Erratum on “An efficient method for computing excess free energy of liquid” [Sci. China Chem., 2018, 61: 135–140]

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In the above referenced publication [1], there is a mistake in the derivation process leading to the final formula for computing excess free energy of liquids, i.e., Eq. (9). Here we provide corrections to Eqs. (7–9).

For the second entropic term in Eq. (4), one can rewrite it in the following format,

$$\begin{aligned}\langle \exp(\beta \Delta E_{w-w}^{\text{int}}) \rangle &= \left\langle \exp \left(\beta \sum_{j>i,i=1}^{N(N-1)/2} \Delta \varepsilon_{ij} \right) \right\rangle \\ &= \left\langle \prod_{j>i,i=1}^{N(N-1)/2} \exp(\beta \Delta \varepsilon_{ij}) \right\rangle \\ &= \left\langle \prod_{j>i,i=1}^{N(N-1)/2} X_{ij} \right\rangle\end{aligned}\quad (7)$$

It is then assumed that the sampling variable $X_{ij} = \exp(\beta \Delta \varepsilon_{ij})$ should be independent of each other and has the same average value, thus we have

$$= \left\langle \prod_{j>i,i=1}^{N(N-1)/2} X_{ij} \right\rangle = \langle X_{12} \rangle^{N(N-1)/2}$$

or

$$\left\langle \prod_{j>i,i=1}^{N(N-1)/2} \exp(\beta \Delta \varepsilon_{ij}) \right\rangle = \langle \exp(\beta \Delta \varepsilon_{12}) \rangle^{N(N-1)/2} \quad (8)$$

The assumption of Eq. (8) should be reasonable for liquids as liquid molecules move randomly across liquids and their interaction energies are not correlated with each other. Using Eq. (8), the second entropic term in Eq. (4) then becomes

$$\begin{aligned}-TS_X &= k_B T \ln \langle \exp(\beta \Delta E_{w-w}^{\text{int}}) \rangle \\ &= k_B T \ln \left[\langle \exp(\beta \Delta \varepsilon_{12}) \rangle^{N(N-1)/2} \right] \\ &= \frac{N}{2} k_B T \ln \left[\langle \exp(\beta \Delta \varepsilon_{12}) \rangle^{(N-1)} \right] \\ &= \frac{N}{2} k_B T \ln \left[\langle \exp(\beta \Delta \varepsilon_1) \rangle \right],\end{aligned}\quad (9)$$

$$\text{where } \Delta \varepsilon_1 = \sum_{j=1}^N \Delta \varepsilon_{1j}.$$

1 Song J, Qiu LQ, Zhang JZH. An efficient method for computing excess free energy of liquid. *Sci China Chem*, 2018, 61: 135–140

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