models of electrolytes) descending directly from realistic models (called parent models) must be developed first. The requirements imposed on the PM are (i) that they reproduce the structure of the parent model as faithfully as possible, and (ii) that they satisfy certain conditions to make the application of the thermodynamic perturbation theory (TPT) of Wertheim [11] possible. Moreover, if the PM to be developed is to correspond to reality, there should be (at least an approximate) direct connection between its parameters and those of the parent model.

The goal of this paper is to make an attempt to derive PMs from ‘first principles’, i.e., from the parent realistic potential without resorting to *ad hoc* adjustments of the parameters to the known experimental data. The obtained agreement/disagreement with the structural properties of the parent model may then indicate to what extent such simple models may be able to serve the required purposes and will justify further potential efforts to develop a general and refined methodology to construct the PMs.

2. THEORETICAL BACKGROUND

A molecular approach starts with the choice of an intermolecular potential model. There seems to be now a general consensus concerning the functional form of realistic pair potentials $u(1,2)$. It is assumed that the molecule contains interaction sites which are the seat of two types of interactions: (1) non-electrostatic interaction generating a strong repulsion at short separations and a weak attraction at medium separations, and (2) long-range Coulombic charge–charge interaction. A common realistic pair potential has thus the form,

$$\begin{aligned} u(1,2) &= u_{\text{non-el}}(1,2) + u_{\text{Coul}}(1,2) \\ &= \sum_{i\in\{1\}} \sum_{j\in\{2\}} \left\{ u_{\text{non-el}}\left(|\mathbf{r}_1^{(i)} - \mathbf{r}_2^{(j)}|\right) + \frac{q_1^{(i)} q_2^{(j)}}{|\mathbf{r}_1^{(i)} - \mathbf{r}_2^{(j)}|} \right\}, \end{aligned} \tag{1}$$

where the LJ potential,

$$u_{\text{LJ}}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right], \tag{2}$$

is usually chosen for the non-electrostatic interaction. In Eq. (1) (1, 2) stands for the separation and orientation of molecules 1 and 2, $\mathbf{r}_k^{(i)}$ is the position vector of site i on molecule k, $r_{ij} = |\mathbf{r}_1^{(i)} - \mathbf{r}_2^{(j)}|$, and $q_k^{(i)}$ is the partial charge of site i of molecule k.

Equation (1) is evidently too complex to be amenable to a straightforward theoretical treatment. Consequently, we have to resort to a perturbation expansion. Given an intermolecular pair potential u, the perturbation expansion method proceeds as follows [12, 13]: (1) u is decomposed into a reference part and a perturbation part, $u = u_{\text{ref}} + u_{\text{pert}}$; (2) the Helmholtz free energy, A, is expanded in powers of (βu_{pert}): $A = A_{\text{ref}} + \beta \Delta A_1(\{u_{\text{pert}}\}) + \cdots$, where β is the inverse temperature, $\beta = 1/(k_B T)$, k_B is Boltzmann's constant, and A_{ref} is the Helmholtz free energy of the reference fluid; and (3) after the correction terms are evaluated, any thermodynamic property X is derived in the form $X = X_{\text{ref}} + \Delta X_1 + \cdots$.

It was well established a long time ago that the perturbation expansion is fast converging if the *structure* of the reference and considered fluids are nearly identical (very similar). For nonpolar fluids this condition leads to a reference defined by short-range *repulsive* interactions [12, 14]. For polar and associating fluids this problem seems to have been resolved over the last decade. It has been found that the structure of polar and associating fluids, defined in terms of the site-site correlation functions, is also determined predominantly by short-range interactions which however may be, unlike the case of nonpolar fluids, both repulsive and attractive [5–7]. In other words, the reference system must incorporate *all short-range forces* of the total potential $u(1,2)$ and may be obtained, e.g., by switching off smoothly the long-range part of the Coulombic interactions [8],

$$u_{\text{ref}}(1,2) = u(1,2) - S(R_{12};\, R',\, R'')u_{\text{Coul}}(1,2), \tag{3}$$

where $S(R_{12};\, R', R'')$ is a switch function which equals zero for $R_{12} < R'$ and unity for $R_{12} > R''$, and R_{12} is the intermolecular separation. It is appropriate to remark that the way of switching is only a technical problem and that its actual implementation is immaterial.

