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## Comments on

**The contact values in asymmetric hard-sphere mixtures, *Molec Phys*, 107, 687 (2009);  
*Molec. Phys.* 106 , 607 (2008).**

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Despite its highly idealized nature, the asymmetric hard-sphere mixture model is still being the subject of continued interest. One of its virtues is the possibility to express the pressure  $P$  solely from the contact value of the radial distribution functions  $g_{ij}(d_{ij})$ , at a given temperature  $T$ , total density  $\rho$  and mole fraction  $x_i$  of species  $i$ :

$$P = \rho k_B T \left[ 1 + \frac{2\pi\rho}{3} \sum_{i,j} x_i x_j d_{ij}^3 g_{ij}(d_{ij}) \right] \quad (1)$$

If  $g_{ij}(d_{ij})$  were known as a function of  $(\rho, x_i, d_{ij})$ , all the thermodynamic properties could be obtained from equation (1). This could be done from simulations but in practice this is only possible for limited values of  $\rho$ ,  $x_i$  and size ratios. This motivated a long series of papers from different groups proposing various ad-hoc expressions for these quantities, in particular for  $g_{22}(d_{22})$  in the high size asymmetry regime,  $R = d_{22}/d_{11} \gg 1$  (for binary mixtures), for its relevance for the modelling of colloids. In the most recent papers [1]-[2] of this series, some contributions were listed (eg [3-7]), besides the pioneering studies of the early seventies [8]-[9]. In the same vein, however, relevant ones were omitted [10-13]. As regards these attempts to parameterize the  $g_{ij}(d_{ij})$ , one first point should be recalled: a given value of  $P$  in equation (1) can be obtained with quite disparate values of the  $g_{ij}(d_{ij})$ . This is for instance implicit in the discussion of refs. [14], [15]: in the colloidal limit  $R \gg 1$  and comparable packing fractions  $\eta_i = \frac{\pi}{6} \rho x_i d_{ij}^3$  of both species, the contribution of the big spheres becomes negligible in the relevant range  $x_2 \ll 1$ . A similar insensitivity of  $P$  in equation (1) was also clearly stated in ref [7]. In ref. [16] we demonstrated this from an integral equations approach. For a size ratio  $R=10$ , the difference (see our comment [16] about this) between our result  $g_{22}(d_{22}) = 25.24$  and the simulation one [17]  $g_{22}(d_{22}) = 18.5$  changes the compressibility factor  $Z=P/\rho k_B T$  from 2.691 to 2.695. We actually showed that the closure of the Ornstein-Zernike integral equations we derived [16] from Rosenfeld's fundamental measure functional [18] reproduces, without any adjustment, most of the available simulation data for the radial distribution function. This holds also for the simulations for  $R=20$ , alluded to in ref. [2] and

