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## Contact values for disparate-size hard-sphere mixtures

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A universality ansatz for the contact values of a multicomponent mixture of additive hard spheres is used to propose new formulae for the case of disparate-size binary mixtures. A comparison with simulation data and with a recent proposal by Alawneh and Henderson for binary mixtures shows reasonably good agreement with the predictions for the contact values of the large-large radial distribution functions. A discussion on the usefulness and limitations of the new proposals is also presented.

**Keywords:** hard-sphere mixtures; radial distribution function; contact values

### 1 Introduction

A well known result in statistical mechanics is the close relationship between the structural and thermodynamic properties of fluids. In the particular case of a multicomponent mixture of (additive) hard spheres (HS), the compressibility factor  $Z \equiv p/\rho k_B T$  (where  $p$ ,  $\rho$  and  $T$  are the pressure, density and temperature of the system and  $k_B$  is the Boltzmann constant) is given by

$$Z = 1 + 4\eta \sum_{i,j} \frac{\sigma_{ij}^3}{\langle \sigma^3 \rangle} x_i x_j g_{ij}(\sigma_{ij}), \quad (1)$$

where  $N$  is the number of components in the mixture,  $x_i$  is the mole fraction of species  $i$ ,  $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$ ,  $\sigma_i$  being the diameter of a sphere of species  $i$ ,  $\eta = (\pi/6)\rho\langle\sigma^3\rangle$  is the packing fraction (with  $\langle\sigma^n\rangle \equiv \sum_{i=1}^N x_i \sigma_i^n$ ) and  $g_{ij}(\sigma_{ij})$  are the contact values of the radial distribution functions (RDFs)  $g_{ij}(r)$ . Hence, in this system, knowledge of the contact values of the RDFs suffices to completely determine the equation of state (EOS). Exact results for  $g_{ij}(\sigma_{ij})$  are unfortunately only known to first order in the packing fraction, where one simply has

$$g_{ij}(\sigma_{ij}) = 1 + \eta \left( 1 + \frac{3}{2} z_{ij} \right) + O(\eta^2), \quad (2)$$

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where

$$z_{ij} \equiv \frac{\sigma_i \sigma_j}{\sigma_{ij}} \frac{\langle \sigma^2 \rangle}{\langle \sigma^3 \rangle}. \quad (3)$$

Therefore, in general one must rely on either approximations or values obtained from computer simulations. Amongst the most important approximate analytical expressions for the contact values are the ones that follow from the solution of the Percus–Yevick (PY) equation of additive HS mixtures by Lebowitz [1], namely

$$g_{ij}^{\text{PY}}(\sigma_{ij}) = \frac{1}{1-\eta} + \frac{3}{2} \frac{\eta}{(1-\eta)^2} z_{ij}, \quad (4)$$

and the results obtained from the Scaled Particle Theory (SPT) [2–5],

$$g_{ij}^{\text{SPT}}(\sigma_{ij}) = \frac{1}{1-\eta} + \frac{3}{2} \frac{\eta}{(1-\eta)^2} z_{ij} + \frac{3}{4} \frac{\eta^2}{(1-\eta)^3} z_{ij}^2. \quad (5)$$

However, neither the PY nor the SPT lead to particularly accurate values and so Boublík [6] and, independently, Grundke and Henderson [7] and Lee and Levesque [8] proposed an interpolation between the PY and the SPT contact values, that we will refer to as the BGHLL values:

$$g_{ij}^{\text{BGHLL}}(\sigma_{ij}) = \frac{1}{1-\eta} + \frac{3}{2} \frac{\eta}{(1-\eta)^2} z_{ij} + \frac{1}{2} \frac{\eta^2}{(1-\eta)^3} z_{ij}^2. \quad (6)$$

These lead, through Eq. (1), to the popular and widely used Boublík–Mansoori–Carnahan–Starling–Leland (BMCSL) EOS [6, 9] for HS mixtures. For binary mixtures the BGHLL values are rather accurate except for asymmetric mixtures in which large hard spheres are present in extreme dilution in a small hard-sphere solvent. Since such mixtures represent good models for colloidal suspensions and there is growing interest in these kinds of systems, there have been many efforts to correct the deficiencies of the BGHLL values [10–20]. In this paper the recent proposal of Ref. [20] is of particular concern, so we also quote it explicitly here. It relies heavily on the proposal of Viduna and Smith (VS) [18] which reads

$$g_{ij}^{\text{VS}}(\sigma_{ij}) = \frac{1}{1-\eta} + \eta \frac{3-\eta+\eta^2/2}{2(1-\eta)^2} z_{ij} + \eta^2 \frac{2-\eta-\eta^2/2}{3(1-\eta)^3} \left( 1 + \frac{\langle \sigma \rangle \langle \sigma^3 \rangle}{2 \langle \sigma^2 \rangle^2} \right) z_{ij}^2. \quad (7)$$

Alawneh and Henderson (AH) [20] restrict themselves to binary mixtures ( $N = 2$ ,  $\sigma_2 \geq \sigma_1$ ) and propose to keep VS's expression for  $g_{11}(\sigma_1)$  but amend  $g_{12}(\sigma_{12})$  and  $g_{22}(\sigma_2)$  as

$$g_{12}^{\text{AH}}(\sigma_{12}) = g_{12}^{\text{VS}}(\sigma_{12}) - \frac{\eta^3}{16(1-\eta)^3} (1-R^{-3}) z_{12}^3 + \frac{5\eta^4}{32(1-\eta)^3} (1-R^{-4}) z_{12}^4 - \frac{\eta^5}{16(1-\eta)^3} (1-R^{-5}) z_{12}^5, \quad (8)$$

$$g_{22}^{\text{AH}}(\sigma_2) = g_{22}^{\text{VS}}(\sigma_2) + \frac{3\eta}{2} (z_{22} - 1) \frac{1-R^{-1}}{R} \exp \left[ \frac{3\eta}{2} (z_{22} + 1) \right]. \quad (9)$$

Here  $R \equiv \sigma_2/\sigma_1$  [21]. With these, they get good agreement for the large-small contact values and reasonably good agreement for the large-large contact values as compared to Molecular Dynamics results for mixtures with size ratios going from  $R = 1$  to  $R = 10$ .

