

## Extended excluded volume: Its origin and consequences\*

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*Abstract:* In contrast to the common intuitive/speculative approach based on an analysis of thermodynamic or structural data of (nonpolar) fluids, the statistical mechanical approach is used to extend the excluded volume concept to all other types of fluids. The (extended) excluded volume incorporates, in addition to common nonelectrostatic interactions defining the shape and size of the molecules, also the short-range part of the repulsive interactions between the embedded Coulombic sites. In this study we show that the extended excluded volume concept correctly predicts the behavior of the partial molar volume (PMV) at infinite dilution in different solvents and, particularly, differences between nonpolar and associating solvents. The concept is then applied to estimate the PMV of methanol in water.

*Keywords:* excluded volume; partial molar volume; primitive models; pseudo-hard bodies; water–methanol mixtures.

### INTRODUCTION

One of the most useful and successful concepts in theories of fluids is the excluded volume one. Its origin goes as far back as to van der Waals [1] at the end of the 19<sup>th</sup> century, who believed that molecules are real entities with their own volume which is inaccessible to other molecules. This idea is also the basis of his famous equation of state and its numerous later modifications [2]. The concept proved to be, even before much later justification provided by statistical mechanics, very fruitful and made it possible to explain a number of properties of nonpolar fluids. In addition to its wide use in chemical thermodynamics, particularly for polymer solutions, it has been applied also to such diverse problems as percolation [3] and even quantum statistical physics [4].

Accepting the idea that molecules may be viewed as certain geometrical objects and that it is their packing within the volume of the system that plays the essential role in determining the properties of fluids, the primary thermodynamic quantity to which the excluded volume concept can be readily applied is the excess volume of mixtures and hence also the partial molar volume (PMV). Whereas this approach seems readily acceptable for nonpolar fluids, it meets with difficulties when applied to polar and associating ones. Aqueous solutions may serve as a typical example. It has been well established experimentally that the PMV of nonpolar compounds at infinite dilution is smaller in water than in organic compounds. Kauzmann [5] attributed this difference to a reorganization of H-bonds of water molecules in the first hydration shell around the solute. Pierotti [6] was apparently the first to attempt

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to explain the difference by the excluded volume approach and argued that the difference is due to the small size of the water molecules. This approach seems to have been supported by subsequent studies [7–9], which used the scaled particle theory (SPT) to describe a mixture of hard spheres (HSs). Since there is no particularly strong solute–solvent interaction in aqueous solutions of nonpolar compounds, application of the excluded volume may be justified, but to argue in terms of HSs is, in this case, very questionable. Frankly, with well-adjusted values of the volume of the HSs, a numerical agreement with experiment can be achieved, which, however, does not mean that it corresponds to physical reality. What is then the “correct” size of the water molecule when it varies from author to author within, approximately, the range  $2.76 \leq \sigma_w [\text{Å}] \leq 3.20$  [9–11]? Consequently, general conclusions drawn from this macroscopic/intuitive approach must be viewed with caution because they cannot reflect the actual molecular mechanisms behind the observed phenomena.

The excluded volume concept was put on a firm theoretical footing for nonpolar fluids by results of molecular simulations and scattering experiments that showed that the structure of these fluids is determined predominantly by the strong short-range repulsive interactions. This finding made it possible to formulate fast converging perturbation theories about a purely repulsive short-range reference system [12,13]. In other words, the reference system is given by the repulsive part of the total interaction Hamiltonian, which can be conveniently modeled by hard bodies (representing the shape and size of the molecules). However, for a long time this was not the case for polar and associating fluids. Theories of these fluids followed their own path of development, particularly because of a lack of physically correct intermolecular interaction models (for the widespread, but as a matter of fact, physically unacceptable and out-of-date models, see [14]). It was not until advances in quantum chemistry and molecular simulations that it became possible to construct more realistic interaction models using the same functional form for all types of fluids and to treat them in a uniform way [15]. Extensive simulations on these models showed that the structure of fluids is, in general, determined primarily by short-range interactions, which, however, need not be only repulsive [16–21]. To be more specific, in addition to common short-range repulsive Lennard–Jones (LJ)-type interactions it is necessary also to include the short-range, both repulsive and attractive, effects resulting from the Coulombic interactions between the charged sites.

