

# A Critique of Some Recent Suggestions to Correct the Kirkwood–Buff Integrals

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This article is a thorough critique of some recent publications by Matteoli, Lepori, Ruckenstein and others who suggested a correction to the Kirkwood–Buff integrals to obtain “better” information on the molecular interactions. It is shown that the suggested “corrected” Kirkwood–Buff integrals are, in fact, less informative than the original integrals. A detailed and critical examination of the arguments that led to the suggested correction reveals some serious flaws. Therefore, it is argued that the corrected Kirkwood–Buff integrals should be “recorrected” to restore their original definition and meaning.

## 1. Introduction

In a recent paper,<sup>1</sup> Matteoli has suggested a new method for interpreting the Kirkwood–Buff (KB) integrals. It was claimed that “a reference state is necessary for the *correct* interpretation of the Kirkwood–Buff integrals,  $G_{ij}$ , of liquid mixtures in terms of interactions between components.” It was also added that “...the present new treatment provides either different or new information in regard to preferential solvation and molecular interactions, with respect to the usual way of examining  $G_{ij}$  data”.

This article is devoted to a critical examination and eventually a refutation of Matteoli’s claims as well as some other similar claims.

Before dwelling on the details, we comment on the general claim that, by using the “corrected”  $G_{ij}$  values with reference to symmetrical ideal (SI) solutions, one can get “better” information on the molecular interactions. This claim can be immediately rejected from the outset; none of the KB integrals provide any information on *molecular interactions*.<sup>2</sup> All of the information provided by the KB integrals is concerned with local densities around a selected molecule. These are dependent in a very complex way on all of the *molecular interactions* in the system. The latter quantities *cannot* be derived from the KB integrals, certainly not by the newly corrected quantities. Furthermore, no “wrong information may be inferred” by using the original KB integrals as claimed by Matteoli.<sup>1</sup>

As I have discussed in a recent monograph,<sup>3</sup> the original KB integrals are useful in providing important information on *local* densities, on the preferential solvation around each species, and on deviations from SI solutions. On page 9801 of the article,<sup>1</sup> the author writes “the analytical expressions of the  $G_{ij}$  of this reference mixture, for which *by definition*, all interactions between species are *indistinguishable*.” Unfortunately, the SI solution is, *by definition*, not characterized by *indistinguishable intermolecular interactions*. Clearly, when all of the intermolecular interactions are indistinguishable, all of the  $G_{ij}$ ’s become equal; hence, there is no preferential solvation (PS). The *necessary* condition for SI solutions is not “indistinguishable” interaction but rather

$$\begin{aligned}\Delta_{AB} &= G_{AA} + G_{AB} - 2G_{AB} \\ &= (G_{AA} - G_{AB}) + (G_{BB} - G_{AB}) = 0\end{aligned}\quad (1.1)$$

Clearly, the condition (1.1) *does not* imply anything regarding the *intermolecular interactions*. This, in itself, already invalidates the Matteoli procedure to obtain more “meaningful” local information. In the next section, we briefly outline the Matteoli procedure. In section 3, we present some numerical results for a simple solvable system where all of the KB integrals (KBIs) can be calculated explicitly. In section 4, we briefly discuss an approximate relation between some KBIs that is observed experimentally. These approximate relations are not exact, however, and cannot be derived from the KB theory. In the Appendix, we shall speculate on the possible motivation for defining the corrected KBIs.

## 2. Procedure for Obtaining the Corrected Kirkwood–Buff Integrals

In this section, we present the procedure used by Matteoli, and others who followed,<sup>4–6</sup> to obtain the so-called “corrected values” of the KBIs.

The approach starts with the exact expressions for the KBIs, obtained by inversion of the KB theory.<sup>7–11</sup> These are for the two-component system

$$G_{AB} = G_{BA} = kT\kappa_T - \rho_T V_A V_B / Q \quad (2.1)$$

$$G_{AA} = kT\kappa_T - \frac{1}{\rho_A} + \frac{\rho_B V_B^2}{x_A Q}$$

$$G_{BB} = kT\kappa_T - \frac{1}{\rho_B} + \frac{\rho_A V_A^2}{x_B Q}$$

where

$$Q = x_A \left( \frac{\partial(\mu_A/kT)}{\partial x_A} \right)_{T,P} = 1 + x_A x_B \left[ \frac{\partial^2(g^{\text{EX}}/kT)}{\partial x_A^2} \right]_{T,P} \quad (2.2)$$

It is easy to show that  $\Delta_{AB} = 0$  is equivalent to  $Q = 1$ , that is, the condition for an SI solution. Plugging  $Q = 1$  into eq 2.1, we get the values of the KBIs in a *hypothetical* SI solution,

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that is,

$$\begin{aligned} G_{AB}^{\text{SI}} &= kT\kappa_T - \rho_T V_A V_B \\ G_{AA}^{\text{SI}} &= kT\kappa_T - \frac{1}{\rho_A} + \frac{\rho_B V_B^2}{x_A} \\ G_{BB}^{\text{SI}} &= kT\kappa_T - \frac{1}{\rho_B} + \frac{\rho_A V_A^2}{x_B} \end{aligned} \quad (2.3)$$

All of the quantities on the right-hand side (rhs) of eq 2.3 are to be evaluated at the *hypothetical SI* solution. Note that, here, the quantities defined in eq 2.3 satisfy the condition

$$\Delta_{AB}^{\text{SI}} = G_{AA}^{\text{SI}} + G_{BB}^{\text{SI}} - 2G_{AB}^{\text{SI}} = 0 \quad (2.4)$$

as it should be.

