

COMMENTS

Comment on “The Kirkwood–Buff Theory of Solutions and the Local Composition of Liquid Mixtures”

Arieh Ben-Naim[†]

Department of Physical Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

Received: August 17, 2007; In Final Form: December 28, 2007

Recently, I have written a detailed critique of some work by Matteoli¹ and Matteoli and Lepori² concerning the Kirkwood–Buff theory.^{3–5} This comment concerns a more recent article by Shulgin and Ruckenstein.⁶ The former authors sought a “correction” to the Kirkwood–Buff integrals (KBI), the latter suggested a correction to the interpretation of the KBI. Both “corrections” are superfluous, once the correct interpretation of the Kirkwood–Buff integrals is accepted.

In the following, I will first present three quotations from a recent article by Shulgin and Ruckenstein,⁶ and then I shall comment on each of these quotations. The italics in these quotations are mine.

(1) “The excess (or deficit) number of molecules i ($i = 1, 2$) around a central molecule j ($j = 1, 2$) was defined by Ben-Naim as

$$\Delta n_{ij}^{\text{BN}} = c_i G_{ij} \quad (1)$$

where c_i is the molar concentration of species i in the mixture and G_{ij} is the Kirkwood–Buff integral defined as

$$G_{ij} = \int_0^\infty (g_{ij} - 1) 4\pi r^2 dr \quad i, j = 1, 2 \quad (2)$$

where g_{ij} is the radial distribution function between species i and j and r , is the distance between the centers of molecules i and j ”.

(2) “However, the following *objections* can be brought to the use of eq 1 for calculating the excess (or deficit) number of molecules around a central molecule. A first objection (1) is that there are many systems for which all the KBIs (G_{11} , G_{12} , and G_{22}) are *negative* at least in certain ranges of composition.^{22,41} As a result, in such cases all $\Delta n_{ij}^{\text{BN}}$ calculated with eq 1 ($\Delta n_{11}^{\text{BN}}$ and $\Delta n_{21}^{\text{BN}}$ around the central molecule 1 and $\Delta n_{12}^{\text{BN}}$ and $\Delta n_{22}^{\text{BN}}$ around the central molecule 2) *would be negative*, and *this is not plausible because then, the density around any molecule in liquid will become lower than that in the bulk*. A second objection examined in detail in the next section is that (2) eq 1 *does not provide the true excess*”.

(3) “The average number of molecules i (n_{ij}) in a sphere of radius R around central molecules j can be calculated using the expression^{40,43}

$$n_{ij} = c_i \int_0^R g_{ij} 4\pi r^2 dr \quad i, j = 1, 2 \quad (5)$$

which can be recast in the form

$$n_{ij} = c_i \int_0^R (g_{ij} - 1) 4\pi r^2 dr + c_i \int_0^R 4\pi r^2 dr \quad (6)$$

As soon as R becomes large enough for $g_{ij} \approx 1$, eq 6 can be rewritten as^{18–19,40}

$$n_{ij} = c_i \int_0^\infty (g_{ij} - 1) 4\pi r^2 dr + c_i \int_0^R 4\pi r^2 dr = c_i G_{ij} + \frac{c_i 4\pi R^3}{3} \quad (7)$$

The difference between n_{ij} and $c_i 4\pi R^3/3$ was considered as the average excess (or deficit) number of molecules i ($i = 1, 2$) around a central molecule j ($j = 1, 2$) and eq 1 was thus obtained.^{3,5,18–19,39–40}

However, the term $c_i 4\pi R^3/3$ includes molecules i *assumed to be located in a volume inaccessible to them because of the presence of the central molecule j* . Therefore, when the average excess (or deficit) number of molecules i ($i = 1, 2$) around a central molecule j is calculated, those i molecules *should be subtracted* from $c_i 4\pi R^3/3$, and the second integral in the right-hand side of eq 6 should be subdivided into two parts... The *true excess* is given by...

$$\Delta n_{ij} = n_{ij} - c_i \int_{R_j}^R 4\pi r^2 dr \quad (9)$$

Quotation (1) is correct, except that Ben-Naim did not *define* the quantity $\Delta n_{ij}^{\text{BN}}$, as stated. It was only interpreted by Ben-Naim as the excess or deficit of particles around a central molecule.^{7,8}

The second quotation (2) contains a similar error as in the Matteoli and Lepori papers.^{1,2} (For more details see refs 4 and 5). It shows that the authors did not grasp the fact that the KBI were *defined* in an *open* system. These integrals are related to fluctuations and cross fluctuations in the number of particles of the different species. As such, the KBI can have *any sign*, positive or negative. The claim that a negative KBI “*is not plausible*” is not relevant to an *open* system, i.e., a system maintained at constant chemical potentials, and to which no conservation-type-of- argument applies.

