

An Excluded Volume Theory of Lattice Fluids Part II- Incorporating Specific Models of Attractive and Repulsive Interaction Energy

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The excluded volume theory of lattice fluids (introduced in Fluid Phase Equilibrium 372 (2014) 126-140) is enhanced by specifying models for both the attractive and repulsive interaction energy terms. This results in an interaction energy function exhibiting a potential well reminiscent of a generalized Lennard-Jones potential. However here the potential well is seen in the Gibbs free energy function at the macro level. It improves the ability of the model to correlate saturated liquid density. The success of this theory is based on the following ideas: (1) Intramolecular and intermolecular bonds can be treated as uncorrelated when modeling the partition function. The method used to separate the bonds, which is based on an application of Bayes' theorem, makes a chain molecule appear to have only one segment in a lattice in which the intramolecular bonds are excluded. (2) The attractive forces active between molecules are thought of as being resolved along the generating lines of an assumed lattice. Resolution of these forces along lattice generating lines results in intermolecular bonds i.e. interaction bonds. The energy in an interaction bond is assumed to be inversely proportional to some power of the separation distance between molecules along the lattice line connecting the two molecules. This results in an interaction potential expressed as a polylogarithm with an argument given by a function of the ratio of density to maximum density. (3) An entropic based repulsive force is introduced that opposes the attractive forces. The repulsive force is assumed to be inversely related to the number of configurations available to a molecule in the lattice. Increasing the available configurations decreases the repulsive component of the interaction energy. (4) Strong energetic effects can be modeled based on a random occupation of lattice sites. For example if the attractive forces between molecules is strong enough to cause clustering the molecular cluster is assumed to randomly occupy lattice sites. The improved model is successfully applied to the vapor liquid equilibrium of ethane, ammonia and water, and to the binary mixtures of propane-butane and R152a-butane.