Steps to a Bridge: Multiscale Modeling of the Thermodynamics of a Fluid

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Prepared for Presentation at the 2004 Annual Meeting, November 11th
Session 46, Computational Chemistry and Molecular Simulation II
Unpublished

Several modern approaches attempting to predict thermodynamic properties of fluids have emerged as computational power has increased. Some involve computations of isolated molecules to determine surface charge densities (Klamt, 1995) and, thus, preferable molecular interactions for use in a statistical framework (Lin and Sandler, 2002; Klamt et al. 2002). Others involve detailing the dynamics of molecular interactions using a combination of functional group interaction schemes with available internal molecular degrees of freedom (Jorgensen et al., 1984; Martin and Siepmann, 1998; Chen et al., 2001). A few avoid the computations altogether and continue to correlate thermodynamic properties to a lattice-fluid model for pure species and mixtures (Sanchez and Lacombe 1976, Taimoori and Panayiotou, 2001). All these models attempt to describe macroscopic behavior using only slightly different vehicles within a very similar statistical approach.

This work uses the benefits of group-contribution methods (consideration of a smaller number of intermediate-sized entities) in a multiscale model of thermodynamic properties of fluid systems. A Gibbs ensemble lattice-fluid is derived assuming that molecules occupy multiple lattice sites. Computational chemistry, Atoms in Molecules (AIM) theory (Bader, 1990) and associated software (AIMPAC) are used to find the electron density profiles of a molecule and to calculate rigorous electrostatic and structural properties for functional groups. These properties are used in a functional group potential energy model to describe interactions between entire molecules through the interactions of the smaller functional groups.

In the past, mixture system properties have been successfully represented by lattice-fluid models that correlate molecular-specific or global parameters to a set of data. This work attempts to predict the excess Gibbs energy of several binary mixture systems (*n*-propanol/*n*-butanol, *n*-propanol/hexane, pentane/ethanol) without correlating model parameters to the experimental vapor/liquid equilibrium data.

Lattice-Fluid Model

The lattice on which the molecules of a fluid system are modeled derives from Knox and coworkers (1984, 1987). The partition function is modified in this work to include the effects of vacancies on the system volume. The independent variables of the system therefore become temperature and pressure, and the system is described using the Gibbs partition function

$$\Delta(N, p, T) = W^{ath} \frac{\left[\prod_{i=0}^{n}(z_i N_i/2)!\right]^2}{I!\prod_{i=0}^{n}\prod_{j=0}^{n} N_{ij}!} \exp\left(-\sum_{i=0}^{n}\sum_{j=0}^{n}\frac{N_{ij}\varepsilon_{ij}}{kT} - \sum_{i=0}^{n}\frac{pN_i b_i}{kT}\right)\prod_{i=1}^{n} f_i^{N_i} \qquad (1.1)$$

where W^{ath} is the number of ways the system can be arranged assuming all interactions are equivalent, n is the number of different molecular species in the system, z_i is the number of contacts on molecule i, b_i is the volume occupied by a molecule or a vacancy, N_i is the number of molecules of species i, f_i is the molecular partition function of species i, N_{ij} is the number of interactions between species i and j, ε_{ij} is the interaction energy between species i and j, and I is the total number of interactions in the system.

To recover the most probable state of the system, the maximum of the Gibbs partition function with respect to all interaction numbers N_{ij} and number of vacancies N_0 must be found. This yields a system of nonlinear equations called the quasi-chemical equations (Guggenheim, 1952). The numbers N_{ij} are found to be related to the interaction energies by

$$\frac{N_{ij}N_{ji}}{N_{ii}N_{jj}} = \exp\left[\frac{-\left(2\varepsilon_{ij}-\varepsilon_{ii}-\varepsilon_{jj}\right)}{kT}\right] = A_{ij}^{\,2} \tag{1.2}$$

The quantity in the parentheses is regularly referred to as the interchange energy.