On a different vein, in recent papers [22–25] three of us have advocated a “universality” approach as a guide to propose simple and accurate approximate expressions for the contact values  $g_{ij}(\sigma_{ij})$  of additive HS mixtures. In this approach, if the packing fraction  $\eta$  is fixed, the expressions for the contact values of

the RDF for all pairs  $ij$  of like and unlike species depend on the diameters of both species and on the composition of the mixture *only* through the single dimensionless parameter  $z_{ij}$  [cf. Eq. (3)], irrespective of the number of components in the mixture. Note that this feature is shared by the PY, SPT and BGHLL results but not by the VS or the AH approximations. The aim of this paper is two-fold. On the one hand, we will assess whether the new simulation data of Ref. [20] comply with the universality ansatz. On the other hand, we will introduce a refinement of some of the simple proposals of Refs. [22–25] that retain the universality feature but are able to improve the performance in the case of highly asymmetric mixtures.

The paper is organized as follows. In Sect. 2 and in order to make the paper self-contained, we provide a rather brief account of the simple proposals based on the universality ansatz and a simple extension to deal with highly asymmetric systems. This is followed in Sect. 3 by a comparison between the AH contact values, those of the new proposals and the simulation data. The paper is closed in Sect. 4 with further discussion and some concluding remarks.

## 2 Proposals for contact values including the “universality” assumption

We start by recalling the main aspects of the “universality” approach that has been used recently [22–25] as a guide to propose simple and accurate approximate expressions for the contact values  $g_{ij}(\sigma_{ij})$  of additive HS mixtures. According to this approach, at a given total packing fraction  $\eta$ ,  $g_{ij}(\sigma_{ij})$  depends on the size and concentration distributions only through the single parameter  $z_{ij}$ :

$$g_{ij}(\sigma_{ij}) = G(\eta, z_{ij}), \quad (10)$$

where the function  $G(\eta, z)$  is a common function for all the pairs  $(i, j)$ , regardless of the composition and number of components of the mixture. Note that the exact contact values to first order in density [cf. Eq. (2)] are consistent with the ansatz (10) with  $G(\eta, z) \rightarrow 1 + \eta(1 + \frac{3}{2}z)$ .

In order to propose specific forms for  $G(\eta, z)$  use is made of three basic consistency conditions. First, in the limit in which one of the species, say  $i$ , is made of point particles (i.e.,  $\sigma_i \rightarrow 0$ ),  $g_{ii}(\sigma_i)$  must take the ideal gas value, except that one has to take into account that the available volume fraction is  $1 - \eta$ . Thus,

$$\lim_{\sigma_i \rightarrow 0} g_{ii}(\sigma_i) = \frac{1}{1 - \eta}. \quad (11)$$

Next, if all the species have the same size,  $\{\sigma_k\} \rightarrow \sigma$ , the system becomes equivalent to a single component system, so that

$$\lim_{\{\sigma_k\} \rightarrow \sigma} g_{ij}(\sigma_{ij}) = g_p(\eta), \quad (12)$$

where  $g_p(\eta)$  is the contact value of the RDF of the single component fluid at the same packing fraction  $\eta$  as that of the mixture.

The third condition is the equality between the pressure in the bulk and near a hard wall [24, 25]:

$$1 + 4\eta \sum_{i,j} \frac{\sigma_{ij}^3}{\langle \sigma^3 \rangle} x_i x_j g_{ij}(\sigma_{ij}) = \sum_j x_j g_{wj}, \quad (13)$$

where  $g_{wj}$  is the wall-particle correlation function at contact. Since a hard wall can be seen as a sphere of infinite diameter [26], the contact value  $g_{wj}$  can be obtained from  $g_{ij}(\sigma_{ij})$  as

$$g_{wj} = \lim_{\substack{\sigma_i \rightarrow \infty \\ x_i \sigma_i^3 \rightarrow 0}} g_{ij}(\sigma_{ij}). \quad (14)$$

In the special case of a pure fluid plus a hard wall, Eq. (13) becomes

$$\lim_{\substack{\sigma_2 \rightarrow \infty \\ x_2 \sigma_2^3 \rightarrow 0}} g_{12}(\sigma_{12}) = 1 + 4\eta g_p(\eta) \equiv Z_p(\eta), \quad (15)$$

where  $Z_p(\eta)$  is the compressibility factor of the pure fluid.

Assuming the validity of the ansatz (10), conditions (11), (12), (13) and (15) become

$$G(\eta, 0) = \frac{1}{1 - \eta}, \quad (16)$$

$$G(\eta, 1) = g_p(\eta), \quad (17)$$

$$1 + 4\eta \sum_{i,j} \frac{\sigma_{ij}^3}{\langle \sigma^3 \rangle} x_i x_j G(\eta, z_{ij}) = \sum_j x_j G(\eta, z_{wj}), \quad z_{wj} \equiv 2\sigma_j \frac{\langle \sigma^2 \rangle}{\langle \sigma^3 \rangle}, \quad (18)$$

$$G(\eta, 2) = Z_p(\eta), \quad (19)$$

respectively. Conditions (16), (17) and (19) are fulfilled by the quadratic proposal [22, 25]

$$G_{e2}(\eta, z) = \frac{1}{1 - \eta} + \left[ g_p(\eta) - \frac{1}{1 - \eta} \right] z + \left[ \frac{1 - \eta/2}{1 - \eta} - (1 - 2\eta)g_p(\eta) \right] z(z - 1). \quad (20)$$

However,  $G_{e2}$  does not satisfy Eq. (18) for an arbitrary number of components  $N \geq 3$ . This is accomplished by a cubic form [23–25]:

$$G_{e3}(\eta, z) = G_{e2}(\eta, z) + (1 - \eta) [g_p^{\text{SPT}}(\eta) - g_p(\eta)] z(z - 1)(z - 2), \quad (21)$$

where

$$g_p^{\text{SPT}}(\eta) = \frac{1 - \eta/2 + \eta^2/4}{(1 - \eta)^3} \quad (22)$$

is the SPT contact value of the pure fluid. The proposals  $G_{e2}$  and  $G_{e3}$  are very flexible in the sense that they can accommodate any reasonable choice for  $g_p(\eta)$ . In particular if  $g_p(\eta) = g_p^{\text{SPT}}(\eta)$  then  $G_{e2}(\eta, z) = G_{e3}(\eta, z)$  and one recovers the SPT contact values given in Eq. (5).