If one further assumes that the SI condition holds for an interval of pressures, so that the chemical potentials of the SI solutions can be differentiated twice with respect to  $P$ , one obtains the relations

$$\begin{aligned} V_A &= V_A^P \\ V_B &= V_B^P \\ (\rho_T)^{-1} &= x_A V_A^P + x_B V_B^P \end{aligned} \quad (2.5)$$

The isothermal compressibility in this ideal (id) system is given by

$$\kappa_T^{\text{id}} = \varphi_A \kappa_A^P + \varphi_B \kappa_B^P \quad (2.6)$$

where  $\varphi_A = x_A V_A^P / (x_A V_A^P + x_B V_B^P)$  and  $\kappa_A^P$  and  $\kappa_B^P$  are the isothermal compressibility of the pure A and B.

Thus, one gets the final results for these *hypothetical* KBIs

$$\begin{aligned} G_{AB}^{\text{id}} &= kT\kappa_T^{\text{id}} - \frac{V_A^P V_B^P}{x_A V_A^P + x_B V_B^P} \\ G_{AA}^{\text{id}} &= G_{AB}^{\text{id}} + (V_B^P - V_A^P) \\ G_{BB}^{\text{id}} &= G_{AB}^{\text{id}} + (V_A^P - V_B^P) \end{aligned} \quad (2.7)$$

Again, we note that the condition for SI solution is obeyed by the quantities defined in eq 2.7 as it should. However, it should be stressed that the  $G_{ij}^{\text{id}}$  values computed from these equations pertain to a *hypothetical SI* solution where, in addition to the assumption  $\Delta_{AB} = 0$ , valid for all compositions, one also assumes that this holds for an interval of pressures to allow the evaluation of first and second derivatives of the chemical potential with respect to  $P$ . The  $G_{ij}^{\text{id}}$ s from eq 2.7 are used to define the new corrected quantities

$$\Delta G_{ij} = G_{ij} - G_{ij}^{\text{id}} \quad (2.8)$$

The reason given for defining these new quantities is<sup>1</sup> “non-zero values of  $\delta x_{ij}$  and  $\delta y_{ij}$  in ideal systems are in a way odd...”; hence, “the interactions are masked by the ever present background of the reference ideal system. To avoid this, it is therefore necessary to clear  $G_{ij}$  of the background by considering the difference  $\Delta G_{ij} = G_{ij} - G_{ij}^{\text{id}}$ ”

As it was pointed out in the original articles about PS,<sup>11</sup> there is nothing “odd” about the findings that ideal solutions do show PS. Therefore, there is no need to “clear  $G_{ij}$  of the background”. *Ideal solutions* and preferential solvation are two different properties of the solution.

Clearly, since  $G_{ij}^{\text{id}}$  pertains to a hypothetical SI system, the resulting corrected quantities are also relevant to this hypothetical system. As discussed in ref 3, the original values of the KBIs, as well as those of PS, are already measured with respect to a “reference state”, that is, a randomly chosen element of volume in the liquid. There is no need to subtract any “ideal” values from the original  $G_{ij}$ . The original KBIs are well-defined quantities and convey meaningful and significant information on the mode of packing of the two components on a microscopic level. If one insists on using a reference state, why not choose an ideal gas state where all  $U_{ij} \equiv 0$ ? In which case, also all  $g_{ij} \equiv 1$  and  $G_{ij} \equiv 0$ . However, this will just bring us back to the original KBI.

In the Appendix, we shall speculate on the possible motivation for extracting an ideal part of the KB integrals. It will be shown that such an extraction is very useful in obtaining excess thermodynamic quantities for mixtures. It is useful, since the excess quantities, thus obtained, are devoid of an undesirable divergence of the chemical potential. However, such a procedure is not useful for the KB integrals.

I believe that the source of the problem stems from eq 4 in Matteoli’s and Lepori’s article,<sup>4</sup> which is rewritten here in their own notation

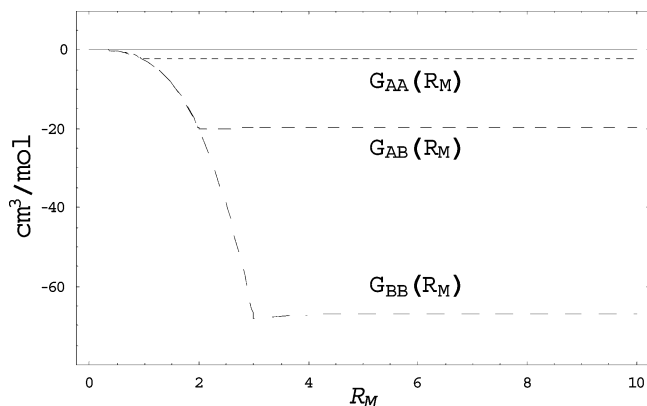
$$\Delta V_{ji} \equiv \bar{V}_j \Delta n'_{ji} = -\bar{V}_i \Delta n'_{ii} \equiv -\Delta V_{ii} \quad (2.9)$$

Here,  $\bar{V}_j$  is the partial molar volume of species  $j$  and  $\Delta n'_{ji} = c_j(G_{ij} - G_{ij}^{\text{id}})$ , where  $c_j$  is the concentration of  $j$ .

