The meaning of Kirkwood-Buff integrals

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Lets perform an imaginary but actually simple experiment, consisting on measuring the mass change of a solution. Put some water into a vessel (the appropriate vessel here is the pycnometer, for precision), as illustrated in Figure 1A. The volume of the vessel is V. The concentration of pure (bulk) water will be called c_{bulk} (molecules/volume), and thus the number of water molecules inside the vessel will be $N_{bulk}(V) = c_{bulk}V$.
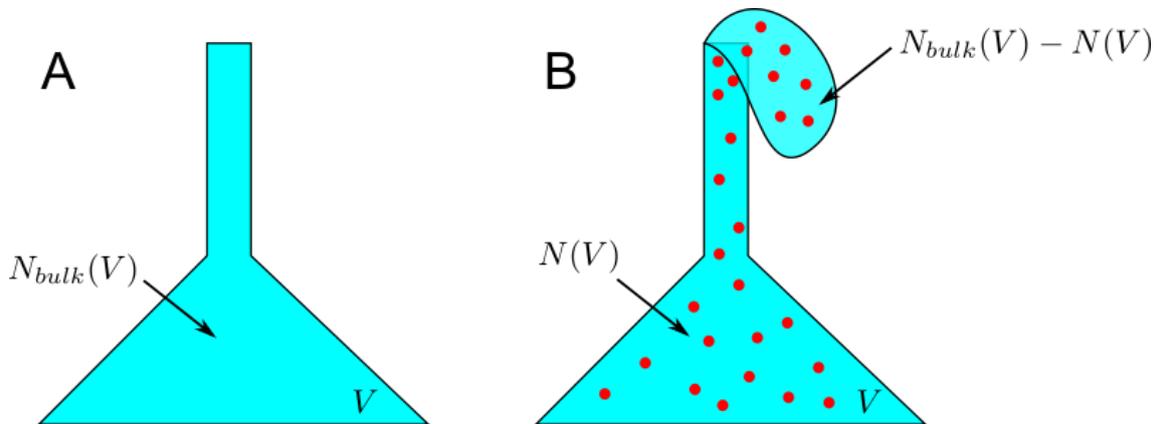

Figure 1: The volume displacement experiment.

Now lets add to this vessel a solute. In one simple case, the solute will simply occupy part of the volume of the vessel, and some solution will leak out of the vessel, as indicated in Figure 1B.

Lets count the number of water molecules inside and leaked out from the vessel. Within the vessel a number $N(V)$ of water molecules remain, and thus the number of leaked molecules will be $N_{bulk}(V) - N(V)$, as indicated in the figure.

The number of leaked molecules, $N_{bulk}(V) - N(V)$, corresponds to a volume of pure water of $[N_{bulk}(V) - N(V)]/c_{bulk}$. In other words, the volume occupied by the water molecules inside the vessel changed by

$$\Delta V = -\frac{N_{bulk}(V) - N(V)}{c_{bulk}}$$

We will define $G(V) \equiv -\Delta V/n_u$, where n_u is the number of mols of solute added, such that

$$G(V) = \frac{N(V) - N_{bulk}(V)}{n_u c_{bulk}}. \tag{1}$$

Therefore, $G(V)$ is the volume of solvent displaced by the insertion of the solute, per mole of the solute.

$G(V)$ can be easily measured given the concentration of the solute in the solution and the masses of the vessel after and before the addition of the solute. The mass difference after solute addition is

$$\Delta m = M_w N_{bulk}(V) - [M_w N(V) + M_u c_u V]$$

where M_w is the mass of a water molecule, M_u is the mass of the solute molecule, and c_u is the concentration (molecules/volume) of the solute in the solution. Simple manipulation leads to the number of molecules leaked from the vessel,

$$N_{bulk}(V) - N(V) = \frac{1}{M_w}[\Delta m + M_u c_u V].$$

Therefore, obtaining $G(V)$ of Equation 1 is simple, and depends only on the measure of the difference in mass of the vessel with pure solvent and with a solution of the solute of interest.

$G(V)$ consists of (minus) the volume of solvent molecules that was displaced, or accommodated, by the addition of the solute, per mole of solute. If the solvent is overall displaced by the solute, $G(V)$ is negative by its definition. If the addition of the solute increases the number of solvent molecules required to fill in the volume V, $G(V)$ is positive, and corresponds the volume that was occupied by the additional solvent molecules in the pure solvent.

Integral from a molecular perspective

Now, lets connect $G(V)$ to the microscopic distribution of the solvent molecules. It is clear by definition that the number of solvent molecules within the volume is the integral over the volume of the concentration of the solvent, that is, in each case,

$$N_{bulk}(V) = \int_V c_{bulk} dV$$

and

$$N(V) = \int_V c(\vec{r}) dV$$

where $c(\vec{r})$ is the concentration, or molecular density, of the solvent at position $\vec{r}$ in the solution. The integrals are computed over the entire volume V.

