Corrigendum

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The A in SAFT: developing the contribution of association to the Helmholtz free energy within a Wertheim TPT1 treatment of generic Mie fluids

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A number of omissions and minor typographical errors have been uncovered in our recent article \cite{1} on the development of the association contribution for use with versions of the statistical associating fluid theory (SAFT) for molecules interacting through intersegment potentials of the Mie (generalized Lennard-Jones) form \cite{2, 3, 4}. These typographical errors in the text have no bearing on the numerical and graphical results presented in Reference \cite{1}, and are reported here to allow other researchers to reproduce the calculations.

Two different algebraic expressions are proposed in Section 4.3 \textit{Novel SAFT-VR Mie association contributions for Mie fluids} of Reference \cite{1} for the association strength (kernel integral) between Mie segments with short-range off-centre square-well association sites (see Figure 1).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Illustration of model of association employed in SAFT approaches. The square-well association sites \(a\) and \(b\) are embedded at a distance \(r^d\) for the centre of the core of the Mie segments, and mediate an association interaction of energy of \(-\frac{1}{2}r_{ab}\) when the site-site distance \(r_{ab}\) is less than \(r^e\).}
\end{figure}

\begin{flushright}
Corrigendum
\end{flushright}
The site-site bonding interaction potential $\Phi_{ab}^{HB}$ between the square-well sites $a$ and $b$ sites is given by

$$
\Phi_{ab}^{HB} = \begin{cases} 
-\varepsilon_{ab}^{HB} & \text{if } r_{ab} \leq r^c \\
0 & \text{if } r_{ab} > r^c 
\end{cases}
$$

(1)

where $r_{ab}$ is the centre–centre distance between sites, $\varepsilon_{ab}^{HB}$ characterizes the depth of the association energy well, and $r^c$ represents the cut-off range of the square-well interaction between sites $a$ and $b$. To fully characterize the geometry of the intermolecular potential model, the distance $r^d$ of each association site from the centre of the corresponding Mie segment must also be specified; the position of the site from the centre is taken to be $r^d = 0.4\sigma$ for all of the molecular models assessed in Reference [1], where $\sigma$ is the diameter of the spherical Mie segment.

In the case of the models characterized by the generic Mie association kernel given by Equation (30) of Reference [1], the geometry of the association site is represented by values of $r^d = 0.4\sigma$ and a cut-off range $r^c = 0.35\sigma$ as stated in the text of the original paper.

A different geometry is employed for the models characterized by the Lennard-Jones (LJ) association kernel given by Equation (32) of Reference [1], where in this case the geometry of the association site is represented by values of $r^d = 0.4\sigma$ and $r^c = 0.4\sigma$; the different value used for the cut-off range of the site-site interaction was not explicitly mentioned in the original paper. This LJ site geometry is also employed to model the associating molecules examined in Reference [4], and in recent applications of the SAFT-VR Mie [2] and SAFT-\(\gamma\) Mie [3] equations of state (unless otherwise stated).

The focus of the development presented in Reference [1] was on the determination of the association contribution to the free energy of single components (generally comprising a single spherical core). In this case the dimensionless number density in the association kernel (32) of Reference [1] is defined as $\rho^* = \rho\sigma^3$, where $\rho^* = N/V$. When the molecules comprise different segments, the appropriate dimensionless number density of the association kernel is the number density of segments $\rho_s^* = \rho_s\sigma_s^3$, where $\rho_s = N_s/V$. In the case of mixtures of molecules comprising different segments, the dimensionless density is defined in terms of the composition-dependent van der Waals one-fluid diameter $\sigma_s$ that characterizes the hypothetical single fluid:

$$
\sigma_s^3 = \sum_{k=1}^{N_G} \sum_{l=1}^{N_s} x_{s,k} x_{s,l} \sigma_{kl}^3,
$$

(2)

where $x_{s,k}$ and $x_{s,l}$ are the mole fractions of segments of types $k$ and $l$ in the system, and $N_G$ is the number of types of groups present. Further details of the use of the association contribution for mixtures of molecules comprising different segment types can be found in Reference [4]; note that the dimensionless density in the association kernel (24) of Reference [4] should also be expressed in terms of the number density of segments $\rho_s^* = \rho_s\sigma_s^3$. 
In SAFT approaches the range of the association interactions is typically quantified with a site-site association volume $K_{ab}$. In the case of the association between sites $a$ and $b$ on different molecules $i$ and $j$ a simple combining rule for $K_{abij}$ can be used to represent the unlike association volume:

$$K_{abij} = \left( \frac{K_{abij}^1 + K_{abij}^2}{2} \right)^3. \quad (3)$$

The corresponding relation for $K_{abij}$ given in Equation (49) of Reference [1] is erroneous and should be disregarded. One should also appreciate that in certain cases the unlike association volume is treated as an adjustable parameter to improve the description of the thermodynamic properties of the associating mixture.

In the case of the mixture of water + methanol examined in Section 7.1 of Reference [1] there is an additional typographical error in the value employed for the binary parameter $k_{ij}$ used to define the unlike dispersion interaction $\varepsilon_{ij}$ (cf. Equation (47) of Reference [1]):

$$\varepsilon_{ij} = (1 - k_{ij}) \sqrt{\frac{\sigma_a^2 \sigma_j^2}{\sigma_{ij}^2}} \sqrt{\varepsilon_a \varepsilon_j}. \quad (4)$$

The value for the water-methanol interaction should be $k_{ij} = 0.02$ (rather than the value of $k_{ij} = 0.04$ incorrectly stated in Reference [1]).

Finally there is a typographical error in the coefficients for the Mie association kernel reported in Table A5 in the Appendix of Reference [1]. In the table, $b_{723}$ (i.e., the coefficient $b_{i,j,k=3}$ for the indices $i = 7$ and $j = 2$) is missing, whereas two different values are given for $b_{423}$. The second of these is the missing value for $b_{723}$, i.e., $b_{723} = -9.27089410962249 \times 10^{-5}$ (the first value reported for $b_{423}$ is correct). The corrected Table A5 is given here. The values of the coefficients for the Mie and LJ association kernels are given correctly, with the coefficients conveniently formatted for computer code, in the downloadable file available as the Supplemental Material link from the home page of Reference [1] (http://www.tandfonline.com/doi/suppl/10.1080/00268976.2015.1029027).


Table A5. \(b_{i,j,k=3}\) coefficients for the association integral correlation in the Mie-based association term, Equation (30). The superfluous coefficient corresponding to \(i = 4\) and \(j = 2\) is crossed out and the missing value for corresponding to \(i = 7\) and \(j = 2\) is indicated as bold.

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