First, note that  $\Delta V_{ji}$  is *defined* in eq 2.9 (as implied by the symbol “ $\equiv$ ” in eq 4 of the original article). Clearly,  $c_j G_{ij}$  is the excess or deficiency of  $j$  particles in the correlation region around an  $i$  particle.  $c_j G_{ij}^{\text{id}}$ , as we have pointed out, has the same meaning but in a hypothetical symmetrical ideal solution. Therefore, it is not clear what the physical meaning of  $\Delta n'_{ji}$  is. Though the quantity  $\bar{V}_j \Delta n'_{ji}$  is *well-defined*, in eq 2.9, its physical meaning is not clear. As it stands,  $V_{ji}$  is the volume change caused by addition of  $\Delta n'_{ji}$  to a solution where the partial molar volume of  $j$  is  $\bar{V}_j$ .

Whatever the meaning of  $\Delta V_{ji}$  is, one *cannot* *redefine* it, as Matteoli and Lepori did, by claiming that “ $\Delta V_{ji}$  can be *defined* as an excess solvation volume, i.e., the volume occupied (or left free) by the excess (or deficit) number of molecules surrounding the central  $i$  species owing only to the interactions among molecules.” This is clearly a *different* definition of  $\Delta V_{ji}$ . Since  $\Delta n'_{ji}$  is the *number* of particles, the volume occupied by such a number of particles is  $\Delta n'_{ji}/c_j$ , where  $c_j$  is the density of the  $j$ th species. This is clearly *different* from the definition of  $V_{ji}$  in eq 2.9 (unless one can show that  $c_j$  is equal to  $1/\bar{V}_j$ , which is not). Thus, we have two *different* definitions of the same quantity, the physical meaning of which is, at best, unclear.

Furthermore, whatever  $\Delta V_{ji}$  means, there is absolutely no justification for writing the equalities in eq 2.9. The justification for writing these equalities seems to be derived from the following statement:<sup>4</sup> “If  $\Delta n'_{ji}$  is positive,  $\Delta n'_{ii}$  must be negative, and the volume occupied by the excess  $j$  molecules must be equal to the volume left free by the  $i$  molecules.” This statement is totally unfounded. As is *well-known*, the KBIs are *defined* in an open system. They are related to the fluctuations



**Figure 1.** The three functions  $G_{ij}(R_M)$  for the system with the same parameters as those in eq 3.22 with  $n = 3$ .

and cross-fluctuations in the number of particles. Therefore, they can have any value: zero, positive, or negative independently. We shall present in the next section some numerical examples demonstrating the invalidity of these claims.

What remains is a procedure of transforming clear, well-defined, and meaningful quantities that provide *local* information on the surroundings of each molecule in the mixture into quantities that have, at best, an unclear meaning.

### 3. Some Numerical Illustrations

In this section, we examine the values of all the local quantities as well the corrected quantities in a system that slightly deviates from an ideal gas mixture. This example is important; a single specific contrary example is sufficient to refute a general claim. It is well-known that, within the second virial approximation, the pair correlation function is determined by the pair potential only, that is,

$$g_{ij}(R) = \exp[-\beta U_{ij}(R)] \quad (3.1)$$

The corresponding KBI in such a system is

$$G_{ij} = \int_0^\infty [g_{ij}(R) - 1] 4\pi R^2 dR \quad (3.2)$$

For a square well potential, it follows that

$$U_{ij}(R) = \begin{cases} \infty & \text{for } R \leq \sigma_{ij} \\ -\epsilon_{ij} & \text{for } \sigma_{ij} \leq R \leq \sigma_{ij} + \delta \\ 0 & \text{for } R > \sigma_{ij} + \delta \end{cases} \quad (3.3)$$

One can write

$$\begin{aligned} G_{ij} &= -\frac{4\pi\sigma_{ij}^3}{3} + \{\exp(\beta\epsilon_{ij}) - 1\} \frac{4\pi}{3} [(\sigma_{ij} + \delta)^3 - \sigma_{ij}^3] \\ &= -V_{ij} + I_{ij} \end{aligned} \quad (3.4)$$

The affinity between the two species has a negative contribution due to the repulsive part of the interaction potential and a positive contribution due to the attractive part. A similar split of  $G_{ij}$  can be done for Lennard-Jones particles. Note, however, that, in the general case,  $I_{ij}$  is determined by both the repulsive and the attractive parts of the potential function.