The quasi-chemical equations for the Gibbs ensemble is a generalization to the equations that govern a system with no vacancies

$$\frac{1}{\psi_i} = \theta_0\psi_0 A_{i0} + \left(1-\theta_0\right)\sum_{j=1}^{n}\Theta_j\psi_j A_{ij} \tag{1.3}$$

where θ_0 is the surface area fraction of vacancies, ψ_i is the residual activity coefficient of molecule i, and Θ_i the surface area fraction of species i in a system with no vacancies. If the number of vacancies is set to zero, the quasi-chemical equations reduce to those for a systems with a fully occupied lattice, such as those described in earlier works (Guggenheim, 1952; Kehiaian et al., 1978; Knox et al, 1984; Knox, 1987; Taimoori and Panayiotou, 2001; Klamt et al., 2002).

The equations presented above describe interactions of entire molecules. The model is able to consider systems where functional group properties and interactions are the entities of interest.

Minimizing the partition function with respect to the number of vacancies results in the equation of state for the system

$$\frac{pb_0}{kT} = \left(\frac{\partial \ln W^{ath}}{\partial N_0}\right)_N - z_0 \ln\left(\psi_0\right) \tag{1.4}$$

This depends on the choice of the athermal ways function. If the Flory expression for the athermal ways function within a pure species (Martinez, 1995) is used, equation (1.4) becomes

$$pb_0/kT = -\ln\left(1-rb_0/V\right) - rb_0\left(1-1/r\right)/V - s\ln\left(\psi_0\right) \tag{1.5}$$

where r is the number of lattice sites occupied by the molecule and s is the average number of contacts per lattice site, whether occupied or unoccupied. This equation is related directly to the result of Taimoori and Panayiotou (2001), derived from a slightly different approach.

In the system of quasi-chemical equations (1.3) and in the equation of state (1.4), parameters describing structural properties (r_i and z_i) and energetics (ε_{ij}) exist. This work attempts to find these molecular-scale quantities through theoretical and computational means.

Structural and Electrostatic Properties of Functional Groups: Atoms in Molecules Theory

To determine fundamental properties for atoms and groups, AIM theory is used. The properties of these atoms are theoretically found to be additive, therefore these atoms can be assembled into functional groups with known properties. The volume of a group, V, enclosed by bordering groups and the 0.001 au isodensity surface (Bader et al., 1987) is used to define how many lattice sites a functional group occupies. The exposed surface area, A_{ex}, is the size of the enclosing 0.001 au isodensity surface and is used to determine the number of interactions in which a functional group can participate. The average distance, denoted as r_{avg}, from the location of the center of the functional group (location of the heavy atom) to the exposed surface area is used to determine the extent of the functional group electron density.

Table 1. Global Model Parameters

Parameter	Value	Description	Origin
b_0	10.0 cm^3/mol	Volume of vacant lattice site in EoS model	AIM volume of neon
	25.7 cm^3/mol	Volume of vacant lattice site in VLE model	AIM volume of methane
$a_{interaction}$	0.071 nm^2	Area occupied by one interaction	Klamt et al., 1998

Electrostatic properties of functional groups are also defined under AIM theory. A partial charge is assigned to the functional group by integration of the electron density within the partitioned space. The polarizability of a group, α, is also quantifiable by calculating changes in the group's dipole moment to orthogonal electric fields (Bader et al., 1992). Higher order electrostatic properties, such as dipole moment vector and quadrupole moment tensor, are definable through AIM but are not used in this work. AIM properties for the functional groups within the molecule are found using the AIMPAC integration software available on the internet. Functional group definitions have been designed around united-atom models (Jorgensen et al., 1984; Martin and Siepmann, 1998; Chen et al., 2001).

An example of functional group properties for molecules in a mixture system of interest is presented in Table 2. Groups with the same definition are assumed to be different unless there are strict symmetries. Calculations exceeding error tolerances are written in italics; these values are estimated by considering the property along a series of similar molecules. All values are given in atomic units.