To accomplish the above perturbation scheme, both the thermodynamic and structural properties of the reference fluid, Eq. (3), must be available, preferably in a closed analytic form. This problem may be solved by another perturbation expansion which results in a mapping of the properties of the reference onto those of an appropriate primitive model (cf. a similar procedure to estimate the properties of a soft-sphere reference for Lennard–Jonesium by those of hard spheres). The next step of the above general perturbation scheme is thus the construction of the primitive model.

3. CONSTRUCTION OF PRIMITIVE MODELS

The above short-range potential model, Eq. (3), serves as the parent model for a PM to be constructed. Maintaining the direct link between the parent and PMs, geometry of the PM must copy that of its realistic parent model, it means the arrangement of the sites and their separation. To approximate the force field of the parent model at short intermolecular separations, the following approach is adopted:

1. The molecule is represented by a fused-hard-sphere (FHS) body resulting from appropriate non-electrostatic repulsive interactions, u_{ij}^{eff}. Specifically, the hybrid Barker–Henderson method is used to determine the HS diameters d_{ij}: potential u_{ij}^{eff} is decomposed at its minimum $R_{ij}^{\min}$ into the repulsive part, u^{rep}, and attractive part; the repulsive part is shifted (see Fig. 1), and the hard core diameter is computed from

$$d_{ij} = \int_0^{R_{ij}^{\min}} \{1 - \exp[-u_{ij}^{\text{rep}}(r)/k_{\text{B}}T]\}dr. \tag{4}$$

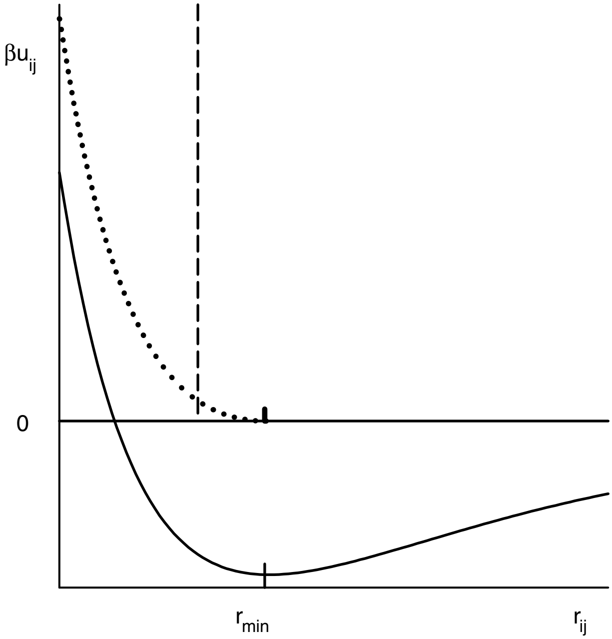

Fig. 1. Construction of the effective site-site repulsive interaction and an effective hard core. The solid line is a sphericalized site-site potential, dotted line is its shifted repulsive part, and the dashed line is the hard-sphere potential obtained from Eq. (4).

2. The Coulombic interactions are represented as follows:
   (i) The repulsive interaction between the like charges is represented by a hard-sphere interaction, u_{HS},

$$u_{\mathrm{HS}}(r_{12};\sigma)=\begin{cases}+\infty & \text{for } r_{12}<\sigma,\\ 0 & \text{for } r_{12}>\sigma,\end{cases} \tag{5}$$

   and

   (ii) the attractive interaction between the unlike charges is represented by a square-well interaction u_{SW}:

$$u_{\mathrm{SW}}(r_{12};\lambda)=\begin{cases}-\epsilon_{\mathrm{HB}} & \text{for } r_{12}<\lambda,\\ 0 & \text{for } r_{12}>\lambda.\end{cases} \tag{6}$$