Before turning to some numerical calculation, it is instructive to examine the corrected quantities discussed in section 2. Within the second virial approximation, we have the expression for the chemical potential of component A

$$\mu_A(T, P, x_A) = kT \ln(x_A \Lambda_A^3) + kT \ln \beta P + PB_{AA} - P x_B^2 (B_{AA} + B_{BB} - 2B_{AB}) \quad (3.5)$$

The partial molar volume of A is

$$\bar{V}_A = \left( \frac{\partial \mu_A}{\partial P} \right)_{T, N_A, N_B} = \frac{kT}{P} + B_{AA} - x_B^2 (B_{AA} + B_{BB} - 2B_{AB}) \quad (3.6)$$

where

$$B_{ij} = -\frac{1}{2} \int_0^\infty \{\exp[-\beta U_{ij}(R) - 1]\} 4\pi R^2 dR \quad (3.7)$$

If the system is a SI solution, then

$$\bar{V}_A = \frac{kT}{P} + B_{AA} = V_A^p \quad (3.8)$$

and similarly

$$\bar{V}_B = \frac{kT}{P} + B_{BB} = V_B^p \quad (3.9)$$

The compressibility of the SI system is thus

$$\kappa_T^{\text{id}} = \varphi_A \kappa_A^p + \varphi_B \kappa_B^p = \frac{1}{P} - \frac{x_A B_{AA} + x_B B_{BB}}{kT} \quad (3.10)$$

We have all the quantities to calculate the hypothetical  $G_{ij}^{\text{id}}$ 's in this system. Thus, the values of  $G_{ij}^{\text{id}}$  in a SI solution, eq 2.7, became

$$G_{AB}^{\text{id}} = kT \kappa_T^{\text{id}} - \frac{V_A^p V_B^p}{x_A V_A^p + x_B V_B^p} \approx -(B_{AA} + B_{BB}) \quad (3.11)$$

$$G_{AA}^{\text{id}} = -2B_{AA} \quad (3.12)$$

$$G_{BB}^{\text{id}} = -2B_{BB} \quad (3.13)$$

Hence, the corrected values as defined by Matteoli are

$$\Delta G_{AA} \equiv G_{AA} - G_{AA}^{\text{id}} = 0 \quad (3.14)$$

$$\Delta G_{BB} \equiv G_{BB} - G_{BB}^{\text{id}} = 0 \quad (3.15)$$

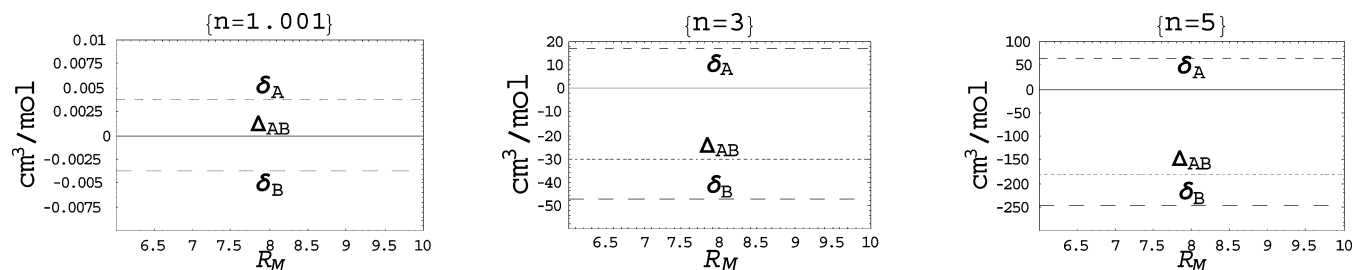
$$\begin{aligned} \Delta G_{AB} &= G_{AB} - G_{AB}^{\text{id}} \\ &= G_{AB} + (B_{AA} + B_{BB}) = \\ &\quad -2B_{AB} + B_{AA} + B_{BB} = -\frac{1}{2} \Delta_{AB} \end{aligned} \quad (3.16)$$

Equations 3.14–3.16 clearly show that the corrected values have no meaning as affinities. Both  $\Delta G_{AA}$  and  $\Delta G_{BB}$  are zero, and  $\Delta G_{AB}$  is nothing but  $\Delta_{AB}$ , that is, the measure of nonideality in this system.