Table 2. AIM properties for *n*-propanol and *n*-butanol

	n-propanol					*n*-butanol					
	CH$_3$	CH$_2$	CH$_2$	O	H	CH$_3$	CH$_2$	CH$_2$	CH$_2$	O	H
q	0.014	0.048	0.476	-1.123	0.585	-0.014	0.042	0.032	0.477	-1.122	0.584
α	13.8	11.7	10.8	7.5	1.1	14.3	11.6	11.7	11.3	7.3	1.1
V	218.4	158.0	151.3	125.9	22.33	222.1	156.0	157.1	151.3	125.8	22.34

A_{ex}	138.7	90.10	*84.36*	74.99	22.72	144.1	83.57	84.48	*83.75*	75.30	22.50
r_{avg}	4.174	4.230	*4.203*	3.550	2.430	4.184	4.266	4.284	*4.203*	3.552	2.428

Interaction Model: Functional Group Interaction Energies

An interaction energy model is being developed to take advantage of the molecular-scale properties found for species in the systems of interest. For each pair of functional groups, the calculated AIM structural and electrostatic properties are used to evaluate appropriate energies for the resulting pair-wise interactions.

A similar work to determine the interaction potential curves for functional groups has been conducted by Siepmann and coworkers (1995, 2001), referred to as Transferable Potentials for Phase Equilibrium (TraPPE). The interaction functions of this work include the same effects as those in the TraPPE force field: a repulsion contribution, a dispersion contribution and a Coulombic contribution. A quantum exchange contribution is included in this work explicitly.

Interaction energies in the mixture systems are calculated for use in the statistical model. Distances coordinating to interaction energy minima are used in favorable interactions, while the sum of r_{avg} values is used for interactions dominated by the repulsion contribution. For the hydrogen bonding interactions, the TraPPE force field does not include a repulsive contribution at short interaction ranges. An interaction distance of 2.0 Å is used, approximately the experimentally determined hydrogen bond distance.

At present, use of the TraPPE force fields gives more accurate predictions of VLE behavior and thus will be used in the statistical model.

Comparison of Lattice-Fluid Model to Pure Species and VLE Data

Pure species volumetric data is considered using the equation of state in (1.4) and the Guggenheim expression for the athermal ways in a pure species (Martinez, 1995). The equation of state takes the form

$$\frac{pb_0}{RT} = \left[\left(1-\frac{b_0}{b}\right)\left(\frac{1}{1-c}\right)-1\right]\ln\left(1-\frac{b}{V}\right)-\left(1-\frac{b_0}{b}\right)\left(\frac{1}{1-c}\right)\ln\left(x_{00}\left(V,T\right)\right) \tag{1.6}$$

where x_{00} is the local composition of vacancies around vacancies.

A table of equation of state parameters for small molecules is located in Table 3. Trends along the values of the parameters are in italics. Within the fluorinated methanes, the decrease of molecular volume b is seen as the number of fluorine atoms in the molecule decreases. Within the noble gases, the surface area parameter decreases from $c=1.0$ for a molecule occupying exactly one lattice site to that of xenon, a relatively bulky sphere occupying lattice sites with no external contacts.

The interaction energy parameters within the inorganic molecules reveal trends in the electrostatic moments of the molecule. The top five species are ordered by increasing dipole moment, as this is reflected in the increasing interaction energy parameter. The bottom four neutral species have similar energies except for carbon dioxide and its large quadrupole moment.

Table 3. Equation of State Parameters that Reproduce the Critical Point of Pure Fluids

molecule	b (cm^3/mol)	c	ε (K)	molecule	b (cm^3/mol)	c	ε (K)
CF$_4$	62.0	0.347	-432	CO	40.6	0.515	-181
CHF$_3$	60.4	0.318	-659	NO	27.1	0.565	-315
CH$_2$F$_2$	56.1	0.311	-856	N$_2$O	43.6	0.44	-537
CH$_3$F	52.6	0.328	-754	H$_3$N	33.8	0.472	-810
CH$_4$	43.4	0.471	-292	H$_2$O	26.6	0.541	-1318
Ne	19.0	0.812	-35.2	N$_2$	39.5	0.516	-175
Ar	33.1	0.574	-196	O$_2$	32.7	0.57	-208
Kr	40.2	0.501	-305	F$_2$	29.7	0.603	-187
Xe	51.6	0.417	-477	CO$_2$	42.2	0.452	-517

The volumetric behavior of (1.6) using the parameters is exemplified when compared to the critical isotherm volumetric data of a species. The equation of state shows behavior like that of an analytic expression around the critical point. The liquid branch overpredicts the pressure of the pure species, while the vapor branch underpredicts the pressure.