The third quotation (3) starts with a correct definition of n_{ij} but then makes a fatal error. The quantity $c_i 4\pi R^3/3$ is the average number of i particles in a spherical volume of radius R . *Nothing more, nothing less!* It has nothing to do with the location of a j particle. Therefore, no “ i molecules should be subtracted...” as suggested by Shulgin and Ruckenstein.

Clearly, the main argument given in quotation (2) results from the confusion of the KBI which is defined in an open system, with a similar integral defined in a closed system.^{7,8} For the KBI integral, no conservation-type argument applies, and implausibility of the signs of the various Δn_{ij} does not exist.

Thus, the two “objections” raised in quotation (2) are a result of misunderstanding the meaning of the KBI. This misunder-

[†] Present address: NIST, 100 Bureau Drive Stop 8380, Gaithersburg, MD 20899.

standing is understandable in view of the subtle difference in the long-range behavior of the pair correlation functions in open and closed systems.^{7–9} The error in quotation (3) is unfortunate. The quantity $c_i 4\pi R^3/3$ has nothing to do with j molecules.

To conclude, let me reiterate the *correct* interpretation of the quantity $\Delta n_{ij}(R_M) = c_i G_{ij}$. The quantity $n_i(R_M) = c_i \int_0^{R_M} 4\pi r^2 dr$ is the average number of i molecules in a sphere of radius R_M . The quantity $n_{ij}(R_M) = c_i \int_0^{R_M} g_{ij}(r) 4\pi r^2 dr$ is the average number of i molecules in a sphere of radius R_M , at the center of which a j molecule is placed. Therefore, the difference $n_{ij}(R_M) - n_i(R_M)$ is the *change* in the average number of i molecules in the sphere of radius R_M , caused by placing a j molecule at the center of the sphere. This interpretation applies to any R_M . This change in the average number of molecules is referred to as *excess or deficit*, according to whether it is positive or negative, respectively. I am not aware of any other valid interpretation of this quantity. Clearly, when a j molecule is placed at the center of the sphere, it can either attract or repel other molecules from that sphere. The larger the size of the j molecule, the larger the negative effect due to the hard core repulsive part of the intermolecular forces.

Thus, what Shulgin and Ruckenstein are offering is not a *new interpretation* of the quantity $c_i G_{ij}$, but an *old interpretation of a different* quantity that has already appeared in ref 10 almost 30 years ago. This interpretation is concerned with only a part

of the KBI, not with the KBI itself. This has been suggested in eq 3.6 of my article in 1977, and reiterated in ref 7. Clearly, if one places larger molecules at the center of the spherical region, the quantity $c_i G_{ij}$ becomes more and more negative.^{7,10} There is nothing implausible in this finding. This is simply the way the KBI behave, not a result of an “incorrect” interpretation of the KBI.

Finally, it is interesting to note that Matteoli and Lepori² refer to $c_j G_{ij}$ as “the excess (or deficit) number of molecules j in the whole space around a central molecule i ”, which is exactly the same as my interpretation given above. Yet, ironically, they support Shulgin and Ruckenstein’s claim that my interpretation is incorrect.

References and Notes

- (1) Matteoli, E. *J. Phys. Chem. B* **1997**, *101*, 9800.
- (2) Matteoli, E.; Lepori, L. *J. Chem. Soc. Faraday Trans.* **1995**, *91* (3), 431.
- (3) Kirkwood, J. G.; Buff, F. P. *J. Chem. Phys.* **1951**, *19*, 774.
- (4) Ben-Naim, A. *J. Phys. Chem. B* **2007**, *111*, 2896.
- (5) Matteoli, E.; Lepori, L. *J. Phys. Chem. B* **2007**, *111*, 3069–3072.
- (6) Shulgin, I. L.; Ruckenstein, E. *J. Phys. Chem. B* **2006**, *110*, 12707.
- (7) Ben-Naim, A. *Molecular Theory of Solutions*; Oxford University Press: Oxford, U.K., 2006.
- (8) Ben-Naim, A. *Chem. Phys.* **2007**, *331*, 283.
- (9) Note that there are some errors in the upper limits of the integrals in Appendix G of ref 7. These were corrected in ref 8.
- (10) Ben-Naim, A. *J. Chem. Phys.* **1977**, *67*, 4884.