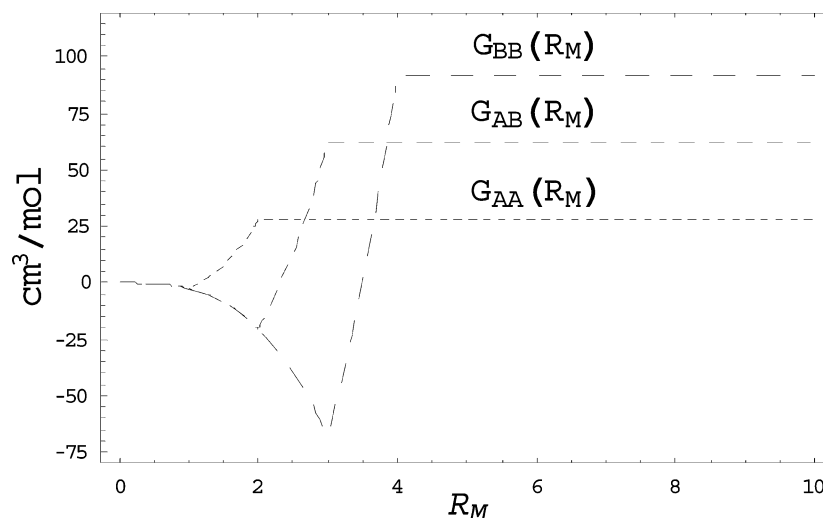
The limiting coefficients of the PS for A and B are in this system

$$\begin{aligned} \delta_{A,A}^0 &= x_A x_B (G_{AA} - G_{AB}) = -2x_A x_B (B_{AA} - B_{AB}) \\ \delta_{B,B}^0 &= x_A x_B (G_{BB} - G_{AB}) = -2x_A x_B (B_{BB} - B_{AB}) \end{aligned} \quad (3.17)$$

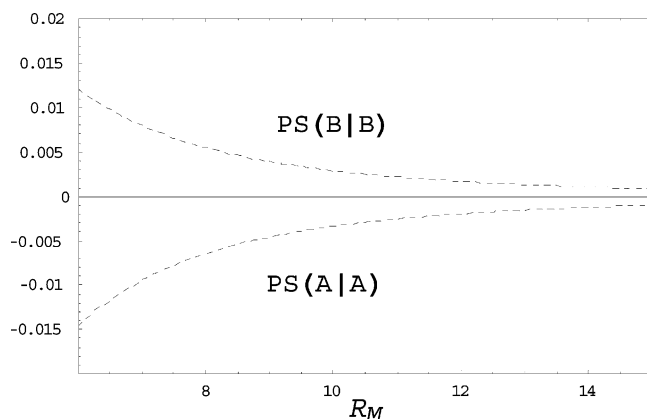
Note that  $\delta_{A,A}^0$  and  $\delta_{B,B}^0$  depend on both the repulsive and attractive parts of the intermolecular interactions and, in



**Figure 2.** Values of  $\Delta_{AB}$ ,  $\delta_A$ , and  $\delta_B$  for the system with the same parameters as those in eq 3.22 and different values of  $n$ .



**Figure 3.** Same as Figure 1 but with the same parameters as those in eq 3.23.



**Figure 4.** Limiting behavior of the PS of A and B at large  $R_M$  with the same parameters as those in eq 3.23.

principle, can have independent values and signs. On the other hand, the same coefficients when calculated by Matteoli's procedure are

$$\begin{aligned}\Delta\delta_{A,A} &= x_A x_B [\Delta G_{AA} - \Delta G_{AB}] = \frac{1}{2} x_A x_B \Delta_{AB} \\ \Delta\delta_{B,B} &= x_A x_B [\Delta G_{BB} - \Delta G_{AB}] = \frac{1}{2} x_A x_B \Delta_{AB}\end{aligned}\quad (3.18)$$

Thus, we see in this case none of the  $\Delta G_{ij}$ 's has the meaning of affinity, between A and B, as do the original quantities  $G_{ij}$ . Furthermore, the two corrected quantities in eq 3.18 have equal magnitudes and they do not have the meaning of preferential solvation. These results show clearly and definitely that the corrected quantities do not have the meaning claimed by Matteoli.

It should be added that, within this approximation, the solvation Gibbs energies of A and B are

$$\Delta G_A^* = 2kT(\rho_A B_{AA} + \rho_B B_{AB}) = 2kT\rho_T(x_A B_{AA} + x_B B_{AB}) \quad (3.19)$$

$$\Delta G_B^* = 2kT(\rho_A B_{AB} + \rho_B B_{BB}) = 2kT\rho_T(x_A B_{AB} + x_B B_{BB}) \quad (3.20)$$

Thus, in this approximation, the solvation Gibbs energies are linear in the mole fraction  $x_A$ .

We next present a sample of calculated results on  $G_{ij}$  and the corresponding derived quantities for a system of particles interacting via the Lennard-Jones pair potential, with different parameters  $\sigma_{ij}$  and  $\epsilon_{ij}$ .

Figure 1 shows the integrals

$$G_{ij}(R_M) = \int_0^{R_M} \{\exp[-\beta U(R)] - 1\} 4\pi R^2 dR \quad (3.21)$$

for the three pairs AA, AB, and BB for a system with parameters [with  $n = 3$ ]

$$\epsilon_{AA}/kT = \epsilon_{BB}/kT = \epsilon_{AB}/kT = 0.01$$

$$\delta = 1, \sigma_{AA} = 1, \sigma_{BB} = n\sigma_{AA}, \text{ and } \sigma_{AB} = (\sigma_{AB} + \sigma_{BB})/2 \quad (3.22)$$

All the curves start at zero at  $R_M = 0$ , then become negative in the region of the repulsive potential, and finally attain a constant value for  $R \geq \sigma_{ij} + \delta$ . Note that, in this case, the limiting values of  $G_{ij}$  (which are the KBIs) are all negative.