In the present paper we briefly explain the way that leads from a complex realistic Hamiltonian to simple short-range models, which after switching off the attractive interactions define a new type of hard bodies, the so-called pseudo-hard bodies (PHBs) [22]. These bodies evidently include, as a special case, common hard bodies, and their use makes it possible to extend, without resorting to any intuitive speculations or ad hoc adjustments, the excluded volume concept to complex associating systems. In addition to general trends and differences in the PMV for HS and PHB solvents, we also present PMV results for methanol–water solutions. In the following section, we outline the method and provide all necessary equations and relations. The next section then contains the obtained results and their discussion.

## THEORY

All statistical mechanical computations/considerations begin by specifying a certain interaction Hamiltonian. Traditional interaction models were different for different classes of fluids [14] and represented an ad hoc modeling of the resulting features of the interactions, but not of their origin. Modern quantum chemistry starts from the fact that in addition to consequences of the quantal nature of the elementary particle interaction there is only one further real physical interaction that can act between molecules, the Coulombic electrostatic interaction. It thus treats molecules of all compounds in a unified way, viewing them as geometrical objects (reflecting their structure) with embedded interaction sites that are, in general, the seat of two types of interactions: (1) a nonelectrostatic (non-el) interaction including a strong repulsion at short separations and a weak attraction (dispersion force) at medium separations, and (2) the long-range Coulombic charge–charge interaction. For small molecules and under

the assumption of pair-wise additivity, it is further assumed that the geometrical arrangement of the sites within the molecule is fixed (rigid monomer). A common realistic intermolecular pair potential is thus given as the sum of a number of various site–site interactions and the total interaction energy between two molecules assumes the form

$$u(1,2) \equiv u(R_{12}, \Omega_1, \Omega_2) = u_{\text{non-el}}(1,2) + u_{\text{Coul}}(1,2) \\ = \sum_{i \in \{1\}} \sum_{j \in \{2\}} \left\{ u_{\text{non-el}}(|\mathbf{r}_1^{(i)} - \mathbf{r}_2^{(j)}|) + \frac{q_1^{(i)} q_2^{(j)}}{|\mathbf{r}_1^{(i)} - \mathbf{r}_2^{(j)}|} \right\} \quad (1)$$

where the LJ potential is usually (but not necessarily) chosen for the nonelectrostatic site–site part,  $u_{\text{non-el}} = u_{\text{LJ}}$ . In eq. 1,  $R_{12}$  denotes the separation between the reference points (arbitrarily chosen points within the molecule; for water commonly the oxygen site) of molecules 1 and 2,  $\Omega_k$  denotes the orientation of molecule  $k$ ,  $\mathbf{r}_k^{(i)}$  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  $k$ .

When examining the general impact of the potential in the above form on the properties of fluids, it turns out that it is the range of the interaction that matters most [16–21]. All the obtained results have shown that the structure of fluids defined by potential (1) is determined primarily by the short-range part of the intermolecular interaction, which may be, in contrast to nonpolar fluids, both repulsive and attractive, and that the long-range Coulombic interactions play only a marginal role and can thus be treated as a perturbation only. We remind in passing that the usual statement [13] “...the *structural* properties of non-polar fluids are determined primarily by *repulsive* interactions” means nothing else than that the *short-range part* of the total pair potential  $u(1,2)$  is the determining factor, which, in this case, happens to be just its repulsive part.

The above finding has made it possible to start developing a theory of polar and associating fluids along the same path as that used for nonpolar fluids [12,13]. It means using a perturbation expansion and well-defined approximations to transform the complex short-range reference system into a simple model that is amenable to a theoretical treatment (cf. the scheme “soft repulsive reference” → “hard-body fluid” for nonpolar fluids). This procedure leads to various “primitive” models that incorporate only caricatures of the attractive Coulombic interactions between unlike sites at short separations and the repulsive interactions between like sites [23,24], see Fig. 1a. Choosing, for the sake of simplicity, the square-well interaction for the attractive part, and the HS model for the repulsive part of the potential of such a model, its explicit form reads as