Taking either the  $g_p(\eta)$  values that follow from the Carnahan–Starling or the Carnahan–Starling–Kolafa (CSK) EOS as input, both approximations  $G_{e2}$  and  $G_{e3}$  yield in general very good predictions for  $g_{ij}(\sigma_{ij})$  in binary and polydisperse mixtures under a wide range of conditions [22–25], which typically implies  $z_{ij} \leq 2$ . However, in the case of very disparate mixtures, the parameter  $z_{ij}$  can take larger values. For instance, in a binary mixture with  $R > 1$  one has

$$z_{22}(x_2, R) = R \frac{1 - x_2 + x_2 R^2}{1 - x_2 + x_2 R^3}. \quad (23)$$

The behaviour of  $z_{22}$  as a function of  $1/R$  is shown in Fig. 1 for different values of  $x_2$ . It follows that, at fixed  $x_2$ , there exists a value  $R = R_{\text{max}}(x_2)$  at which  $z_{22}$  reaches a maximum  $z_{22}^{\text{max}}(x_2)$ . The peak  $z_{22}^{\text{max}}(x_2)$  becomes narrower and higher as  $x_2$  decreases, its location moving to the left (larger values of  $R$ ). An

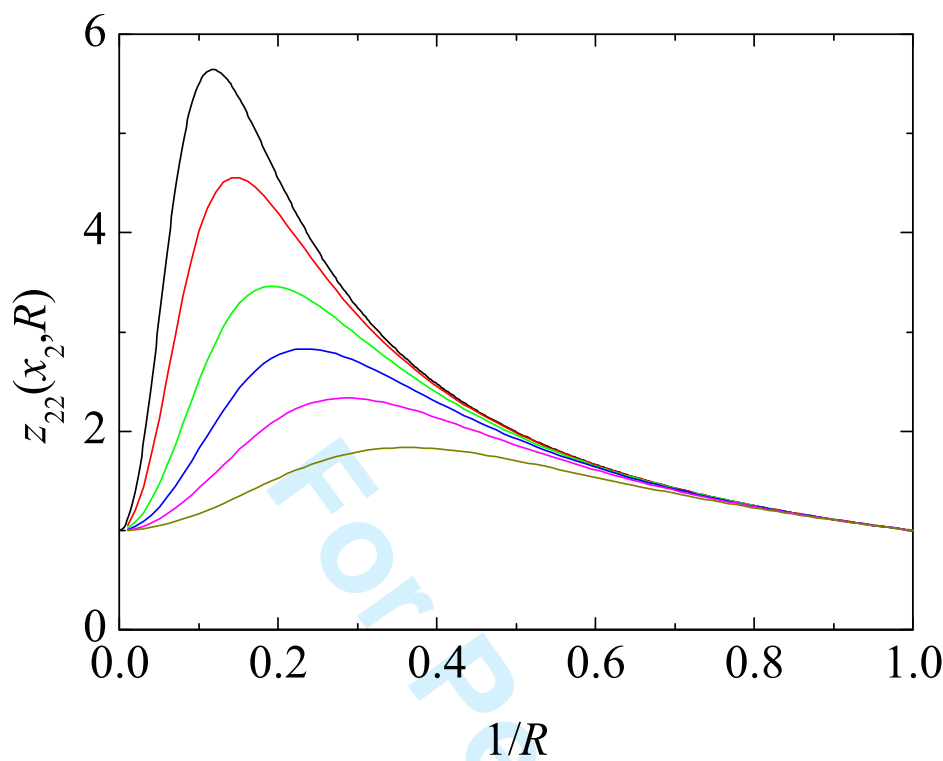


Figure 1. (Colour online) Plot of  $z_{22}(x_2)$  as a function of  $1/R$  for, from top to bottom,  $x_2 = 0.001, 0.002, 0.005, 0.01, 0.02$  and  $0.05$ .

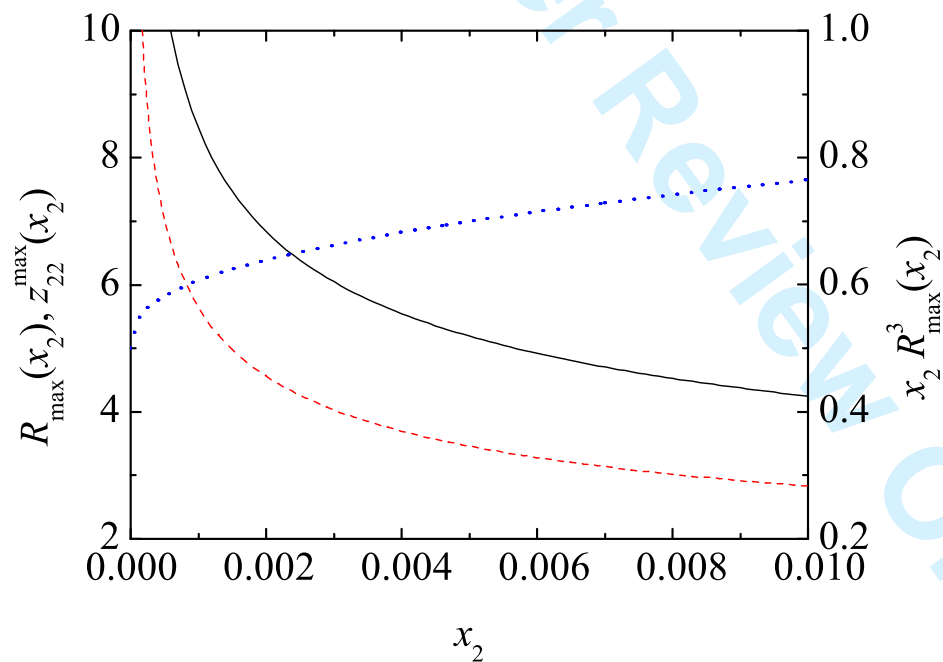


Figure 2. (Colour online) Plot of  $R_{\max}(x_2)$  (solid line) and the corresponding  $z_{22}^{\max}(x_2)$  (dashed line). Also shown is the behaviour of the quantity  $x_2 R_{\max}^3(x_2)$  (dotted line, right vertical scale) as a function of  $x_2$ .

