



An excluded volume theory of lattice fluids part II-incorporating specific models of attractive and repulsive interaction energy



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ABSTRACT

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. The result is 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. The attractive component of the interaction potential, though based on a lattice model, can be cast as arising from a radial distribution function and as such the model is seen as a bridge between lattice fluid models and models based on the radial distribution method. 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. 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 force 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.

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1. Introduction

This article further develops the excluded volume theory (EVT) of lattice fluids originally proposed in Ref. [1] by giving mathematical form to the attractive and repulsive interaction energy models. The theory again assumes that intermolecular interactions cause a time weighted average ordering of molecules into a lattice structure in both the liquid and vapor states. Lattice sites are considered to be locations of local minima in interaction energy. The constant buffeting of molecules due to thermal motion knocks molecules from one lattice site to another. A lattice site is assumed to be the most likely place to find a molecule.

The lattice is viewed as a molecular network with attractive connections between molecules occurring along the lattice generating lines. The network is considered to be a supermolecule [2–4]. Each type of network connection is assigned an interaction energy characteristic of the type of connection. The strength of the connection is assumed to be related to the separation distance in the lattice. The attraction between molecules is assumed to be opposed by a repulsive force, due to thermal motion, that is assumed to be related to a loss of configurational entropy.

The theory allows the development of models for thermodynamic properties and phase behavior for pure fluids and mixtures with all types of species ranging from simple non-polar molecules to complex associating and electrolyte components.

Mean-field lattice fluid models, MFLF, have been in continuous use for about the last seventy five years. Today they are widely used

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to model polymer properties and to a lesser extent to model vapor–liquid equilibrium of smaller molecules. Comprehensive reviews of a number of these models have been done, see for example [5–9]. The most widely used of these models rely on the lattice statistics of either Flory [10] or Guggenheim [11]. Flory's theory is often referred to as the Flory-Huggens theory because Huggens [12] developed it independently at about the same time as did Flory.

In an MFLF the energy associated with intermolecular interactions is treated as independent of all other energy modes. It is assumed that interaction energy depends on how molecules are distributed within the volume containing them and on the number of available configurations. Interaction energy is defined as the amount by which the energy exceeds the value it would have if all molecules were infinitely far apart from each other. If the total energy is E when the molecules are contained in volume V and E_0 when separated, interaction energy $E_I = E - E_0$. If E_I is negative molecules are attracted to each other. If they repel each other work must be done to bring them together and so E_I is positive.

The interaction partition function Q_I , ignoring internal degrees of freedom, is defined as

$$Q_I = \sum_j \Omega_j e^{-E_{Ij}/kT}. \quad (1)$$

where N is the number of molecules, T is temperature, Ω_j is the number of configurations with interaction energy E_{Ij} , k is Boltzmann's constant. The configurational degeneracy Ω is defined as $\Omega = \sum_j \Omega_j$.

A configurational degeneracy weighted interaction energy is defined as

$$e^{-E_I/kT} = \frac{\sum_j \Omega_j e^{-E_{Ij}/kT}}{\Omega}. \quad (2)$$

This allows the Helmholtz free energy F_I to be written as

$$F_I = E_I - RT \ln \Omega = E_I - TS_c. \quad (3)$$

where $S_c = R \ln \Omega$ is the configurational entropy. The equilibrium value of the interaction energy U_I is

$$U_I = -T^2 \partial(E_I/T) / \partial T = E_I - T \partial E_I / \partial T = E_I + TS_T. \quad (4)$$

where $S_T = -\partial E_I / \partial T$ is the thermal entropy.

The Bragg-Williams lattice gas, BWLG, is the simplest lattice model and serves to illustrate important aspects of a MFLF [5]. In it molecules are assumed to exist in a one dimensional lattice, with one molecule per lattice site, see Fig. 1. All lattice sites have the same fixed size. Compressibility is modeled by allowing some of the sites to be vacant. Only nearest neighbors contribute to the interaction energy. There is no interaction between vacant sites and between vacant sites and occupied sites. Molecules are assumed to be randomly distributed in the lattice.