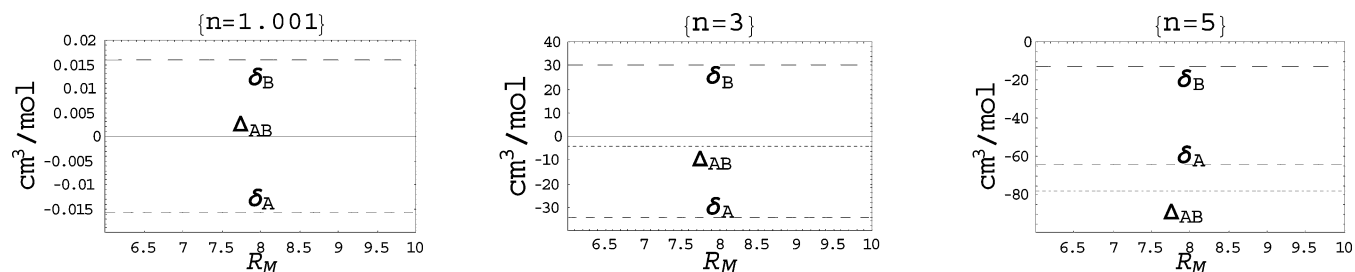


Figure 5. Same as Figure 2 but with the same parameters as those in eq 3.23.

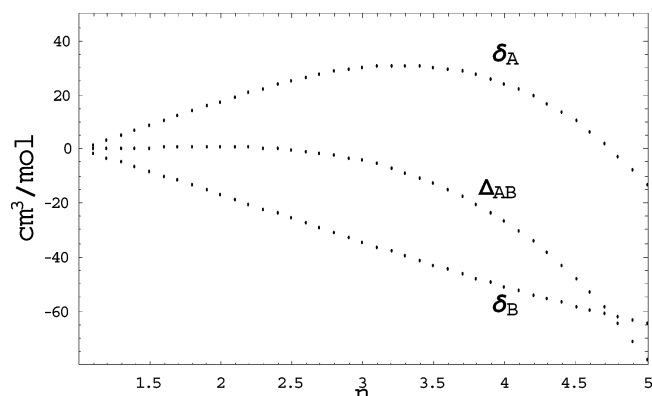


Figure 6. Variations of  $\Delta_{AB}$ ,  $\delta_A$ , and  $\delta_B$  with  $n$ , for a system with the same parameters as those in eq 3.23.

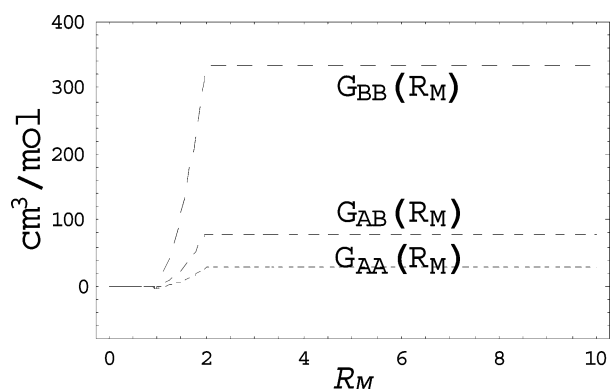


Figure 7. Same as Figure 1 but with the parameters given in eq 3.24 and  $n = 3$ .

This reflects the dominance of the repulsive interaction over the relative weak attractive part of the potential.

Figure 2 shows the values of  $\Delta_{AB}$ ,  $\delta_A$ , and  $\delta_B$  for three different values of  $n$  in eq 3.22. Note that, for  $n = 1.001$ , the system is nearly an SI solution; that is,  $\Delta_{AB} \approx 0$ ,  $\delta_A$  and  $\delta_B$  have different signs but are nearly equal in absolute magnitude. As we increase the size difference to  $n = 3$  and  $n = 5$ , the extent of nonideality becomes more and more negative.  $\delta_A$  and  $\delta_B$  now have different values but again different signs.

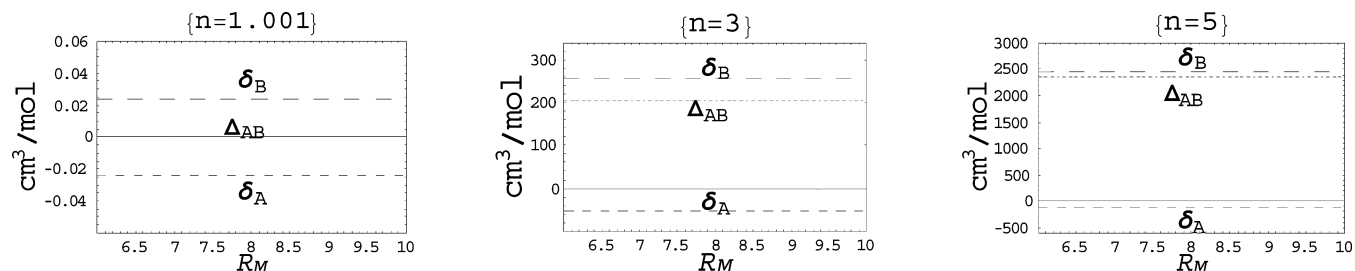


Figure 8. Same as Figure 2 but with the parameters of eq 3.24.