$$u_{\text{PM}}(1,2) = \sum_{i,j \in \{S\}} u_{\text{HS}}(|\mathbf{r}_i^{(1)} - \mathbf{r}_j^{(2)}|; d_{ij}) + \sum_{\substack{i,j \in \{P\} \\ i,j \in \{N\}}} u_{\text{HS}}(|\mathbf{r}_i^{(1)} - \mathbf{r}_j^{(2)}|; d_{ij}) \\ + \sum_{i,j \in \{P,N\}} u_{\text{SW}}(|\mathbf{r}_i^{(1)} - \mathbf{r}_j^{(2)}|; \lambda) \\ \equiv u_{\text{FHS}}(1,2) + \sum_{\substack{i,j \in \{P\} \\ i,j \in \{N\}}} u_{\text{HS}}(|\mathbf{r}_i^{(1)} - \mathbf{r}_j^{(2)}|; d_{ij}) \\ + \sum_{i,j \in \{P,N\}} u_{\text{SW}}(|\mathbf{r}_i^{(1)} - \mathbf{r}_j^{(2)}|; \lambda) \quad (2)$$

where  $u_{\text{FHS}}$  is the common interaction between fused-hard-sphere (FHS) bodies forming the “true” core of the molecules, the summation in the second term on the right-hand side of the above equations runs over all pairs of like charges, in the third term over all pairs of unlike charges

$$u_{\text{HS}}(r_{12}; d) = +\infty, \text{ for } r_{12} < d$$

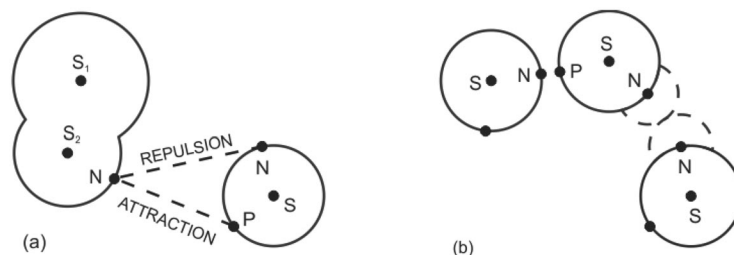
$$= 0, \text{ for } r_{12} > d$$
(3)

and

$$u_{\text{SW}}(r_{12}; \lambda) = -\epsilon_{\text{HB}}, \text{ for } r_{12} < \lambda$$

$$= 0, \text{ for } r_{12} > \lambda$$
(4)

Furthermore, we denoted the sites that bear charges as P (positive charge) and N (negative charge), and the sites with nonelectrostatic interactions as S.