Predictions of vapor/liquid equilibrium for binary mixture system are accomplished by calculating the activity coefficients of the species in the liquid phase. Activity coefficients are determined through the total Gibbs energy found from the Gibbs ensemble in (1.1). The first derivative of the excess Gibbs energy with respect to the number of molecules of type i yields

$$\ln(\gamma_i) = \ln(\gamma_i^{ath}) + \sum_{j=0}^{m} Z_j v_{ij} \ln(\psi_j / \psi_j^{\text{pure i}}) \tag{1.7}$$

where Z_j is the number of contacts of group j, v_{ij} is the number of groups of type j in species i, and the $\psi_j^{\text{pure i}}$ is the activity of group j in a system of pure i.

For the athermal, or combinatoric, contribution γ_i^{ath}, the Guggenheim expression rederived for a Gibbs ensemble is used. The Guggenheim athermal ways function for a lattice system occupied by both molecules and vacancies is given by

$$W^{ath} = \left[\prod_{i=1}^{n}\left(\frac{\rho_i}{\sigma_i}\right)^{N_i}\right]\left[\left(\sum_{i=0}^{n} r_i N_i\right)! \bigg/ \prod_{i=0}^{n} N_i!\right]\left[\left(\sum_{i=0}^{n} q_i N_i\right)! \bigg/ \left(\sum_{i=0}^{n} r_i N_i\right)!\right]^{\frac{z_0}{2}\kappa} \tag{1.8}$$

where $q_i = z_i/z_0$ and

$$\frac{z_0}{2}\kappa = \sum_{i=1}^{n}(r_i - 1)x_i \bigg/ \sum_{i=1}^{n}(r_i - q_i)x_i \tag{1.9}$$

If the original definition of q_i is satisfied, namely $q_i = r_i - 2(r_i - 1)/z_0$, then (1.8) reduces to the original Guggenheim athermal ways expression.

After the activity coefficients have been calculated for the species in the liquid phase, the pressure of the vapor phase is given by

$$p = x_1\gamma_1 p_1^{sat} + x_2\gamma_2 p_2^{sat} \tag{1.10}$$

where p_i^{sat} is the experimentally determined saturated vapor pressure of species i at the mixture system temperature.

Calculated pressures for three mixture systems are compared to experiment in Figures 1-3. For the systems presented, the TraPPE force field is used throughout, and the experimental vapor pressures are used to reproduce the limiting behavior. For the alcohol/alkane mixture systems, the experimental liquid volume for the pure species is used to guarantee that the pure species contribution to the activity coefficient comes from a system with a liquid-like volume.

Also within the alcohol/alkane systems, the functional group activity coefficient for the hydrogen atom in both the pure alcohol and mixture system is set to zero. In relating the quasi-chemical equations (1.3) to the work of Knox (1987), the functional group activity coefficient of i is found more generally to be

$$\psi_i = \sqrt{x_{ii}/\theta_i} \qquad (1.11)$$

where x_{ii} is the local composition of group i around i, and θ_i is the surface area fraction of group i. If we assume the probability of a hydrogen atom occurring around another hydrogen atom in the liquid system is negligible, then it is assumed that $\psi_0 = 0$.
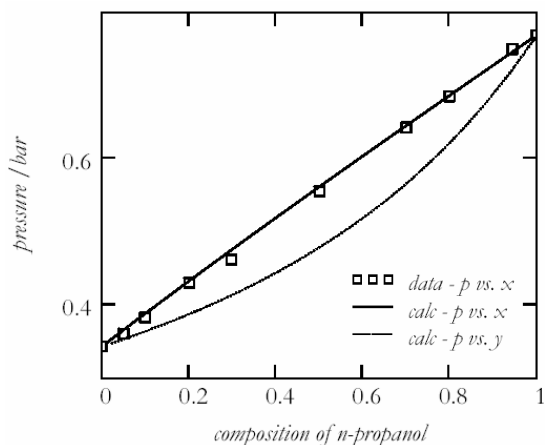

