Fluid Phase Equilibria 372 (2014) 126–140

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Models of free energy in lattice fluids—An excluded volume theory

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ARTICLE INFO

Article history:
Received 17 December 2013
Received in revised form 26 March 2014
Accepted 28 March 2014
Available online 13 April 2014

Keywords:
Helmholtz free energy
Equation of state
Lattice cell model
Vapor–liquid equilibrium
Free volume

ABSTRACT

A new method of modeling free energy in a lattice fluid is developed and shown to be capable of correlating non-ideal behavior in vapor–liquid equilibria. The success of the analysis is based largely on two ideas. The first is to express the partition function as the product of two partition functions one for intramolecular bonds (internal degrees of freedom) and one for intermolecular bonds (molecular interactions) and then to treat these bond types separately in the analysis of interaction energy and configurational degeneracy. The transformation used to separate the bond types makes a molecule look like it is monatomic in the transformed lattice and significantly reduces the complexity of the analysis. It also excludes the molar cell volume associated with intramolecular bonds from the total cell volume in the transformed lattice. The second idea is that when the molecular configuration for the system being modeled is specified appropriately, strong energetic effects can be accounted for based on a random distribution. Interaction energy is modeled using a modified mean field theory in which a nearest neighbor interaction is defined to occur between the closest neighbors in line of sight. All nearest neighbor interactions separated by the same distance are assigned the same interaction energy. This allows interaction energy to depend on separation distance. Pure component models are developed and compared with experimental data for four distinct cases: (1) linear molecules (*n*-alkanes); (2) molecules that form clusters (water); (3) polymers and non-linear molecules (benzene); and (4) helium which exhibits quantum effects as a liquid. The simplest form of the equation of state derived is shown to be capable of predicting pure component phase equilibrium behavior in reasonably good qualitative agreement with observed behavior. The size factors in the model are shown to be well correlated with the acentric factor. A multicomponent model is developed and compared with experimental data for the non-ideal binary mixture of 1,1-difluoroethane (HFC152a) and *n*-butane (azeotrope formation).

1. Introduction

The work presented in this article explores a new approach for deriving equations of state (EOS) using the methods of applied statistical mechanics in a lattice fluid. Literature on the development of lattice models is extensive [1–19]. A good review of the type of analysis undertaken in this article can be found in [1].

The models developed here assume 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.

The lattice is viewed as a molecular network with connections between molecules occurring along lattice generating lines. The network is considered to be a supermolecule [20–22], see Fig. 1(a). Each type of network connection is assigned an interaction energy characteristic of the type of connection. This energy connection can be further developed by assuming the strength of a connection is related to the separation distance in the lattice. This is done in the water model.

Fluid particles can always be considered to be randomly distributed throughout the volume they occupy because on average they always completely and uniformly fill that space. When building applied statistical mechanics models of fluids using hard spheres an understanding of the nature of the particle being modeled is important to the success of the model. In the water model developed below the particle is not a water molecule but instead a cluster of water molecules. This abstraction has been demonstrated to be useful [23–25]. It is the cluster that is considered to be randomly distributed. An individual cluster may not be long lived but any fleeting existence is assumed

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http://dx.doi.org/10.1016/j.fluid.2014.03.030
0378-3812/

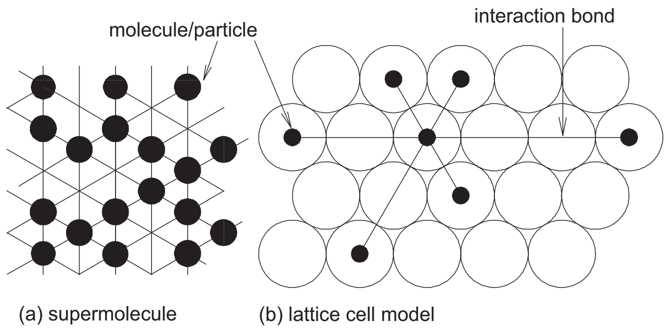

Fig. 1. Two views of the lattice used in this work. (a) Lattice network connected supermolecule. (b) Lattice cell model used showing interaction bonds.

to be averaged out so that a cluster behaves like a long lived entity.

Models are developed and compared with experimental data for: (1) linear molecules (n-alkanes); (2) molecules that form clusters (water); (3) polymers and non-linear molecules (benzene); and (4) helium which exhibits quantum effects as a liquid. The analysis is extended to mixtures and applied to the non-ideal mixture of HFC152a and butane at 273 K and 293 K.