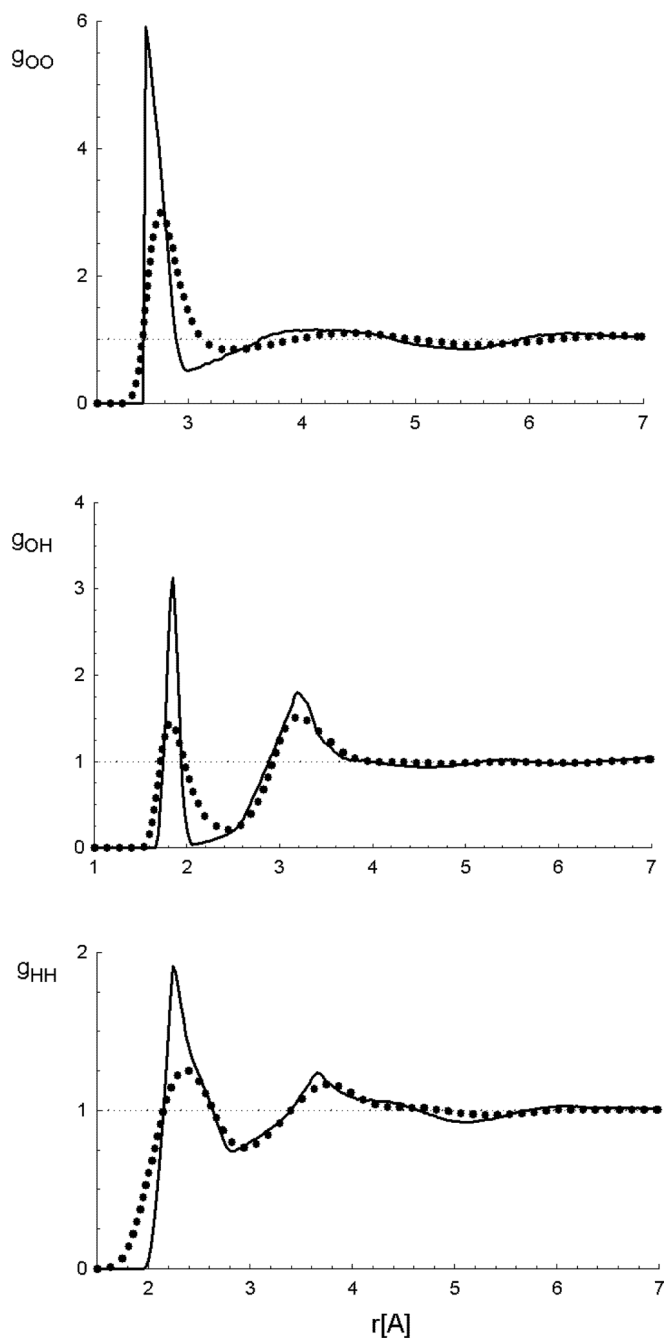
**Fig. 1** Schematic representation of the site–site interactions (a) in the primitive models with indicated repulsive and attractive interactions, and (b) in the associated PHBs. Two spheres can get to contact unless site (N) on one sphere meets another site (N) on the other sphere.

Despite its simplicity, potential (2) captures all the features of the electrostatic interactions at short intermolecular separations and should thus, in the light of the aforementioned statement on the predominant effect of the short-range interactions, reproduce the structure of the parent realistic model. That this is indeed the case has already been demonstrated in a series of papers [16–21], and therefore we only show here the results for water, see Fig. 2. When the repulsive HS interaction term in eq. 2 is switched off, one gets the same general form as in a majority of intuitive models mimicking H-bonding, i.e., a hard body with attractive sites [23]. Since H-bonding is likely the most important interaction in associating fluids, these models are often used to explain, albeit only *qualitatively*, some of their properties, and also serve as the basis for correlations of experimental data, such as the statistical association fluid theory (SAFT) methods [25]. On the other hand, by switching off the attractive interaction in eq. 2 (i.e., the last term), only the repulsive interaction terms remain, defining the so-called PHB, and hence also a certain excluded volume [22]. However, unlike common hard bodies resulting from eq. 2 by neglecting *all* interactions between the Coulombic-like sites, the PHB is not a real body but an object with a flavor of nonadditive interactions. This is the essence of the approach and a very important feature of this purely repulsive short-range model. A schematic representation of the interactions in the PHB fluid is shown in Fig. 1b.

Studies of fluids of PHBs are a challenge for theoreticians, and so far no theory describing their properties has been developed. We thus have to resort to either empirical extensions of methods available for conventional hard-body fluids [26–29] or to a parameterization of simulation data [30]. For the numerical evaluation of the PMV, it is convenient to use variable  $\zeta = x_S/(1 - x_S)$  instead of the mole fraction  $x_S$ . The PMV of the HS solute is then given by

$$\psi_S(P, T, \zeta) = v_{\text{mix}}^* + \frac{\partial v_{\text{mix}}^*}{\partial \zeta}$$
(5)

where  $v_{\text{mix}}^* = V/N\sigma_W^3$  is the reduced volume of the mixture per molecule.



**Fig. 2** Comparison of the site–site correlation functions of the primitive model of water (full lines) with those of the full parent realistic TIP4P model (filled circles).