explicit expression for  $R_{\max}(x_2)$  can be derived by differentiation of  $z_{22}$  with respect to  $R$ , which yields a cubic equation for  $R$  whose real solution is

$$R_{\max}(x_2) = \frac{1}{2} \left[ 1 + (2x_2^{-1} + 2x_2^{-1}\sqrt{1-x_2} - 1)^{1/3} + (2x_2^{-1} + 2x_2^{-1}\sqrt{1-x_2} - 1)^{-1/3} \right]. \quad (24)$$

A plot of  $R_{\max}(x_2)$  and the associated values of  $z_{22}^{\max}(x_2)$  is shown in Fig. 2. In the limit  $x_2 \rightarrow 0$  one gets



$R_{\max} \rightarrow (2x_2)^{-1/3}$ , so that  $\lim_{x_2 \rightarrow 0} x_2 R_{\max}^3 = 1/2$ . For  $x_2 > 0$  one has  $x_2 R_{\max}^3 > 1/2$ . This means that, when  $z_{22}$  reaches its maximum value, the partial volume fraction occupied by the big spheres is always larger than half the one occupied by the small ones. Figure 2 shows that  $z_{22}^{\max}(x_2)$  can reach rather high values for sufficiently small  $x_2$ . In particular,  $z_{22}^{\max}(x_2) > 2$  if  $x_2 \leq 0.036$ , irrespective of the value of  $R$ . Since  $G(\eta, z)$  is a monotonically increasing function of  $z$ , the larger  $z_{22}$ , the higher  $g_{22}(\sigma_2)$ . Thus, Eq. (24) gives the value of  $R$  at which  $g_{22}(\sigma_2)$  has a maximum, according to the ansatz (10). Note that  $R^{\max}(x_2)$  is independent of  $\eta$ .

The polynomial forms (20) and (21) are constructed by imposing exact properties at  $z = 0$ ,  $z = 1$  and  $z = 2$ . On the other hand, in disparate mixtures where one can have values of  $z$  higher than 2, Eqs. (20) and (21) are not accurate enough. In fact, again in the binary case, there exists evidence indicating that  $g_{22}(\sigma_2)$  grows exponentially for large  $R$ , as explicitly incorporated in the AH proposal [20], Eq. (9). This translates, in the context of the ansatz (10), into an exponential dependence of  $G(\eta, z)$  on  $z$  for large  $z$ . Thus, here we propose to amend Eqs. (20) and (21) as

$$G_{e2+}(\eta, z) = \begin{cases} G_{e2}(\eta, z), & 0 \leq z \leq 2, \\ Z_p(\eta) \exp[A_{e2}(\eta)(z - 2)], & 2 \leq z, \end{cases} \quad (25)$$

$$G_{e3+}(\eta, z) = \begin{cases} G_{e3}(\eta, z), & 0 \leq z \leq 2, \\ Z_p(\eta) \exp[A_{e3}(\eta)(z - 2)], & 2 \leq z, \end{cases} \quad (26)$$

where  $A_{e2}(\eta)$  and  $A_{e3}(\eta)$  are determined by requiring continuity of the first derivative at the matching point  $z = 2$ . Their expressions are

$$A_{e2}(\eta) = \frac{1}{Z_p(\eta)} \left[ \frac{2 - 3\eta/2}{1 - \eta} - 2(1 - 3\eta)g_p(\eta) \right], \quad (27)$$

$$A_{e3}(\eta) = \frac{1}{Z_p(\eta)} \left[ \frac{4 - 9\eta/2 + \eta^2}{1 - \eta} - 4(1 - 2\eta)g_p(\eta) \right]. \quad (28)$$

Note that the amended proposals (25) and (26) also share with Eqs. (20) and (21) the flexibility to accommodate any reasonable choice for  $g_p$ . In what follows we will use the one corresponding to the CSK EOS, namely

$$g_p^{\text{CSK}}(\eta) = \frac{1 - \eta/2 + \eta^2(1 - 2\eta)/12}{(1 - \eta)^3}. \quad (29)$$

### 3 Comparison with simulation data

Once the new universal proposals have been introduced, the question now arises as to whether the available simulation data are consistent with the universality ansatz. Were this to be the case, for a given packing fraction  $\eta$  plots of  $g_{ij}$  vs  $z_{ij}$  of different mixtures should lie on a common curve and this will be tested next.

The approximations  $G_{e2}(\eta, z)$ ,  $G_{e3}(\eta, z)$ ,  $G_{e2+}(\eta, z)$  and  $G_{e3+}(\eta, z)$ , given in Eqs. (20) (21), (25) and (26), respectively, complemented with the CSK expression for  $g_p(\eta)$  given in Eq. (29), are compared with simulation data of  $g_{ij}(\sigma_{ij})$  [20, 27] in Figs. 3–6. We can observe that  $G_{e2}$  and  $G_{e3}$  perform very well for  $0 < z < 2$ , except for the higher values of  $g_{22}(\sigma_2)$  in that region (see the insets of Figs. 3–6). Since, by construction, both  $G_{e2}$  and  $G_{e3}$  give the correct value at  $z = 2$  [cf. Eq. (19)], the deviations of the simulation values of  $g_{22}(\sigma_2)$  from the theoretical curves in the region  $0 < z < 2$  can be interpreted as a