2. Canonical partition function

The canonical partition function Q is treated as the product of a molecular partition function $q(T)$ that depends on temperature T and an interaction partition function $q_I(T, \theta)$ that depends on temperature and volume fraction θ. Total volume V is divided into M equal cells each with volume v. When only one molecule occupies one cell volume fraction is N/M, where N is the number of molecules.

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 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 partition function is

$$Q = q(T)^N q_I(T, \theta)^N = q(T)^N \sum_n \Omega_n e^{-E_{I,n}/kT}. \tag{1}$$

where Ω_n is the number of configurations with interaction energy $E_{I,n}$ and k is Boltzmann's constant. The sum of all Ω_n is the configurational degeneracy Ω.

A configurational degeneracy weighted interaction energy is defined as

$$e^{-E_I/kT} = \frac{\sum_n \Omega_n e^{-E_{I,n}/kT}}{\Omega}. \tag{2}$$

This allows the Helmholtz free energy F to be written as

$$\frac{F}{kT} = -\ln\ Q = \frac{E_I}{kT} - \ln\ \Omega - N \ln q(T). \tag{3}$$

The equilibrium value of the interaction energy, denoted by U_I, is related to E_I; $U_I = -T^2 \partial(E_I/T)/\partial T$. The two are the same when E_I does not depend on temperature. The model of E_I is presented in the next section.

3. Interaction energy

The lattice cell model used in this work is a modification of the Lennard-Jones and Devonshire (LJD) [26] lattice cell model to allow for vacant lattice cells, see Fig. 1(b). LJD cell theory is a lattice based model of the liquid state [27]. It is the prototype microscopic model used to predict the liquid–vapor critical point of a simple fluid [27]. In its simplest form it is used to introduce mean field theory in a number of standard texts and extensions of the model are in use today for research applications [27–29].

In standard mean field theory interactions occur only between nearest neighbors. All nearest neighbor interactions have the same energy. And nearest neighbors are adjacent to each other. Here a nearest neighbor is redefined to mean the nearest neighbor in direct line of sight along a lattice generating line. Nearest neighbors can be separated by any number of vacant lattice cells.

To start the analysis a molecule is treated like a single particle occupying one cell with a time weighted average location at a lattice point, i.e. at the center of a lattice cell. Fig. 1(b) illustrates how interactions are accounted for in this model. A black dot represents a particle residing in a cell which is represented by a white circle. In the illustration a particle makes six nearest neighbor intermolecular bonds. When an adjacent cell is unoccupied the bond extends through the cell to the first occupied cell. Bonds are shown occurring between nearest neighbors along lattice generating lines. Three types of bonds are shown: three-first, two-second and one-third nearest neighbor. Each type of bond is assigned a characteristic energy. An individual particle appears to be affected by only its nearest neighbors. But this is not so because all particles are connected to each other through the network. Interaction energy resides in the network. It is accounted for through nearest neighbor bonds. The network connected particles is seen as a supermolecule as illustrated in Fig. 1(a).

N particles can make $(z/2)N$ connections in the lattice. Here z is the lattice coordination number. In a volume divided into M cells, the maximum possible number of connections is $(z/2)M$. Define an interaction bond fraction Y as the ratio of the actual number of interaction bonds to the maximum possible number of bonds so that;

$$Y = \frac{(z/2)\,N}{(z/2)\,M} = \frac{N}{M} = \frac{vN}{vM} = \theta. \tag{4}$$

Interaction bonds are classified according to their separation along a lattice generating line as illustrated in Fig. 1(b). A first nearest neighbor bond occurs between adjacent particles on a lattice line. The number of first neighbor bonds is $(z/2)MY^2$. This results from assuming the time weighted position of a particle is at a lattice site. A second neighbor bond occurs between particles separated by one vacant site. The number of second neighbor bonds is $(z/2)MY(1-Y)Y$. The number of n^{th} neighbor bonds is $(z/2)MY(1-Y)^{n-1}Y$. The total number of bonds is

$$\frac{z}{2}MY^2\sum_{n=1}^{\infty}(1-Y)^{n-1} = \frac{z}{2}MY^2\frac{1}{Y} = \frac{z}{2}N; \tag{5}$$

the sum extends to infinity because of the large number of particles.

It is assumed that all n^{th} neighbor bonds have the same energy ω_n. Therefore the total interaction energy is

$$E_I = \frac{z}{2}MY^2\sum_{n=1}^{\infty}(1-Y)^{n-1}\omega_n = \frac{z}{2}NY\sum_{n=1}^{\infty}(1-Y)^{n-1}\omega_n. \tag{6}$$