Denoting the charged sites as O and H, and the remaining sites as S, the PM assumes then the following functional form:

$$
\begin{aligned}
u_{\mathrm{PM}}(1,2) = & \sum_{\substack{i,j\in\{\mathrm{S,O,H}\}\\ \{i,j\}\neq\{\mathrm{O,H}\}}} u_{\mathrm{HS}}(|\mathbf{r}_i^{(1)}-\mathbf{r}_j^{(2)}|;d_{ij}) \\
& + \sum_{\substack{\{i,j\}=\{\mathrm{O,O}\}\\ \{i,j\}=\{\mathrm{H,H}\}}} u_{\mathrm{HS}}(|\mathbf{r}_i^{(1)}-\mathbf{r}_j^{(2)}|;d_{ij}) \\
& + \sum_{\substack{i,j\in=\{\mathrm{O,H}\}\\ i\neq j}} u_{\mathrm{SW}}(|\mathbf{r}_i^{(1)}-\mathbf{r}_j^{(2)}|;\lambda).
\end{aligned} \tag{7}
$$

The first term defines the FHS core, and the second term adds additional hard-core interaction originating in the repulsion between the like charges. These two terms together define the pseudo-hard body [15]. Finally, the last term represents the attractive interaction (H-bonding) between the like charges. The goal of the theoretical modeling is to find the optimized values of the potential parameters, d_{ij}, λ, and ϵ_{HB} without resorting to *ad hoc* adjustments or reducing at least to minimum the advance knowledge of the properties of the parent model.

4. RESULTS AND DISCUSSION

In this paper we exemplify the above outlined method by constructing the PM for two associating fluids, methanol and water, and one (quadru) polar fluid, carbon dioxide, using the following realistic potentials: Optimized Potential for Liquid Simulation (OPLS) model of Jorgensen for methanol [16], Simple Point Charge (SPC) potential for water [17], and for carbon dioxide the potential used by Harris and Young (referred to as EPM2 potential) [18]. Geometry of these three molecules is depicted in Fig. 2 along with a schematic sketch of the corresponding FHS cores; for the potential parameters and other details we refer the reader to the original papers.

To get the parameters of the hard-core repulsions, one might use directly the repulsive parts of the respective LJ site-site interactions. This route may however be used only for non-associating fluids; the short-range part of the Coulombic interactions is known to be indispensable for associating fluids, and no site-site interaction can therefore be treated separately without any regard to other sites [6]. To account for the composite influence of all sites in associating fluids, we will use therefore ideas of the RAM perturbation theory [19]. This theory defines a sphericalized