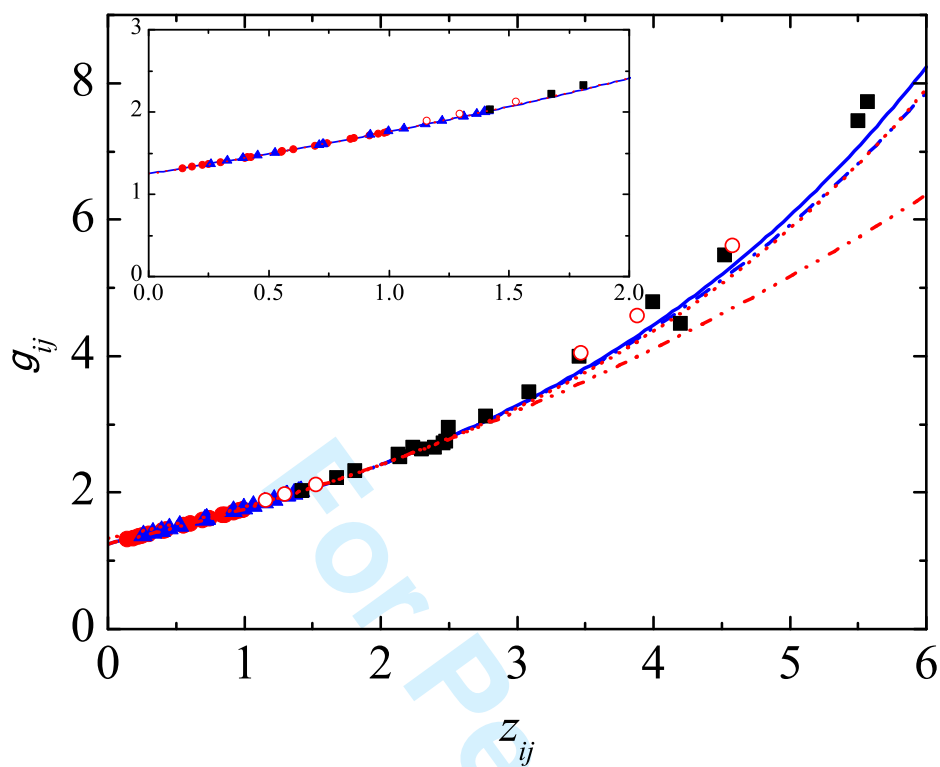


Figure 3. (Colour online) Plot of  $g_{ij}(\sigma_{ij})$  as a function of  $z_{ij}$  for  $\eta = 0.2$ . Dash-dot-dot line:  $G_{e2}(\eta, z)$ ; dash-dot line:  $G_{e3}(\eta, z)$ ; dotted line:  $G_{e2+}(\eta, z)$ ; solid line:  $G_{e3+}(\eta, z)$ ; solid circles: simulation data of  $g_{11}(\sigma_1)$  from Ref. [20]; solid triangles: simulation data of  $g_{12}(\sigma_{12})$  from Ref. [20]; solid squares: simulation data of  $g_{22}(\sigma_2)$  from Ref. [20]; open circles: simulation data of  $g_{w1}$  and  $g_{w2}$  from Ref. [27]. The inset shows the region  $0 \leq z_{ij} \leq 2$ . Note that  $G_{e2+}(\eta, z)$  and  $G_{e3}(\eta, z)$  are practically indistinguishable at this density.

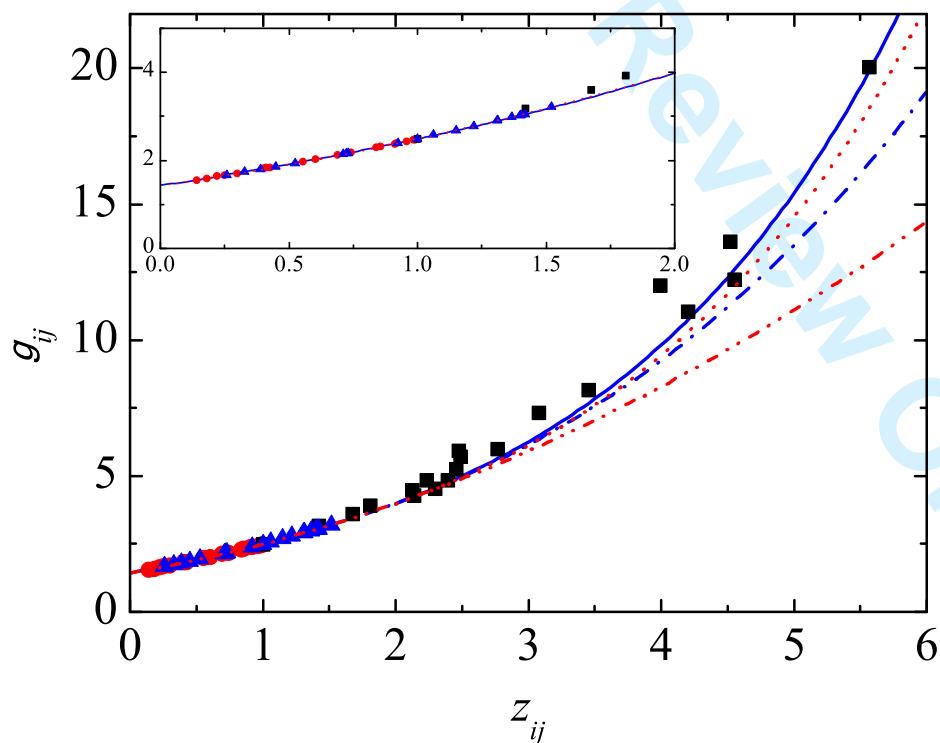


Figure 4. (Colour online) Same as in Fig. 3, but for  $\eta = 0.3$ . At this density there are no simulation data for  $g_{wj}$ .

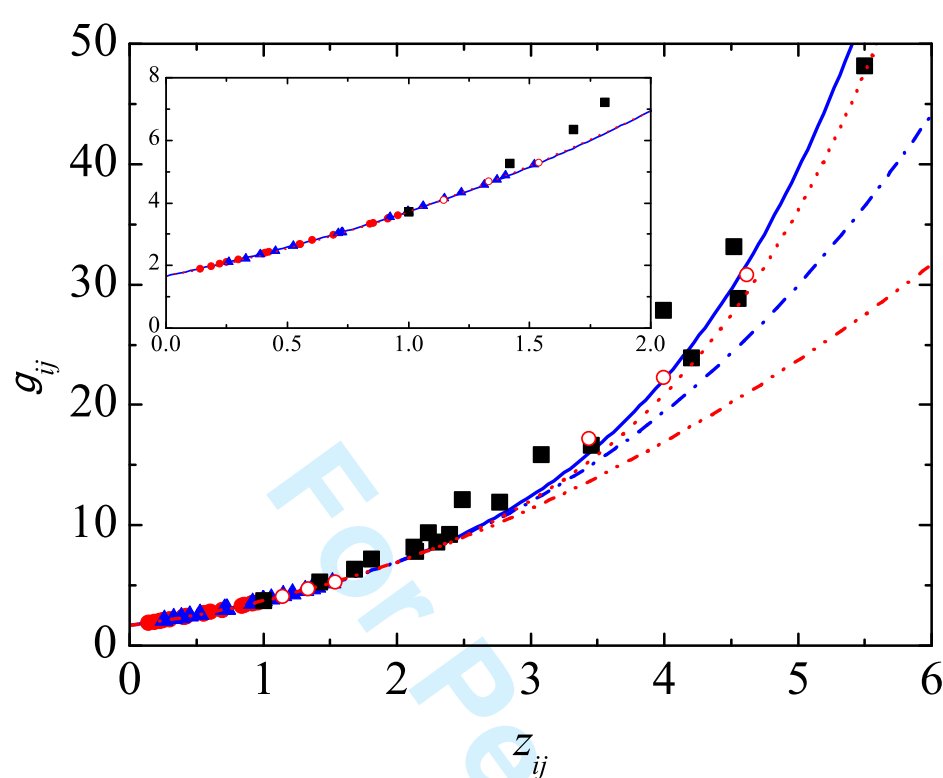


Figure 5. (Colour online) Same as in Fig. 3, but for  $\eta = 0.4$ .