Figure 3 shows the values of  $G_{ij}(R_M)$  for a system with parameters as in eq 3.22, but with  $n = 3$  for this figure.

$$\epsilon_{AA}/kT = \epsilon_{BB}/kT = \epsilon_{AB}/kT = 1$$

$$\delta = 1, \sigma_{AA} = 1, \sigma_{BB} = n\sigma_{AA}, \sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2 \quad (3.23)$$

Note that here all three curves start as in Figure 1, but the limiting values of  $G_{ij}$  (i.e., the KB integrals) are all positive. In this case, the attractive part of the potential dominates the value of all  $G_{ij}$ , in contrast to the behavior shown in Figure 1.

Figure 4 shows the limiting behavior of the PS(A|A) and P(B|B) for the same parameters as those in eq 3.23, with  $n = 3$ , and at one composition,  $x_A = x_B = 1/2$ . Note that PS(A|A) and PS(B|B) approach zero at  $R_M$  from negative and positive values, respectively.

Figure 5 shows again the limiting values of  $\Delta_{AB}$ ,  $\delta_A$ , and  $\delta_B$  as in Figure 2 but with the parameters in eq 3.23. As in Figure 2, for  $n = 1.001$ , the system is almost an SI solution, and  $\delta_A$  and  $\delta_B$  have different signs but almost the same absolute values. When we increase the size difference to  $n = 5$ , we see that  $\Delta_{AB}$  becomes negative but  $\delta_A$  and  $\delta_B$  both become negative. More detailed dependence of these quantities on  $n$  is shown in Figure 6 corresponding to the same parameters as those in eq 3.23.

In the next three figures, we use the same model but with the same diameters and different  $\epsilon_{ij}$ 's, that is,

$$\epsilon_{AA}/kT = 1, \epsilon_{BB} = n\epsilon_{AA}, \epsilon_{AB} = \sqrt{\epsilon_{AA}\epsilon_{BB}}, \delta = 1, \sigma_{AA} = 1, \sigma_{BB} = 1, \sigma_{AB} = 1 \quad (3.24)$$

Figure 7 shows  $G_{ij}(R_M)$  for this system with  $n = 3$ . Note the larger limiting values of  $G_{ij}$  (the KBIs), reflecting the dominance of the attractive part of the potential.

Figure 8 shows similar plots to Figure 5, but now as an increase  $\Delta_{AB}$  becomes positive whereas  $\delta_A$  and  $\delta_B$  have different signs. A more detailed dependence of  $\Delta_{AB}$ ,  $\delta_A$ , and  $\delta_B$  on  $n$  is shown in Figure 9. Note that the behavior of these quantities is quite different from Figure 6. From this example, it is clear that  $\delta_A$  and  $\delta_B$  can have either the same or the opposite sign and that there is nothing "absurd" or "odd" in finding that  $\delta_A$  and  $\delta_B$  have opposite signs.



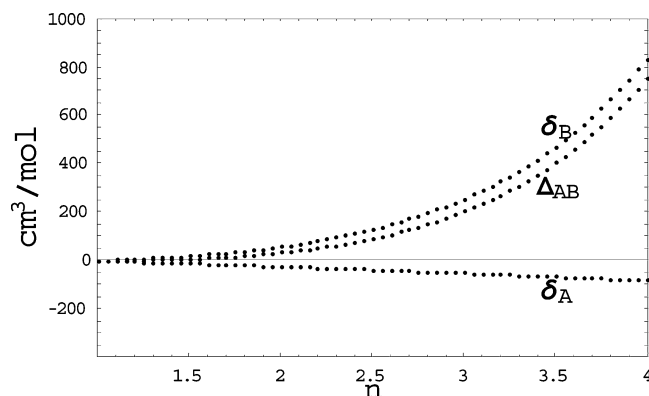


Figure 9. Same as Figure 7 but with the parameters of eq 3.24.

#### 4. Values of the KB Integrals at the “Edges” of the Composition Range

We examine here the values of  $G_{ij}$  and the derived quantities at the “edges” of the composition range,  $x_A \approx 0$  and  $x_A \approx 1$ . In these regions, we have

$$Q = \frac{x_A}{kT} \frac{\partial \mu_A}{\partial x_A} = 1 \quad (4.1)$$

At the edges of the composition range, the chemical potential is linear in  $kT \ln x_A$ . Therefore, one can easily obtain the results<sup>3</sup>

$$G_{AA} \text{ (at } x_A = 1) = kT\kappa_A \text{ (pure A)} - V_A^P \text{ (pure A)} \quad (4.2)$$

$$G_{AB} \text{ (at } x_A = 0) = kT\kappa_B \text{ (pure B)} - V_A^0 \text{ (at } x_A = 0) \quad (4.3)$$

