

SATURATED PHASE EQUILIBRIA AND PARAMETER ESTIMATION OF PURE FLUIDS WITH TWO LATTICE-GAS MODELS

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ABSTRACT

Accurate and reliable prediction of saturated pure fluid properties is essential for subsequent extension to multicomponent mixtures. The conventional cubic equations of state are accurate in correlation of non-polar fluid properties but often give poor results when applied to fluids with permanent dipole or quadrupole moments. A simple alternative to the cubic equations are the lattice-gas equations of state, pioneered by Guggenheim, Simha, Sanchez and Lacombe, and Kleintjens and Koningsveld. We compare the performance here of the Sanchez-Lacombe (SL), Kleintjens-Koningsveld (KK), and Peng-Robinson (PR) equations of state in correlating the properties of pure non-polar and polar fluids. We also correlate the characteristic parameters in the two lattice-gas equations with critical and molecular properties. The KK model with four parameters, one of which is temperature-dependent, correlates the saturated fluid properties of polar fluids better than the SL model with three parameters. Both equations of state give better results for polar fluids than the conventional cubic equations, particularly in the prediction of saturated liquid densities.

INTRODUCTION

The lattice-gas model is an old concept. The rudiments of the theory were introduced by Bragg and Williams (1934) to describe lattice imperfections in crystals. The model can also be used to describe liquid-vapor phase equilibria as pointed out by Fowler and Guggenheim (1939). Recently, the lattice-gas model has been applied to computation of pure fluid and binary vapor-liquid equilibria of polar fluids and their mixtures by Sanchez and Lacombe (1976a,b; 1980) and by Kleintjens and Koningsveld (1979, 1980, 1982, 1983). Both applications are based on a regular lattice populated by molecules which occupy multiple lattice sites and vacancies, or "holes", which occupy a single lattice site.

Sanchez and Lacombe's treatment is statistical in nature and relies on using the mean field approximation to the configurational degeneracy term in the isothermal-isobaric ensemble. (Sanchez and Lacombe 1975a; Guggenheim 1944). This approximation is repeated in assuming that only nearest-neighbor segment interactions contribute to the overall configurational energy.

Kleintjens and Koningsveld took a substantially different approach and derived the Helmholtz free energy of mixing holes and molecules. This free energy contains three pieces: (1)

an athermal entropy of mixing, (2) a non-athermal entropy of mixing, and (3) a surface-area weighted energy of interaction between holes and molecules. This third contribution was originally suggested by Staverman (1937). Kleintjens and Koningsveld's primary contribution is the non-athermal entropy correction, which accounts for the decrease in entropy of mixing below that given by athermal mixing due to local ordering of holes and molecules.

In this paper, we compare the performance of the Sanchez-Lacombe (SL) and Kleintjens-Koningsveld (KK) equations of state in modeling liquid-vapor phase equilibria of pure polar and non-polar liquids. In a previous paper (Kilpatrick and Chang 1986), we have correlated the parameters of the KK equation with critical and group-contribution molecular properties. We do the same here for the SL equation.

SL EQUATIONS

The pressure equation of state obtained by Sanchez and Lacombe (1976a) upon minimizing the total Gibbs free energy with respect to volume is:

$$P' = T' \left[\ln \left(\frac{1}{1-\rho'} \right) - \left(1 - \frac{1}{r} \right) \rho' \right] - \rho'^2 \quad (1)$$

Here, the dimensionless pressure, molar density, and temperature are defined according to:

$$P' = \frac{P}{P^*} \quad , \quad P^* = \frac{\epsilon^*}{v^*} \quad (2)$$

$$\rho' = \frac{\rho}{\rho^*} \quad , \quad \rho^* = \frac{M}{rv^*} \quad (3)$$

$$T' = \frac{T}{T^*} \quad , \quad T^* = \frac{\epsilon^*}{k} \quad (4)$$

The characteristic parameters of the SL equation are thus either macroscopic -- P^* , T^* , and ρ^* -- or the corresponding molecular quantities -- ϵ^* , r , and v^* . In the above equations, M is the molecular weight, ϵ^* is the interaction energy between non-bonded molecular segments, v^* is the volume of an Avogadro's number of lattice sites, r is the number of lattice sites occupied by a molecule, and k is Boltzmann's constant.