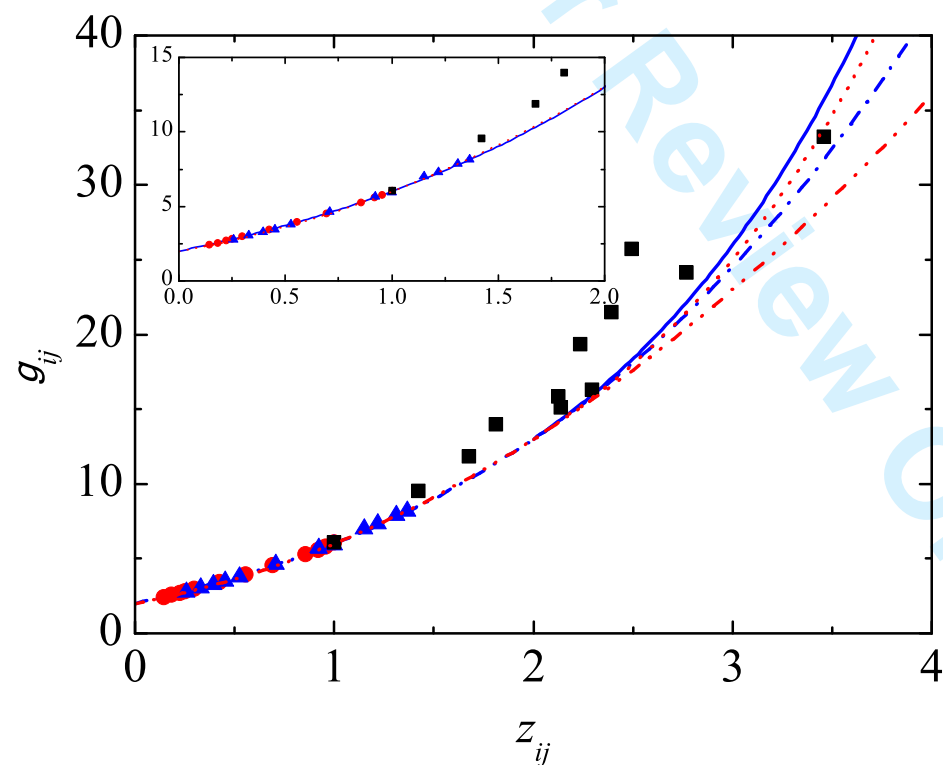


Figure 6. (Colour online) Same as in Fig. 3, but for  $\eta = 0.5$ . At this density there are no simulation data for  $g_{wj}$ .

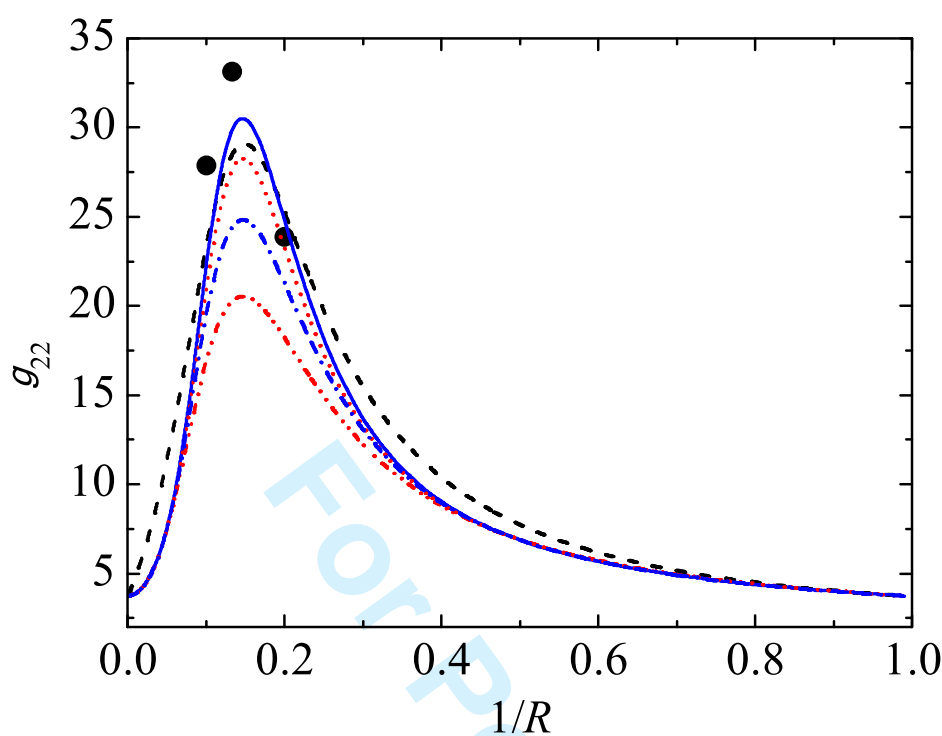


Figure 7. (Colour online) Plot of  $g_{22}(\sigma_2)$  as a function of  $1/R$  for  $\eta = 0.4$  and  $x_2 = 0.002$  (as given by different approximations) and simulation results from Ref. [20]. Dash-dot-dot line:  $g_{22}^{e2}(\sigma_2)$ ; dash-dot line:  $g_{22}^{e3}(\sigma_2)$ ; dotted line:  $g_{22}^{e2+}(\sigma_2)$ ; solid line:  $g_{22}^{e3+}(\sigma_2)$ ; dashed line:  $g_{22}^{AH}(\sigma_2)$ ; solid circles: simulation data of  $g_{22}(\sigma_2)$  from Ref. [20].

manifestation of the approximate character of the universality ansatz (10). This seems to be confirmed by the scatter of the simulation data of  $g_{22}(\sigma_2)$  for  $z > 2$ . On the other hand, the overall behaviour of  $g_{22}(\sigma_2)$  in that region seems to be reasonably well captured by both  $G_{e2+}$  and  $G_{e3+}$ .