Another interpretation of eqs 4.2 and 4.3 is

$$-G_{AA} \text{ (at } x_A = 1) = V_A^{*P} \text{ (the volume change to put A at a fixed position in pure A)} \quad (4.4)$$

$$-G_{AB} \text{ (at } x_A = 0) = V_A^{*0} \text{ (the volume change to put A at a fixed position in pure B)} \quad (4.5)$$

In all of the examples of real systems, at liquid densities, we observe that the two quantities in eqs 4.2 and 4.3 are nearly the same. This is probably a result of the small value of the term  $kT\kappa$  and nearly equal values of  $V_A^P$  and  $V_A^0$ . However, these are not exactly equal! There is no reason that these should be exact, neither for liquid mixtures<sup>3</sup> nor for gaseous mixtures, as discussed in section 3.

#### 5. Conclusion

The conclusion of the critical examination of the procedure of “correcting” the KB integrals is inevitable. One should abandon the corrected quantities in favor of the original KB integrals.

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#### Appendix

In this appendix, I take the liberty to speculate on the possible motivation for seeking corrected KB integrals, by subtracting

an ideal KBI. My speculation is based on a comment by one reviewer who wrote “ $\Delta G_{ij}$  are to  $G_{ij}$  as  $X^{\text{EX}}$  are to  $X_{\text{mix}}$ .” I believe this analogy between the excess functions,  $X^{\text{EX}}$ , and the excess KBIs is misleading for the following reason.

Excess functions are defined by

$$X^{\text{EX}} = X^{\text{real}} - X^{\text{ideal}} \quad (\text{A.1})$$

where  $X$  is any thermodynamic quantity.

The idea of subtracting an ideal part from the real thermodynamic quantity is to eliminate a *property* of the ideal solution. For example, the chemical potential of a component A in a *real* solution has the form<sup>3</sup>

$$\mu_A = \mu_A^*(\rho_A, T) + kT \ln \rho_A \quad (\text{A.2})$$

In an ideal dilute solution, the chemical potential has the form

$$\mu_A^{\text{id}} = \mu_A^{*\text{ideal}}(T) + kT \ln \rho_A \quad (\text{A.3})$$

where now  $\mu_A^{*\text{ideal}}(T)$  is not a function of  $\rho_A$ .

Clearly, in both cases, the chemical potential has a divergent part as  $\rho_A \rightarrow 0$ . Therefore, by subtracting  $\mu_A^{\text{id}}$  from  $\mu_A$ , we eliminate the divergent part of the chemical potential. This has some convenience. The main point, however, is that the *thing* that is eliminated, that is, the divergent part  $kT \ln \rho_A$ , is a *property* of the chemical potential both in an ideal and in a real solution. Therefore, by subtracting the ideal part, we are left with a nondivergent quantity.

Matteoli defined the “excess” value,  $\Delta G_{ij}$ , as

$$\Delta G_{ij} = G_{ij}^{\text{real}} - G_{ij}^{\text{ideal}} \quad (\text{A.4})$$

By doing so, one hopes to eliminate some property of the ideal value,  $G_{ij}^{\text{ideal}}$ . As stated in the article,<sup>1</sup> “the... $G_{ij}$  of this reference mixture, for which by definition, all interactions between species are indistinguishable”. Thus, what Matteoli wanted to achieve by subtracting  $G_{ij}^{\text{ideal}}$  is to subtract a *property* that was *assigned* to  $G_{ij}^{\text{ideal}}$  but actually does not belong to  $G_{ij}^{\text{id}}$ . This is said explicitly in the following:<sup>1</sup> “the interactions are masked by the ever present *background* of the reference ideal system. To avoid this, it is therefore necessary to *clear*  $G_{ij}$  of the *background* by considering the difference  $\Delta G_{ij} = G_{ij} - G_{ij}^{\text{id}}$ .” (The italics are mine.)

As we have seen in this article, one cannot “clear” a “background” from  $G_{ij}$  by subtracting  $G_{ij}^{\text{id}}$  that does not contain that background. In other words, an ideal solution *does not* “by definition” have the *property* that “all interactions between species are indistinguishable”. Therefore, by taking the difference in eq A.4, one *does not* eliminate the *property* that is referred to as “background”. Therefore, the whole analogy between excess functions and excess KB integrals is invalid. Unfortunately, the analogy is very appealing, and perhaps, this is the reason why a few followers accepted it uncritically.

#### References and Notes

- (1) Matteoli, E. *J. Phys. Chem. B* **1997**, *101* (47), 9800–9810.
- (2) The word “interaction” is used in the literature in different senses, sometimes referring to the direct intermolecular interactions and sometimes to the potential of mean force (PMF). Even if one understands the term “interaction” as the potential of mean force, the KBIs are integrals over the PMF and do not provide any details on the PMF themselves. However, it is clear from the content of ref 1 that the author is referring to the *direct* interactions between the molecules.
- (3) Ben-Naim, A. *Molecular Theory of Solutions*; Oxford University Press: Oxford, U.K., 2006.

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