Sanchez and Lacombe formulate the total Gibbs free energy of the pure fluid-hole system in the isothermal-isobaric ensemble and obtain the configurational degeneracy using Guggenheim's (1944) estimate in a mean field approximation. The result for the dimensionless molar Gibbs free energy (i.e. chemical potential for a pure fluid) is:

$$G' = \frac{G}{Nr\epsilon^*} = -\rho' + P'V' - T' \left[(v'-1)\ln(1-\rho') + \frac{1}{r}\ln\left(\frac{\rho'}{\omega}\right) \right] \quad (5)$$

In equations (5), ω is related to the "flexibility" of the molecule, the number of lattice sites which it occupies, and a so-called asymmetry number. For purposes of constructing phase equilibria, the dimensionless molar Gibbs free energy is equated for liquid and vapor densities, ρ'_l and ρ'_v , respectively, at the same temperature T' . Thus the quantity ω is seen to cancel as the term $T' \ln \omega / r$ and it does not appear in the equation of state for P' (equation (1)).

KK EQUATION

The KK equation for pure fluids has been described thoroughly elsewhere (Kleintjens 1979, 1983; Kleintjens and Koningsveld 1982, 1983; Nitsche *et al.* 1984; Kuan *et al.* 1986; Kilpatrick and Chang 1986). The dimensionless Helmholtz free energy of mixing molecules and holes is:

$$A = \frac{\Delta F}{N_0 RT} = \phi_0 \ln \phi_0 + \frac{1}{m_1} \phi_1 \ln \phi_1 + \left[\alpha_{01} + \frac{g_{01}(1-\gamma_{01})}{(1-\gamma_{01}\phi_1)} \right] \phi_0 \phi_1 \quad (6)$$

Here, ΔF is the dimensional Helmholtz free energy of mixing, $N_0 = n_0 + n_1 m_1$ is the total number of lattice sites, n_0 the number of lattice sites occupied by vacancies, n_1 the number of molecules on the lattice and m_1 the number of lattice sites each molecule occupies. The volume fractions of the lattice occupied by vacancies and molecules are ϕ_0 and ϕ_1 , respectively.

Molecules interact on the lattice through an enthalpic interaction parameter, g_{01} , which is weighted by the difference between unity and the ratio of surface areas of interaction for molecule and vacancy, γ_{01} . The term α_{01} is intended to correct for entropic effects which are not accounted for in the athermal contribution. The enthalpic interaction parameter is fit to a quadratic function of inverse absolute temperature:

$$g_{01}(T) = g_{01,0} + \frac{g_{01,1}}{T} + \frac{g_{01,2}}{T^2} \quad (7)$$

The pressure and chemical potential equations are obtained from the dimensionless Helmholtz free energy and are given in previous publications. Phase equilibrium between saturated liquid and saturated vapor is computed with both the KK and SL equations by setting the temperature, and then solving for equality of pressure and equality of chemical potential of the liquid and vapor phases in terms of the two unknowns: saturated liquid and vapor molar density or, equivalently, saturated liquid and vapor molecule volume fractions, ϕ_1 . Standard Newton iteration with first-order temperature continuation is used as the numerical algorithm.

PARAMETER ESTIMATION AND SATURATED FLUID PROPERTIES

There are three parameters in the SL equation: ϵ^* , v^* , and r (or equivalently T^* , P^* , and ρ^*). These three parameters are obtained by optimizing the fit of the SL equation to experimental saturated density and vapor pressure data. The objective function is the unweighted sum of relative percent deviations between experimental and calculated vapor pressures and saturated densities for n data:

$$SSR = \sum_{i=1}^n \left(\frac{P_{i,exp}^{vap} - P_{i,calc}^{vap}}{P_{i,exp}^{vap}} \right)^2 + \sum_{i=1}^n \left(\frac{\rho_{i,exp}^l - \rho_{i,calc}^l}{\rho_{i,exp}^l} \right)^2 + \sum_{i=1}^n \left(\frac{\rho_{i,exp}^v - \rho_{i,calc}^v}{\rho_{i,exp}^v} \right)^2 \quad (8)$$

A Powell search optimization routine is employed to minimize SSR .