Once the question of universality has been examined, in order to complement the perspective of the present results, in Figs. 7–10 we illustrate some other issues. In particular, we want to assess the performance of the theoretical approximations obtained with the universality assumption, denoted by  $g_{22}^*(\sigma_2)$  (where the asterisk will be either  $e2$ ,  $e3$ ,  $e2+$  or  $e3+$  depending on whether one uses  $G_{e2}(\eta, z)$ ,  $G_{e3}(\eta, z)$ ,  $G_{e2+}(\eta, z)$  or  $G_{e3+}(\eta, z)$ , respectively, to compute the contact value) and that of the AH approximation  $g_{22}^{AH}(\sigma_2)$  [cf. Eq. (9)] as compared to simulation data. Hence, in Fig. 7 we have plotted  $g_{22}(\sigma_2)$  as a function of  $1/R$  taking  $x_2 = 0.002$  and  $\eta = 0.4$ , while in Fig. 8 the large-large contact value has been plotted as a function of  $x_2$  for  $\eta = 0.4$  and  $R = 5$ . These plots suggest that the new approximations may indeed improve the already reasonable agreement between the AH formula and simulation results, but all theories seem to underestimate the height of the peak in the  $g_{22}(\sigma_2)$  vs.  $1/R$  plot. The region of interest, namely relatively large  $R$  and small  $x_2$ , is further examined in Figs. 9 and 10 which illustrate two additional points. On the one hand, one can clearly see that the curves are almost indistinguishable for low densities (up to  $\eta \simeq 0.2$  in these cases) but at higher densities the new proposals  $G_{e2+}(\eta, z)$  and  $G_{e3+}(\eta, z)$  indeed improve on the performance of the earlier ones  $G_{e2}(\eta, z)$  and  $G_{e3}(\eta, z)$ . On the other hand, they also show that, in the high density region, the AH formula performs a little bit better than either  $G_{e2+}(\eta, z)$  or  $G_{e3+}(\eta, z)$  as  $R$  becomes larger.

#### 4 Concluding remarks

The above results deserve some further consideration. In this paper, following the universality approach that some of us have followed for some years, we have introduced two new proposals [cf. Eqs. (25) and (26)] for the contact values of HS mixtures which improve on the earlier proposals in the case where one has disparate in size mixtures. These proposals fulfill certain exact conditions and are rather flexible, requiring as their only input the contact value of the one-component system.

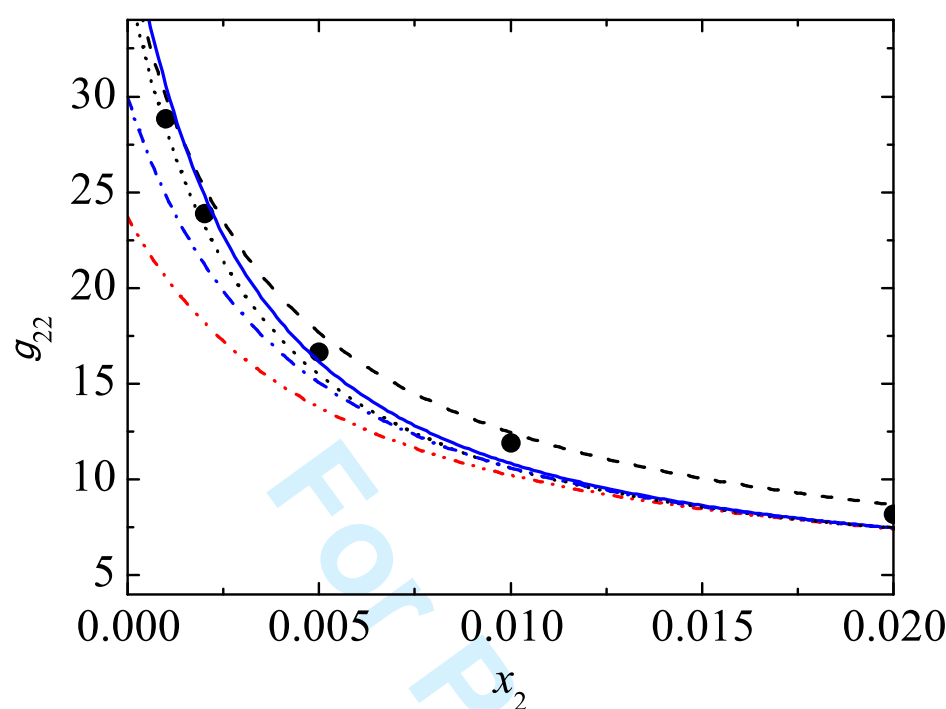


Figure 8. (Colour online) Plot of  $g_{22}(\sigma_2)$  as a function of  $x_2$  for  $\eta = 0.4$  and  $R = 5$  (as given by different approximations) and simulation results from Ref. [20]. Dash-dot-dot line:  $g_{22}^{e2}(\sigma_2)$ ; dash-dot line:  $g_{22}^{e3}(\sigma_2)$ ; dotted line:  $g_{22}^{e2+}(\sigma_2)$ ; solid line:  $g_{22}^{e3+}(\sigma_2)$ ; dashed line:  $g_{22}^{AH}(\sigma_2)$ ; solid circles: simulation data of  $g_{22}(\sigma_2)$  from Ref. [20].