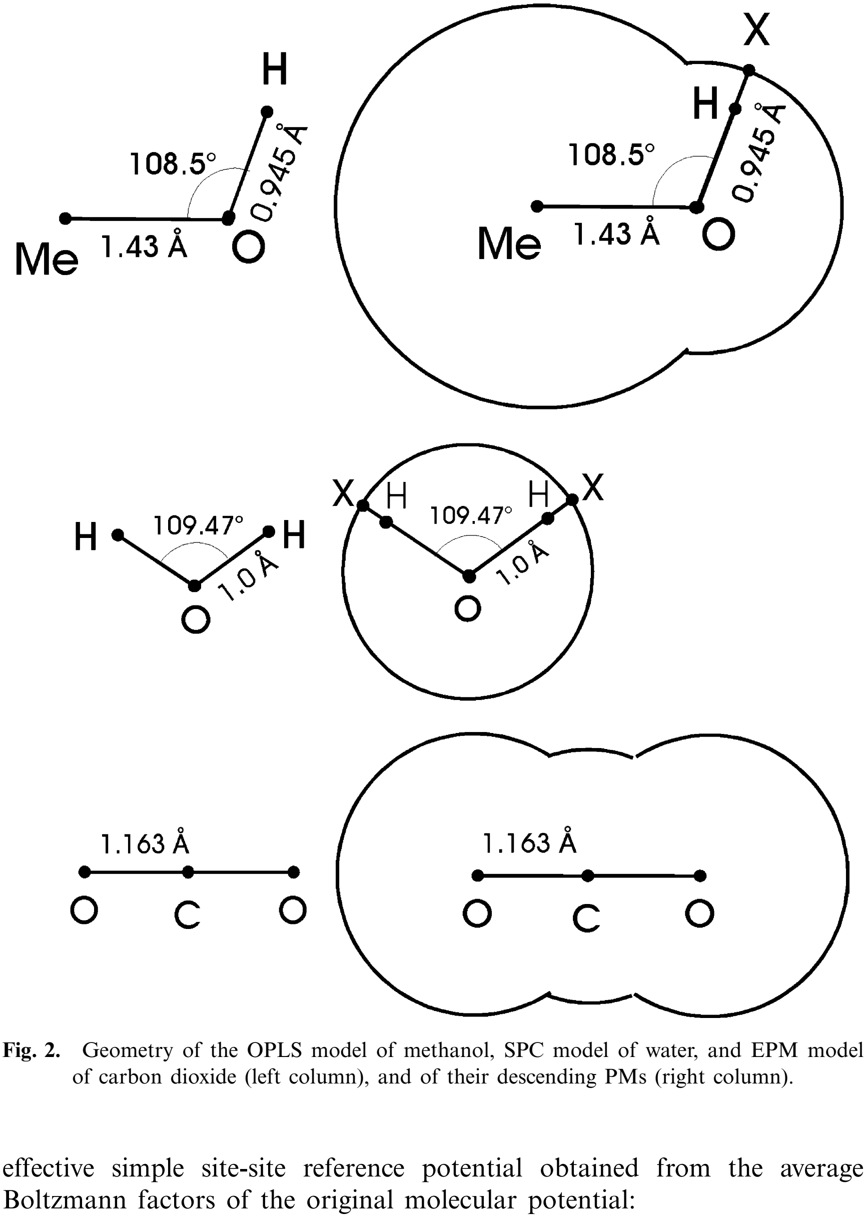

Fig. 2. Geometry of the OPLS model of methanol, SPC model of water, and EPM model of carbon dioxide (left column), and of their descending PMs (right column).

effective simple site-site reference potential obtained from the average Boltzmann factors of the original molecular potential:

$$u_{ij}^{\mathrm{RAM}}(r_{ij}) = -k_{\mathrm{B}}T \ln\left[\int_{r_{ij}=\mathrm{const}} \exp[-u(1,2)/k_{\mathrm{B}}T]d(1)d(2)\right], \qquad (8)$$

where the angular brackets denote an unweighted angular average. This method is known to provide quite accurate site-site correlation functions. Here we are concerned with effective short-range repulsions of the individual sites defined by these potentials. To this end, we use these potentials in the hybrid Barker–Henderson method explained above.

The hard cores of methanol and water obtained using the average Boltzmann factors are listed in Table I along with those for carbon dioxide obtained directly from the site-site LJ potentials. A remark concerning these diameters seems appropriate here. The diameters of the dumbbell and triatomics cores have been determined from the $Y_i - Y_i$ interactions (where Y_i denotes any site) which also implies that the cross interaction, $d_{Y_iY_j}$, is pair-wise additive, $d_{Y_iY_j} = (d_{Y_i} + d_{Y_j})/2$. We may however use the above method, Eq. (4), to determine the cross diameters directly. Agreement/disagreement between the two results may indicate consistency/inconsistency of the method. As it can be easily verified, the used method gives diameters to a high degree of consistency. For example, if we consider methanol, then from the direct method we get for the O-Me interaction $d_{\mathrm{OMe}} = 3.291\,\text{Å}$, which compares excellently with the arithmetic mean of d_{OO} and d_{MeMe} given in the table.