Concerning mixtures of HSs, the most commonly used equation of state is the Boublik–Mansoori–Leland–Carnahan–Starling (BMLCS) equation, which in the case of pure fluids reduces to the Carnahan–Starling equation (for a comprehensive review on hard-body fluids, see ref. [26]). However, recently reported results were based on the less accurate SPT equation of state, but with

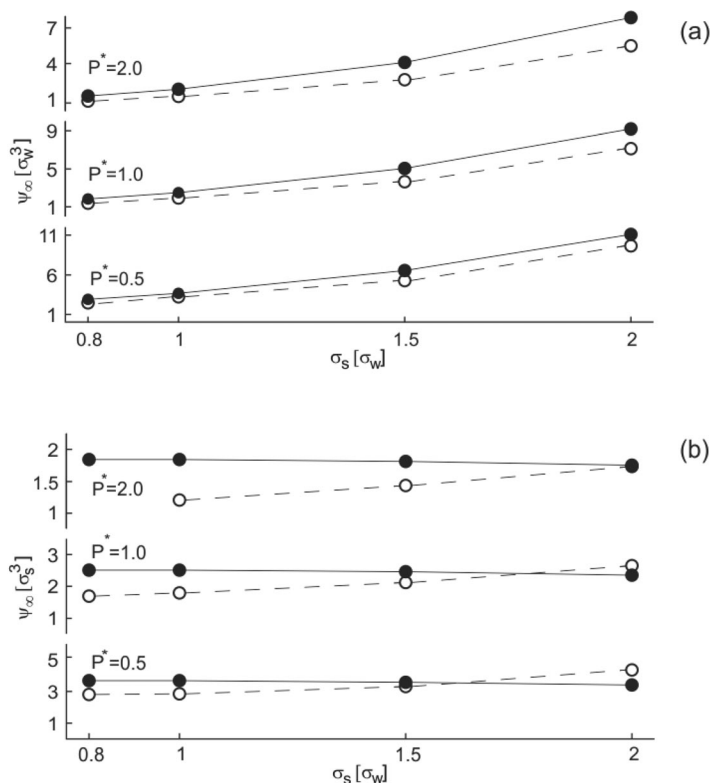
respect to other inherent uncertainties the differences between the two are negligible [7]. By differentiating the SPT equation of state with respect to the number of molecules of the solute Lee derived the following analytic expression for the PMV of an HS solute of diameter  $\sigma_S$  at infinite dilution [7]:

$$\psi_{\text{SPT},\infty} = \frac{v_W}{C} (t^3 + 3At^2 + 3A^2t + A^2B) \quad (6)$$

where  $A = (1 - \xi)/(1 + 2\xi)$ ,  $B = (1 - \xi)/\xi$ ,  $C = (1 + 3A + 3A^2 + A^2B)$ ,  $\xi$  is the relative packing density of the pure solvent defined as the ratio of the physical volume of 1 mol of HSs of diameter  $\sigma_W$  and the molar volume,  $v_W$ , of the pure solvent, and  $t = \sigma_S/\sigma_W$ .

## RESULTS AND DISCUSSION

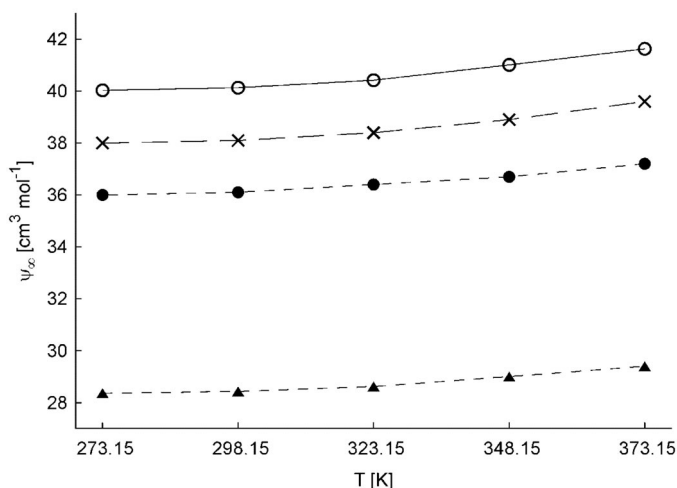
The first issue we want to address is the role of the relative size of the solute and solvent molecules. To this end, let us consider first a solution of HSs of different diameters  $\sigma_S$  in the solvent of HSs of diameter  $\sigma_W$ . In Fig. 3a, we plot the dependence of the PMV of spheres S on the ratio  $\sigma_S/\sigma_W$  at different pressures. As it is seen, this dependence along isobars is always monotonously increasing. In Fig. 3b, we then show the dependence of the PMV of the same sphere S in solvents of different diameters  $\sigma_W$ . As we see, the trend in this case is opposite: with increasing ratio  $\sigma_S/\sigma_W$  (i.e., smaller solvent molecules) the PMV is very slowly decreasing. This behavior corresponds to the original finding of Lee [7] and is also in full agreement with the trends obtained by Graziano [9] for aqueous solutions of alkanes and n-alcohols.