It follows that $G(V)$ can in principle be computed by

$$G(V) = \frac{1}{n_u c_{bulk}} \left[\int_V c(\vec{r}) dV - \int_V c_{bulk} dV \right]$$

or, by noting that c_{bulk} is a constant for the integration,

$$G(V) = \frac{1}{n_u} \int_V \frac{c(\vec{r})}{c_{bulk}} dV - \int_V \frac{c_{bulk}}{c_{bulk}} dV = \frac{1}{n_u} \int_V \frac{c(\vec{r})}{c_{bulk}} dV - \int_V dV = \frac{1}{n_u} \int_V \left[\frac{c(\vec{r})}{c_{bulk}} - 1 \right] dV$$

We define now the distribution function $g(\vec{r})$, as

$$g(\vec{r}) = \frac{c(\vec{r})}{c_{bulk}} \tag{2}$$

in such a way that $G(V)$ can be written in its most common form,

$$G(V) = \frac{1}{n_u} \int_V [g(\vec{r}) - 1] \, dV \tag{3}$$

Therefore, $G(V)$ can be computed from the distribution of the solvent molecules inside the volume V, connecting the microscopic distribution of the solvent molecules to the macroscopic observation of mass change of the solution.

Identical solute and solvent

What happens if the solute and the solvent are the same? In this case, the $N(V) - N_{bulk}(V)$ is simply the number of molecules added to the vessel, and the volume displaced is simply the volume of the solvent associated with this number of molecules, with the same density. Therefore, since $c_{bulk} = N_{bulk}(V)/V$ and $n_u = -(N(V) - N_{bulk}(V))/N_A$, where N_A is Avogadro's number, Equation 1 becomes

$$G(V) == \frac{N(V) - N_{bulk}(V)}{[-(N(V) - N_{bulk}(V))/N_A][N_{bulk}(V)/V]} = -\frac{N_A}{N_{bulk}(V)}V$$

or simply

$$G(V) = -\frac{V}{n_{bulk}(V)}$$

where $n_{bulk}(V)$ is the number of moles of solvent that fit in the volume V with bulk density. $V/n_{bulk}(V)$ is the molar volume of the solvent in bulk, thus, in this case, $G(V)$ turns out to be simply (minus) the molar volume of the solvent.

The meanings of the $g(\vec{r})$ (Equation 2) and of the corresponding KB integral (Equation 3) must be clarified in this case. If all molecules are considered equally, the integral of $g(\vec{r})$ over the entire volume is simply the volume of the vessel,

$$\int_V \frac{c(\vec{r})}{c_{bulk}} dV = \frac{1}{c_{bulk}} \int_V c(\vec{r}) dV = \frac{N(V)}{c_{bulk}} = V$$

and thus, the corresponding $G(V)$, from Equation 3, is zero. This is not consistent with the macroscopic interpretation given above. Therefore, $c(\vec{r})$ must not be interpreted as the density of the solvent in general, but as the density of the solvent molecules that were in the vessel *before* the addition of the new solvent molecules, which are to be interpreted as an additional solute. With this interpretation $c(\vec{r}) < c_{bulk}$, and the integral of the distribution function corresponds to the displaced volume of solvent.

Limit of $G(V)$ for very small additions of solute

We considered above the case of the addition of a finite ammout of solute, n_u, to a vessel containing the pure solvent, and defined $G(V) = -\Delta V/n_u$ from the volume of solvent molecules leaked by the addition of the solute. In the limit where n_u is very small, we can write

$$\lim_{n_u \to 0} G(V) = -\frac{dV}{dn_u}$$

This is a more precisely defined property. It is the volume leaked from the vessel by the addition of the solute to a solution with properties identical to those *prior* to the addition of the solute. That is, in the example above, it is the volume leaked from the vessel associated to the addition of a very small amount of solute to pure water. This is not the most general scenario, as the addition of the solute might occur to a solution already with a finite concentration the solute.

In the general case, for every possible *original* solution, the addition of a solute will cause a volume change. The volume of solution leaked will be associated to the corresponding $G(V)$ integral, which is a property associated to the addition of the solute to a solution of concentration c_{bulk}, without significant change in this concentration.

We can be more rigorous, therefore, if we associate the macroscopic volume change in the solution with

$$\Delta V = \int_{n_0}^{n_1} \frac{dV}{dn_u} dn$$

where we integrate the volume change with the addition of the solute for all concentrations between the first and second concentrations experimentally probed. Of course, if the concentrations are close enough, we expect dV/dn_u to be constant, and Equation 1 holds exactly.