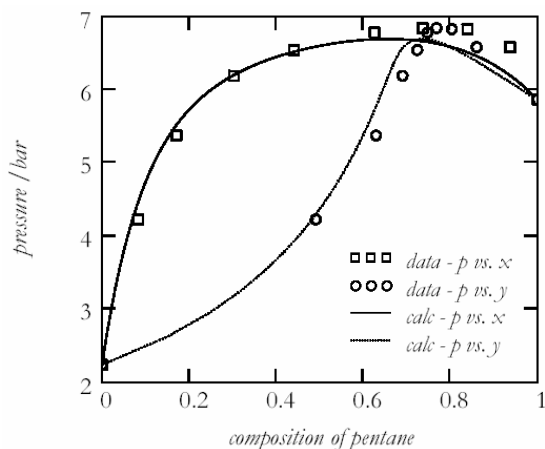Figure 1. VLE of *n*-propanol/*n*-butanol at 363.15 K: Model Compared to Experiment

Figure 2. VLE of pentane/ethanol at 372.7 K: Model Compared to Experiment
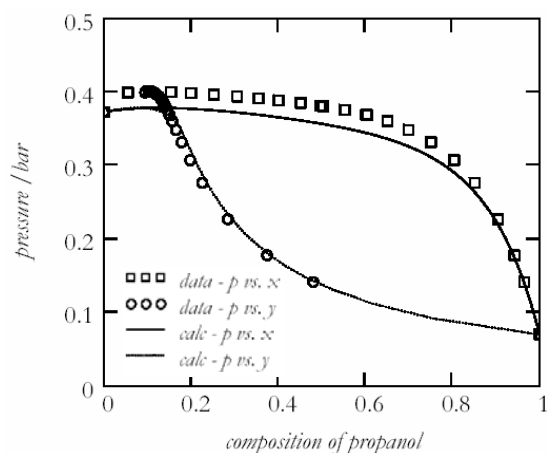
Figure 3. VLE of propanol/hexane at 313.15 K: Model Compared to Experiment

Discussion and Conclusions

This work demonstrates that macroscopic system mixture properties are qualitatively (and nearly quantitatively) describable using the methods described above. These methods do not include correlating any molecule-specific or global model parameters to any mixture data. It is anticipated that full quantitative predictions are possible if the model parameters (vacancy volume, area of interaction) are optimized to predict the macroscopic properties, as in recent VLE models such as COSMO-RS and COSMO-SAC.

The use of liquid volumes in the alkane/alcohol systems are necessary to predict a liquid-like state for the pure species. In general, the model equations (1.3) and (1.4) do not properly predict a liquid-like volume for linear alkanes at the system temperatures above. The experimental liquid volume would not be necessary if the model predicts this liquid root, as in the *n*-propanol/*n*-butanol system. A version of the model will be created that allows for the study of these interaction wells and their effect on phase equilibrium of pure alkanes.

Thus far, the predictions using the TraPPE interaction parameters with the quasi-chemical fluid model give a representation of the liquid phase properties most affected by a mixture process. The interaction model under development yields interaction curves in good agreement with most TraPPE curves, except for those interaction schemes involving two highly charged alkyl groups. Here again, the AIM charges are larger than those in TraPPE, which leads to a more repulsive interaction scheme. It is anticipated that when this issue is resolved, the interaction scheme utilizing AIM properties can be used as successfully in the statistical model as the TraPPE interactions.

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