**Fig. 3** The PMV at infinite dilution,  $\psi_{\infty}$ , of hard spheres in the HS (filled circles) and PHB water (open symbols) solvents, respectively, as a function of the relative size of the solute's HSs at different pressures  $P^* = P\sigma_i^3/k_B T$ , where (a)  $i = W$  and (b)  $i = S$ .

Next, we want to address the primary and most important issue of this communication, namely, what may be the origin of the drop in the PMV of nonpolar solutes when transferred from a nonpolar solvent to water, and to what extent the excluded volume concept can, if at all, capture this feature. To make the computations consistent and to avoid any ad hoc manipulations or adjustments, we consider two solutions: (1) HSs in the HS solvent and (2) the same HSs in the PHB solvent whose molecules are made of the original HSs by adding the repulsive “ears” (recalling that these “ears” do not interact with the solute). To keep contact with the real world, for the solvent we use the PHB water-like model that descends from the likely most popular realistic TIP4P water model [31]. It means that this PHB water comprises an HS (the core of the molecule) with two embedded repulsive sites (for details, see ref. [32]). The perturbation theory calculations performed on the parent TIP4P model yielded a HS diameter of  $\sigma_W = 2.652 \text{ \AA}$  [32], which is slightly less than one of the values considered by Graziano [9]. We remind in passing that other TIPnP models of water yield practically identical values of  $\sigma_W$ . This PHB water is used as the solvent for HS solutes of different diameters, case 2 above. Then, to examine the effect of the “ghost” repulsive sites, these sites are removed and the solvent is just the fluid of HSs of diameter  $\sigma_W$ , case 1. To obtain the PMV at infinite dilution, we used eq. 6 for the HS solvent and eq. 3 from ref. [30] for the PHB solvent. The results for a series of values of  $\sigma_S$  and  $\sigma_W$  and a number of reduced pressures are shown also in Fig. 3. To answer the question raised above, one has to compare the PMV of a given HS solute in the PHB solvents and in the corresponding HS solvents. As one can see, for smaller ratios of  $\sigma_S/\sigma_W$  the PMV of HSs in the PHB solvent is smaller than that in the HS solvent, supporting thus the claim that the drop of the PMV in water is due to the small size of water molecules. However, this trend is reversed for larger  $\sigma_S/\sigma_W$  ratios at lower pressures, which means that the behavior of the PMV depends also on pressure. Nonetheless, if we recall that in real fluids the compressibility factor of reference hard-body fluids is about 10 (and the reduced pressures are thus quite high), then the original claim remains valid.

As the final example, we consider the water–methanol mixture, which is of great interest from both the scientific and engineering points of view. Realistic methanol is modeled by the common 3-site OPLS potential [33]. The descending primitive model, and hence also the PHB model, are then made up of a hard heteronuclear dumbbell core with one embedded P-site (for details and parameters of the model, see ref. [34]). We performed Monte Carlo simulations on this mixture and the obtained PMV at infinite dilution of methanol, along with experimental data, is plotted in Fig. 4 as a function of temper-



**Fig. 4** The PMV at infinite dilution,  $\psi_\infty$ , of methanol in water modeled as a mixture of HSs (filled circles and triangles), a mixture of PHBs (open symbols), and their comparison with experimental values (crosses). Filled circles:  $\sigma_W = 2.8 \text{ \AA}$ ,  $\sigma_S = 3.83 \text{ \AA}$ ; triangles:  $\sigma_W = 3.2 \text{ \AA}$ ,  $\sigma_S = 3.83 \text{ \AA}$ .