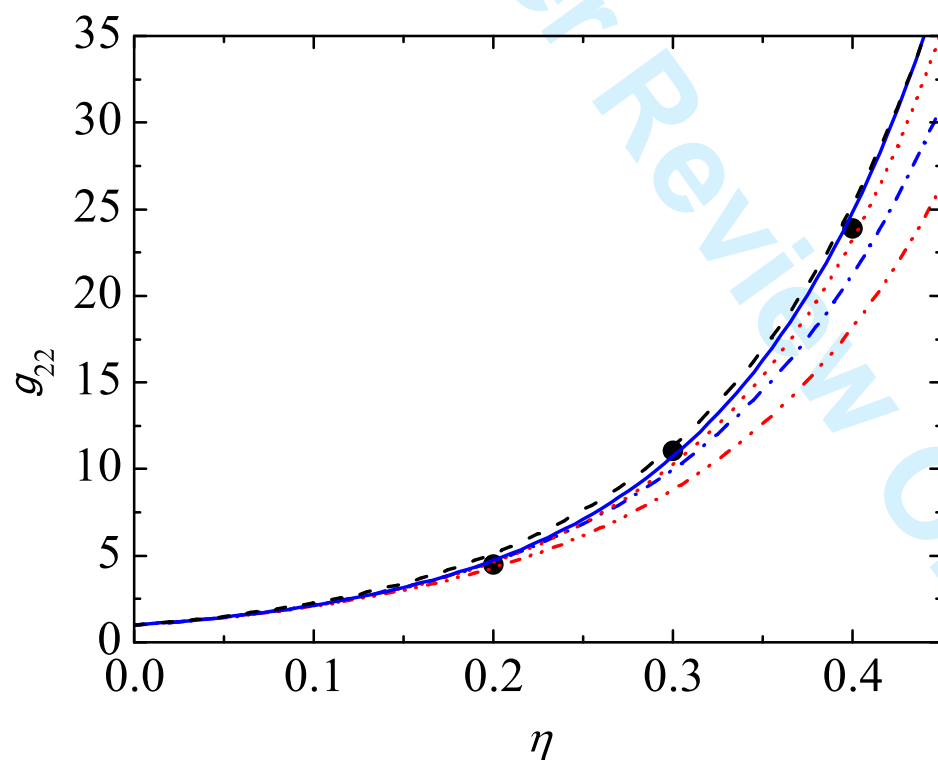


Figure 9. (Colour online) Plot of  $g_{22}(\sigma_2)$  as a function of  $\eta$  for  $x_2 = 0.002$  and  $R = 5$  (as given by different approximations) and simulation results from Ref. [20]. Dash-dot-dot line:  $g_{22}^{e2}(\sigma_2)$ ; dash-dot line:  $g_{22}^{e3}(\sigma_2)$ ; dotted line:  $g_{22}^{e2+}(\sigma_2)$ ; solid line:  $g_{22}^{e3+}(\sigma_2)$ ; dashed line:  $g_{22}^{AH}(\sigma_2)$ ; solid circles: simulation data of  $g_{22}(\sigma_2)$  from Ref. [20].

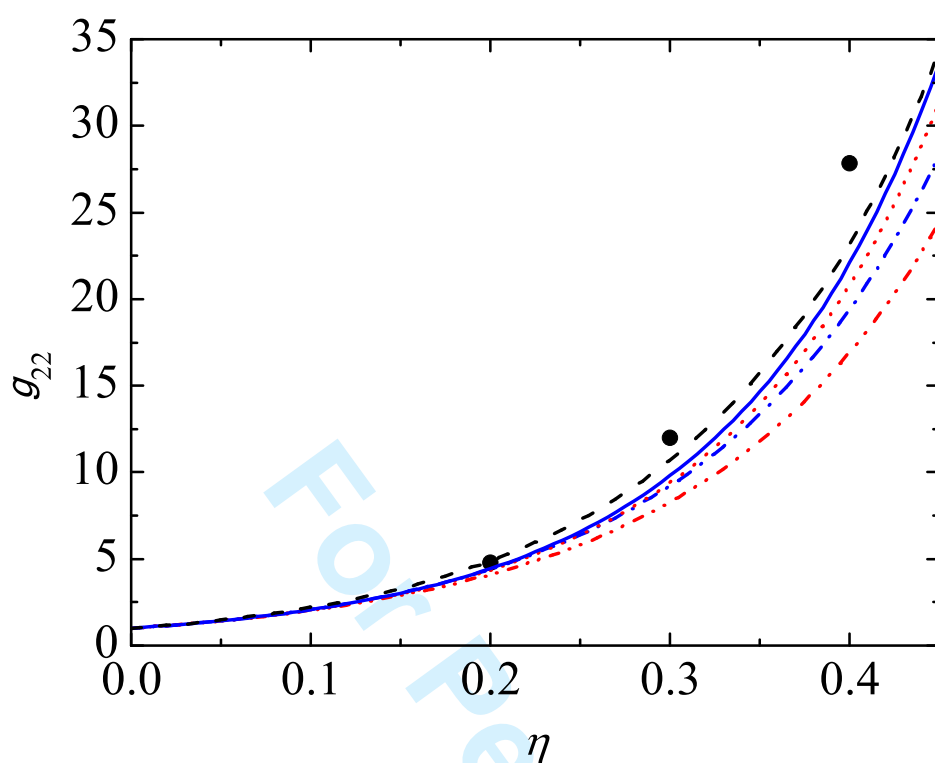


Figure 10. (Colour online) Same as in Fig. 9, but for  $x_2 = 0.002$  and  $R = 10$ .

The comparison with recent computer simulation data [20,27] indicates that the universality assumption may have some limitations but, since there are many technical difficulties in simulating mixtures with large  $R$  and very small  $x_2$ , one cannot reach definite conclusions on this issue on the basis of these limited data. On the other hand, the new proposals following the universality assumptions for the large-large contact values seem nevertheless to yield reasonably good agreement both with the simulation results and with the recent proposal by Alawneh and Henderson [20].

It is clear that the AH formulae do not obey the ansatz (10). First, the non-universal character of Eq. (7) is due to the appearance of the combination  $\langle\sigma\rangle\langle\sigma^3\rangle/\langle\sigma^2\rangle^2$ . In addition, the values given by Eqs. (8) and (9) depend on  $1 - R^{-n}$ . As mentioned above, our analysis of the universality issue in the light of the simulation results suggests that the ansatz (10) may break down at some point and hence whether the AH proposal is universal or not would not be particularly relevant. However, a more serious problem with the AH formulae is that Eq. (9) fails to reduce to the exact result to first order in  $\eta$  given in Eq. (2). In contrast, all the universal approximations quoted in this paper as well as the VS approximation yield such result in the appropriate limit. Whether or not the universality feature is confirmed or discarded depends on the availability of further simulation results. Our hope is that this paper may encourage the performance of such simulations.

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