With the hard-core parameters now completely defined, it remains to estimate the parameters corresponding to the Coulombic interaction between the O- and H-sites, i.e., the depth and range of the square-well attraction. Since this attraction is to approximate the slowly decaying Coulombic interaction, it is natural to try to make its range as long as possible. On the other hand, there are certain general conditions which H-bonding must satisfy and which set upper limits on the SW range. One constraint results from a general requirement that two molecules cannot be double bonded. Nonetheless, this criterion does not prevent H-sites to form simultaneously two bonds which would make application of the TPT practically impossible. We will therefore impose on λ a stronger condition that the H-site may not form more than one hydrogen bond. This is a simple purely geometrical problem which must be solved for each specific arrangement of the sites (see, e.g., Ref. 20). The resulting values of λ for the PM of methanol and water are shown in Table I. No such criterion exists for polar fluids, and for a first rough estimate of λ for CO_2, we simply set $\lambda = 1.5 d_{\mathrm{OO}}$.

It is evident that the range λ must affect the formation and structure of the H-bond network. Secondly, the H-site is located deeply inside the O-sphere which makes the bonding angle over which H-bonds can be established very wide which must ultimately lead to loss of required strong directionality of H-bonding. This effect is known also from constructions of realistic models, and we will follow therefore the pattern established by studies of realistic models and place an auxiliary interaction site mimicking

Table I. Parameters of the Primitive Models of Methanol (3-site model, $MeOH_3$), Water (3-site model, EPM3), and Carbon Dioxide (CO_2)

$MeOH_3$	
d_{OO}	2.64 Å
d_{MeMe}	3.92 Å
d_{XX}	2.11 Å
λ	1.636 Å
EPM3	
d_{OO}	2.620 Å
d_{XX}	2.096 Å
λ	1.703 Å
CO_2	
d_{CC}	2.530 Å
d_{OO}	2.942 Å
λ	4.596 Å

the *interaction* of hydrogen (and labeled as X-site) on the surface of the O-site, i.e., we set $|O-X| = \frac{1}{2}d_{OO}$ (cf., e.g., placement of the negatively charged M-site away from the oxygen site in the TIP4P model of water [21]). Since the X-site is not a part of either the OPLS model or the SPC model, we cannot use Eq. (4) to directly determine the range of the repulsion between the X-sites. We performed therefore test simulations and checked the dependence of the probability distribution of bonding angles and found that the optimal value of d_{XX} is about 0.8 d_{OO} which, coincidentally, equals the value found for the extended primitive models of water [22].

We used the PMs with the parameters summarized in Table I in Monte Carlo simulations; methanol and water have been considered at ambient conditions, carbon dioxide at $T = 320\,\text{K}$. The obtained site-site correlation functions are compared with those of the corresponding realistic parent models in Figs. 3–5. For all three compounds and g_{ij}'s considered, we get qualitative agreement. The location of maxima on g_{ij}'s determine the shells around an arbitrary chosen particle and they agree; the main difference is thus found for their height which is related to the strength of interaction (temperature). Accounting for simplicity of the method, the agreement (in some cases even semi-quantitative) must thus be considered as surprisingly good.

5. CONCLUSIONS

This paper should be viewed as a feasibility study whether primitive models (i.e., models without any long range interactions) for polar and