In the KK equation, there are four parameters: M_1 , α_{01} , γ_{01} , and g_{01} , the last of which is temperature-dependent according to equation (7). The volume per lattice site v_0 is set equal to $25 \text{ cm}^3/\text{mole}$ for all fluids. The three parameters m_1 , α_{01} , and γ_{01} , and the three coefficients in the temperature dependence of g_{01} are determined by minimizing SSR using a Powell search. The optimized parameter sets for 26 polar and non-polar fluids obtained in this way are presented in Table I for the Sanchez-Lacombe equation. The comparable optimized parameter sets for the

KK equation and the literature sources for the experimental data are given by Kilpatrick and Chang (1986).

A summary of the average absolute deviations between calculated and experimental saturated densities and vapor pressures for 23 polar and non-polar fluids as obtained with the two lattice-gas models and with the Peng-Robinson model for comparison is given in Table 2. Both lattice-gas equations are accurate in correlating saturated liquid densities of both polar and non-polar fluids with average absolute deviations rarely exceeding 2.0%. The saturated vapor densities are considerably better correlated by the KK equation within 2-5% for most fluids while the SL equation was within 3-8% for most fluids. The vapor pressure predictions with both equations are comparable, rarely giving average deviations exceeding 4%. The exceptional fluid is acetic acid whose pressure and vapor density is poorly correlated by both equations. This is likely due to the known dimerization of acetic acid in the vapor phase and should be properly treated by a chemical equilibrium model.

TABLE 1: Optimized Sanchez-Lacombe Equation of State Parameters

Fluid	r	z^* (cal/mole)	v^* (cc/mole)
Methane	4.980	408	6.678
Ethane	6.051	619	7.647
Propane	7.028	713	8.740
n-Butane	7.574	804	10.17
n-Pentane	8.089	878	11.36
n-Hexane	8.966	920	11.93
n-Heptane	9.880	955	12.38
n-Octane	10.35	1000	13.19
n-Nonane	11.54	1009	13.10
n-Decane	11.94	1048	13.87
Acetic Acid	9.660	1080	5.215
Methyl Ether	7.907	743	6.378
Ethyl Ether	9.040	838	8.978
Methanol	12.26	878	2.627
Ethanol	14.89	829	2.817
n-Propanol	15.72	843	3.411
Water	8.720	1220	1.793
Ammonia	8.106	765	2.614
Carbon Dioxide	8.390	557	3.239
Carbon Monoxide	5.625	272	5.340
Sulfur Dioxide	8.406	791	4.252
Nitrous Oxide	8.810	603	4.415
Hydrogen Chloride	6.591	640	4.025
Hydrogen Sulfide	6.354	736	4.908
Ethyl Acetate	10.54	906	7.597

Three of the most difficult polar fluids to model accurately are water, ammonia, and methanol; in particular, the saturated liquid density is poorly predicted by the Peng-Robinson equation with average deviations ranging from 13-24% for the three fluids. Modified cubic equations, such as those proposed by Heyen (1980) and Patel and Teja (1982), can give substantially improved results for saturated liquid densities of these strongly polar fluids but the additional parameters introduced by these modifications defy correlation. In Figures 1-3, we compare the saturated densities predicted by the KK and SL equations and the corresponding experimental values for the three fluids water (Figure 1), ammonia (Figure 2), and methanol (Figure 3). The KK model is superior to the SL model for these three fluids, particularly in the vicinity of the critical point. This is likely due to the temperature dependence of the g_{01} function used in the