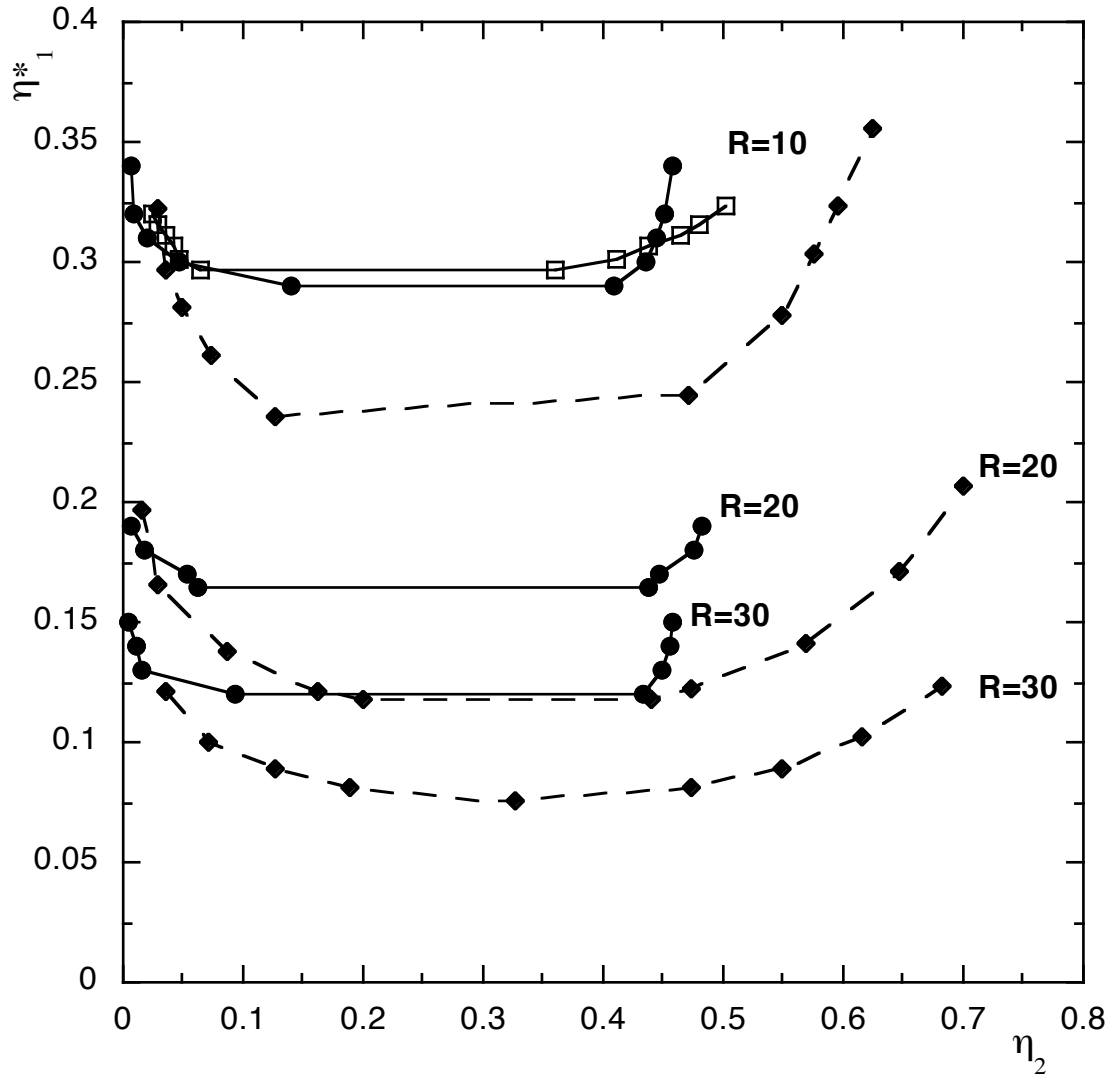
considered in our group [19]-[21]. Besides the limited set of available simulations and since the pressure is not a sensitive criterion, one should consider other properties for discriminating between various proposals for  $g_{ij}(d_{ij})$ . Among these, the fluid-fluid binodal is one immediate candidate. While this was not done in refs [1]-[2], phase separation was found possible in [22] and its study from parameterized EOS became a central point in refs. [11]-[13]. Besides the pioneering studies on phase instability in highly asymmetric mixtures by integral equation (see e.g. [14],[15], [23]) and other methods [24], the fluid-fluid binodal has actually been obtained by simulations of the effective fluid in ref. [25]. From the integral equations we proposed [16], we also computed it [26] in the true mixture and found good agreement with that of the effective fluid (see the figure).. It is not possible to cite here all the relevant literature on this subject (see for example for recent work [27]-[28]; one may also find general references in a recent review on related subjects [29]). But since these calculations required a large amount of numerical work, the parameterized  $g_{ij}(d_{ij})$  in equation (1) should still be useful to study the binodals. Figure 1 showing the binodals we have computed from the new proposal of Santos et al [1], suggests some improvement upon previous estimates [12] but work still remains to be done before reaching quantitative accuracy. Even so, acceptable binodals can be obtained with poor contact values [11]. One should thus consider simultaneously several physical quantities, other characteristics of the phase diagram as well as the maximum number of internal constraints (see for example [30]) before reaching a useful conclusion about the future of this route using parameterized contact values. Therefore, any progress might result only from consideration of all relevant contributions, in the vein of these ad-hoc ansatzs, integral equations or density functional theories and simulations.

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Fluid-Fluid binodal for hard-sphere mixtures with  $R=10, 20, 30$



$\eta_1^*$  is the effective packing fraction of the small spheres,  $\eta_2$  the packing fraction of the big ones. Diamonds : computed from equation 26 in ref. [1]. Circles: simulation of the effective fluid [25]. Squares: true mixture for  $R=10$  [26], from the integral equation of ref. [16].