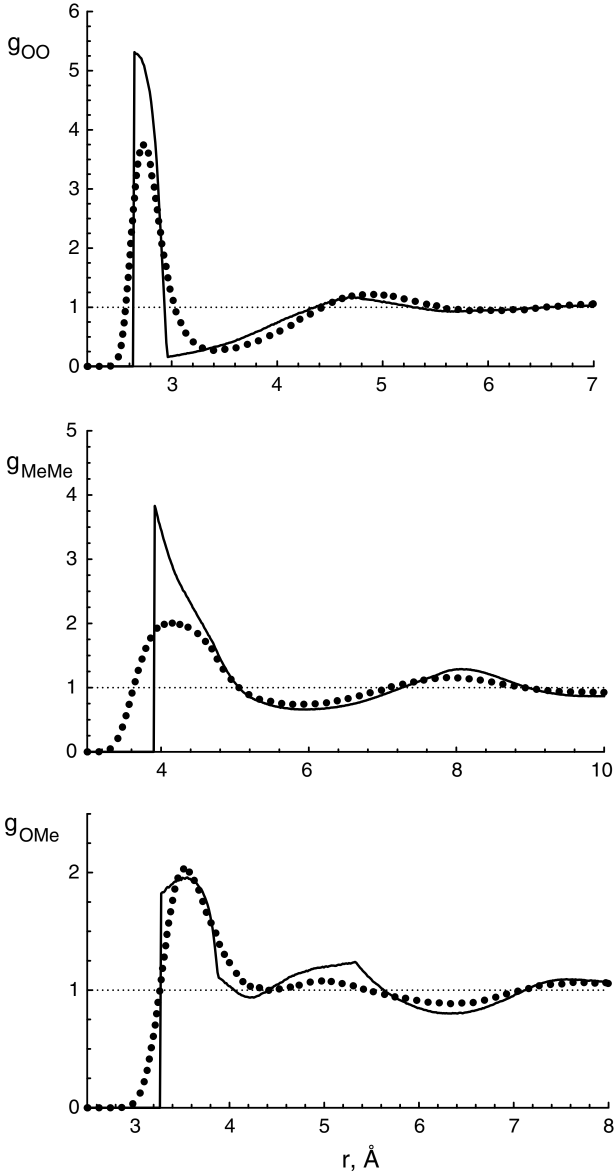

Fig. 3. Comparison of the site-site correlation functions of the PM of methanol with those of its realistic parent model.

