

GENERALIZED EXCLUDED VOLUME: ITS ORIGIN AND EFFECTS

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The idea of the existence of an excluded volume (i.e., an impenetrable volume of molecules) formed the basis of the intuitive van der Waals (vdW) equation. After putting this idea on a rigorous statistical mechanical footing, the excluded volume has been used to interpret, or even estimate semi-quantitatively, a number of properties of fluids. All these facts are a consequence of the predominant effect of short-range repulsive forces acting between the molecules. This concept of the ordinary excluded volume however fails for fluids in which, in addition to omnipresent repulsive interactions at short separations, also specific short-range attractive interactions play an important role as, e.g., for associating fluids.

To model associating fluids at a very simple level, we introduced some time ago the so called primitive models which have formed later the basis of nowadays widespread SAFT method. The models mimic, by means of a square-well attraction and hard sphere repulsion, the interactions between the unlike and like interaction sites embodied to molecules, respectively, at short separations. When all attractive interactions are switched off one gets then the so called pseudo-hard body (PHB). These PHB's may be viewed as a counterpart of hard spheres and play the same role for understanding the behavior of associating fluids and developing theory thereof which hard spheres have played for simple fluids.

After a brief introduction of PHB's and their peculiar properties, a number of examples is presented showing that such generalized excluded volumes are able to explain naturally, without any parameter fitting, anomalous properties of aqueous solutions.