

# Molecular Association in the Chemical and the Physical Picture: Pure Fluids, Binary Mixtures and Ionic Solutions

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In the chemical models, ion pairs and other associates are presumed to exist in a chemical equilibrium with monomers while simulations, based on the intermolecular interactions only, do not require the assumption of associates. Ion pairs and associates result from the analysis of the simulation results employing appropriate definitions, e.g., using geometric and energetic criteria.

Analytical theories are based on the expansion of the partition function in terms of Mayer-f-functions. A representation in terms of connected Graphs agrees formally with the chemical picture describing the matter by a set of association equilibria. The further analysis led to a representation in terms of irreducible clusters and the number density, the Virial expansion. Both expansions are equivalent. The partition function is formally represented by a mass action law. However, it disagrees with the chemical expectation and does not represent the association determined in experiments, which requires that the number of particles must be always positive and that associates vanish in the high temperature limit, while complete association is expected at low temperatures. Only, if bound states are explicitly introduced a mass action law can be derived that agrees with the chemical picture. This will be demonstrated for pure fluids, binary mixtures and a cartoon of an ionic model in one-dimensional systems and also for simple cases in three dimensions. The Onsager book-keeping rule, to which in a complete theory the definition of the associate should not affect the thermodynamics, is satisfied for one dimensional systems.