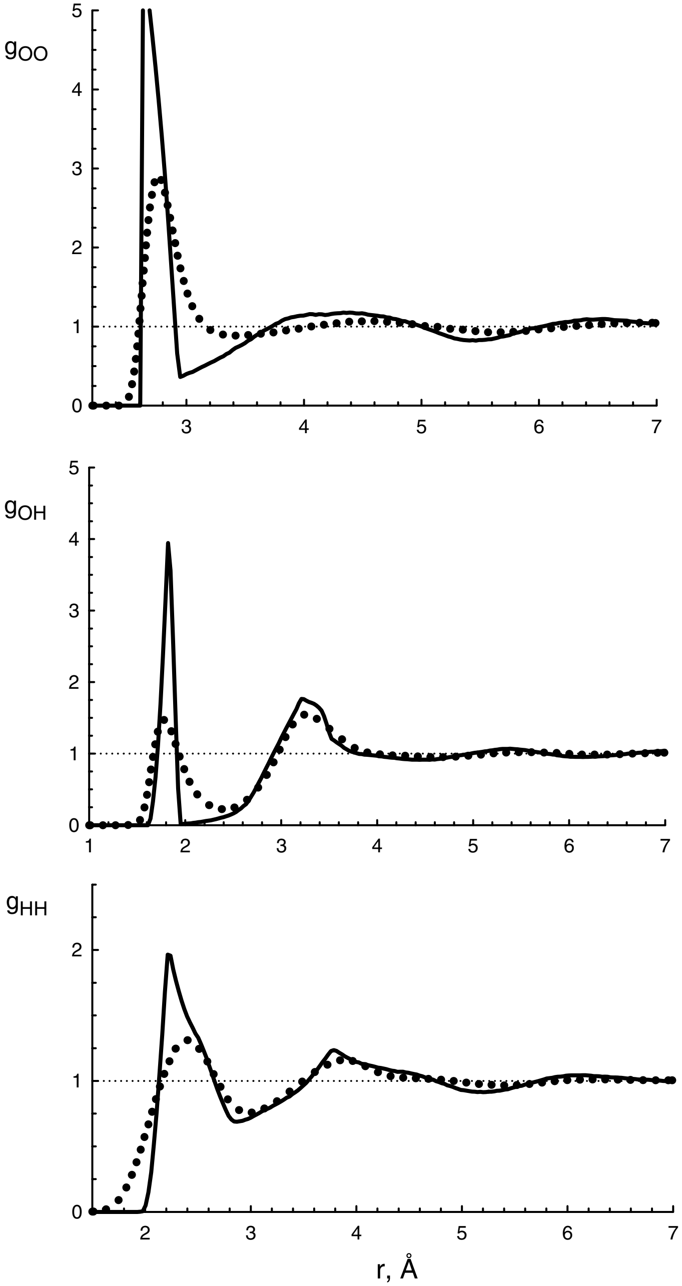

Fig. 4. Same as Fig. 3 for water.

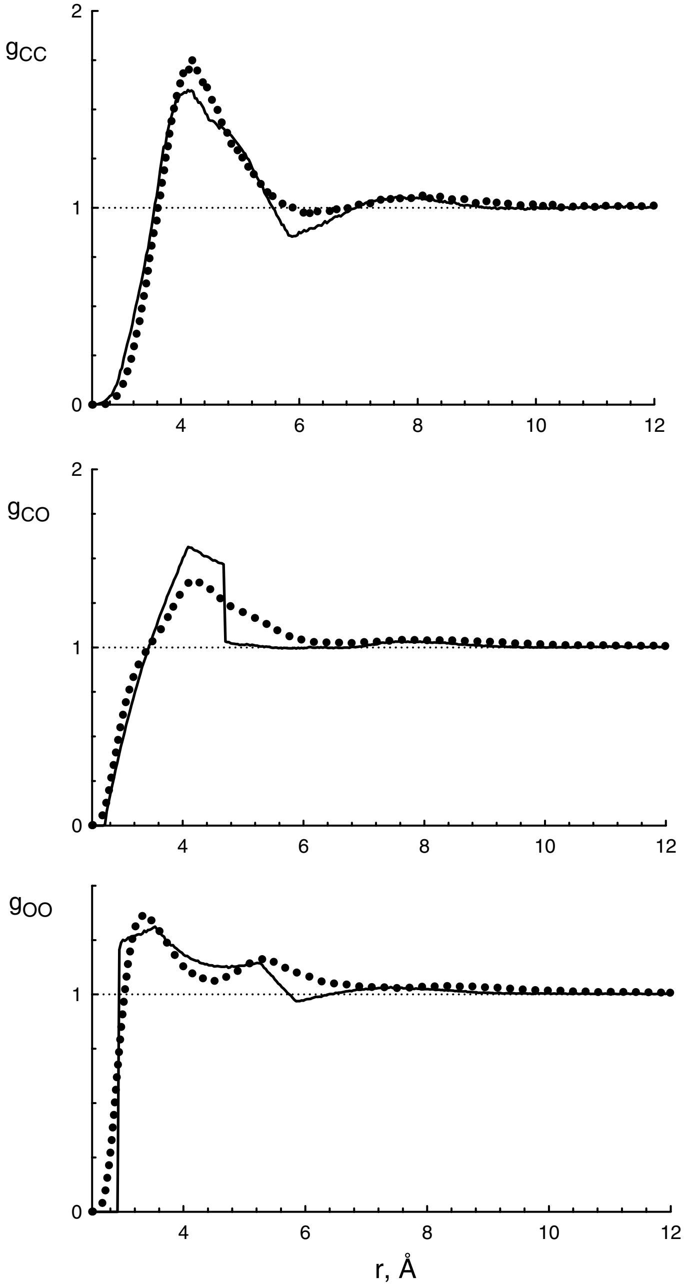

Fig. 5. Same as Fig. 3 for carbon dioxide.

associating fluids may be constructed directly from the complex realistic potential models. With the exception of auxiliary sites, we have used well defined theoretical arguments to set the parameters of the primitive models. Comparison of the site-site correlation functions of the primitive and realistic models shows quite good agreement thus pointing to a sound basis of the method which justifies further research along this line with the ultimate goal to develop a molecular-based theory of polar and associating fluids.

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