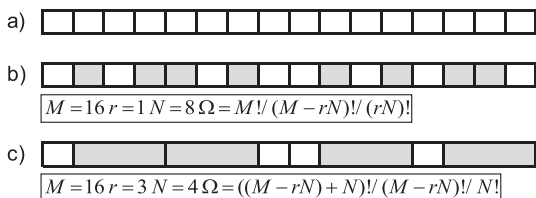


Fig. 1. A pure component in a one dimensional lattice. a) Empty lattice. b) Partially occupied lattice $r = 1$. c) Partially occupied lattice $r = 3$.

In a lattice with M sites and N molecules, see Fig. 1(b), the configurational degeneracy is $\Omega = M! / ((M - N)! N!)$ and the number of nearest neighbors is $N\theta$. Where $\theta = N/M$ is the occupied site fraction. The total interaction energy is $N\theta w$; where the w is the interaction energy between two nearest neighbor molecules.

The BWLG can be improved by assuming that a molecule occupies r contiguous sites, see Fig. 1(c). The configurational degeneracy is now $\Omega = ((M - rN) + N)! / ((M - rN)! N!)$. The number of nearest neighbors is $M((1 - \lambda)\theta)^2 / (1 - \lambda\theta)$. Where $\lambda = (r - 1)/r$ is the ratio of intramolecular bonds to total bonds made by the molecules. $\lambda\theta$ is the probability that two adjacent sites are occupied by segments from the same molecule, see Guggenheim's eq. (3.5) [11]. It is also the probability that any link between two adjacent lattice sites is an intramolecular bond. And $1 - \lambda\theta$ is the probability that any given link is not an intramolecular bond. Bonds can be between individual segments in the same molecule, individual segments in different molecules, vacant sites and between a vacant site and an individual molecular segment. The configurational degeneracy, using Stirlings approximation of a logarithm, can be written as

$$\Omega = \zeta^N \frac{M! (\lambda\theta)^{(r-1)N} (1 - \lambda\theta)^{M - (r-1)N}}{(M - rN)! (rN)!}. \quad (5)$$

where ζ is a constant characteristic of a molecule and is not used in determining thermodynamic properties. In words eq. (5) shows that the configurational degeneracy can be obtained by first calculating the number of configuration available to all segments treated as though they were not attached to molecules. Then to reduce this number by the probability that there are $(r - 1)N$ intramolecular bonds and by the probability that there are $M - (r - 1)N$ other types of nearest neighbor bonds.

In Flory's original theory [10] compressibility is ignored and so vacant lattice sites are replaced by solvent molecules. His configurational degeneracy is obtained from eq. (5) by assuming that the probability of an intramolecular bond is small so that $1 - \lambda\theta \approx 1$. This is appropriate at low density. It overestimates the available configurations because it fails to exclude impossible configurations in which segments from the same molecule occupy the same lattice site [10]. Despite this mathematical simplification Flory's model accurately describes the nontrivial power law nature of polymer properties for dilute through semi dilute solutions [8].

Guggenheim's configurational degeneracy [11] for random mixtures attempts to exclude those impossible configurations allowable in Flory's model. To do this he introduced the quantity $zq = zr - 2(r - 1)$ which gives the number of sites adjacent a molecule that are not occupied by segments from the same molecule. He uses zq to work out the probability of the different ways two adjacent sites can be occupied provided the molecule is a simple linear chain. He derived his equation for Ω by equating the rates of evaporation and condensation at low pressures for a mixture in vapor liquid equilibrium using the site occupancy probabilities. He used an argument similar to the one used by Langmuir to derive the Langmuir adsorption isotherm [13]. Guggenheim's Ω can be obtained from eq. (5) by assuming that the ratio of intramolecular bonds to total bonds made by the molecules is $\lambda = 2(r - 1)/z/r$ and assuming the total number of nearest neighbor bonds other than intramolecular bonds is $zM/2 - (r - 1)N$. Unfortunately the resulting equation for Ω predicts negative configurational entropy at typical liquid densities [10,14]. At low density it is nearly the same as Flory's equation. The same unphysical result occurs in Guggenheim's quasi-chemical approximation [14–16]. Attempts to correct this are given in Refs. [8,14,16].

The fact that these two models are still in use today is a testament to the enormous mathematical simplification, achieved by

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