ature. As we see, the theoretical results slightly overestimate the experimental values and both curves run practically parallel with a difference of about  $2 \text{ cm}^3/\text{mol}$ . The same mixture was also considered by Graziano [9], who treated the methanol molecule as an HS of diameter  $3.83 \text{ \AA}$  and water as an HS of  $\sigma_{\text{W}} = 2.8 \text{ \AA}$ . His results are also shown in Fig. 4. As it is seen, this HS mixture underestimates the experimental data with nearly the same difference as the PHB mixture overestimates it. As we already mentioned in the Introduction, the HS diameter of the water molecule is not a unique quantity and the used values reported in literature go up to  $3.2 \text{ \AA}$ . If this value is used with the same methanol sphere then we get the result that strongly underestimates the experiment, see Fig. 4, which, again, corresponds to the trends shown in Fig. 3. As it is seen, by varying the HS ratio it may be possible to reach agreement with experimental data. In fact, as already mentioned above, realistic water models yield for the hard core of the primitive model the diameter about  $2.6 \text{ \AA}$ . When this value is used along with the methanol value  $3.83 \text{ \AA}$ , then we get for the PMV the experimental value  $40.1 \text{ cm}^3/\text{mol}$ . This coincidence points again to the sensitivity of the PMV results on the chosen values of the hard-core diameters, which is a warning that any general conclusions should be made with caution.

From the above discussion it is evident that when the excluded volume concept is applied to real systems, the crucial point is the choice (or an estimate) of the volume (size) of the molecules and this aspect deserves thus some comments. There are at least two issues associated with this concept, (i) the HS approximation itself used in applications and intuitive/speculative considerations, and (ii) the methods used to estimate a “size” of the molecules.

Ad (i). It has been well known that the shape of molecules plays a very important role and that with a few exceptions no real compounds can be treated as “spherical”. Specifically, methanol is at least a diatomics and thus far from argon-like. Its shape is dumbbell-like, and no HS fluid can estimate the properties of the hard dumbbell fluid; more accurately, some property may be estimated over a certain limited range of densities with an adjusted HS diameter, but other properties are then usually well off. Consequently, any good numerical agreement of the HS approximation with experiment is and must be only a numerical fit and cannot be the base for any reasoning.

Ad (ii). No real molecule possesses a hard core, it is only a certain simplifying (but useful) view. To reach it via well-defined and justified approximations and not by intuition one must start from an interaction Hamiltonian and the way to simplified systems goes then via a perturbation expansion. If we manage to set up a fast converging expansion about a hard-body reference then we can claim that such a reference may be viewed as a reasonable certain effective hard core. All other approaches are only a speculation. For instance, if the LJ potential is divided into reference and perturbation parts at the potential parameter  $\sigma$  and it is then claimed that the HSs of diameter  $\sigma$  represent the hard core (which is often the case in intuitive arguments), the resulting perturbation computations yield rather poor results. It is the collective behavior that determines the properties of dense systems, and hence also “effective” parameters, and this must be accounted for. Nonetheless, it should be borne in mind that neither the statistical mechanical approach provides a unique value for the size of molecules. It depends evidently on the choice of the interaction model but, as we already mentioned above, at least for water different models yield (nearly) the same values for the core, which points to a certain consistency of the approach.

## CONCLUSIONS

The common excluded volume concept is based on the simple idea of impenetrable molecules and supported by results of molecular theories for nonpolar fluids. However, it has lacked any theoretical support for polar and associating solvents. We have shown that this concept can be extended to fluids with complex interactions, particularly to associating ones, if the intermolecular interaction model is considered in the form of a site-site model with embedded Coulombic sites. The excluded volume incorporates then naturally also the effect of the repulsive interactions between the like charges at short intermolecular separations. We have focused on the PMV at infinite dilution, which is known from



experiment to discriminate between different solvents. The extended volume concept predicts correctly, without resorting to any additional assumptions or approximations, decrease of the PMV of nonpolar solutes in water, but claims based solely on the relative size of the solute and solvent molecules are not justified. This phenomenon must be accompanied by (results from) some restructuring of the solvent, but what actually takes place on the molecular level in the solution with purely repulsive interactions only is an additional interesting problem that waits for its solution by molecular simulations.

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