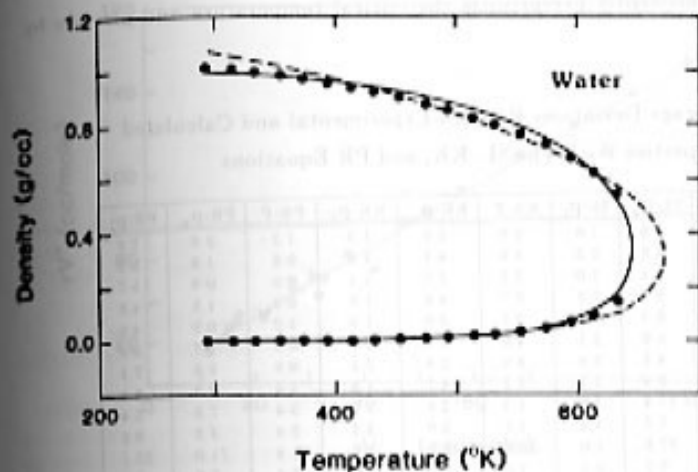


Figure 1.
Density-temperature
vapor-liquid equilibria of
water: experimental data
(o), SL equation (---),
KK equation (—).

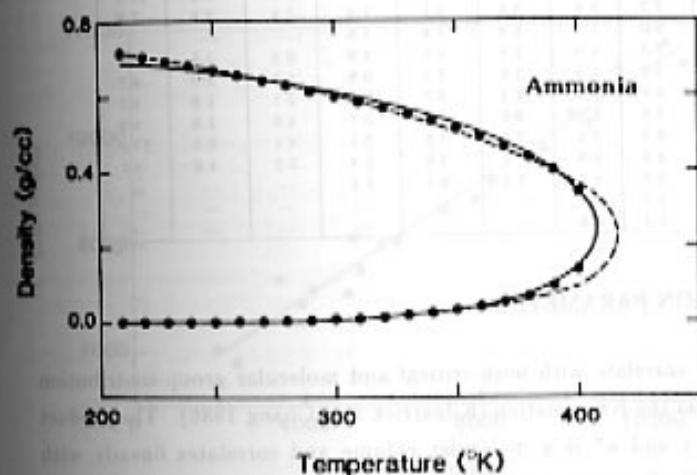


Figure 2.
Density-temperature
vapor-liquid equilibria of
ammonia (curves and data
as in Figure 1).

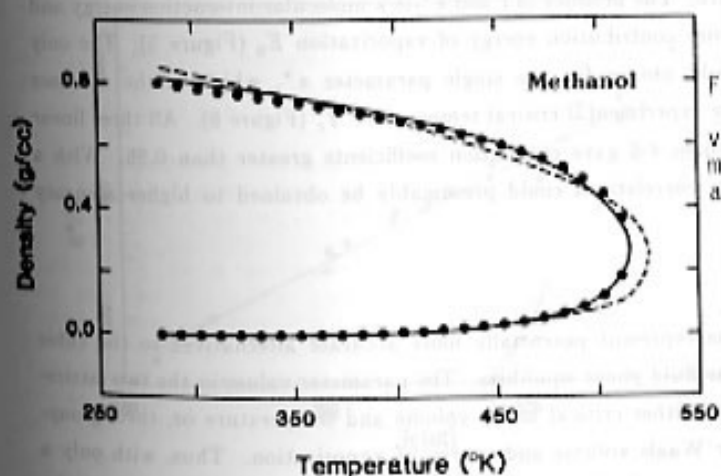


Figure 3.
Density-temperature
vapor-liquid equilibria of
methanol (curves and data
as in Figure 1).

KK model. The SL equation consistently overpredicts the critical temperature and pressure by about 2-4%.

TABLE 2: Absolute Average Deviations Between Experimental and Calculated Saturated Properties With The SL, KK, and PR Equations

Fluid	SL-P	SL- p_c	SL- T_c	KK-P	KK- p_c	KK- T_c	PR-P	PR- p_c	PR- T_c
Methane	2.3	3.6	1.8	2.0	5.6	1.3	1.2	2.6	7.8
Ethane	1.4	5.6	2.3	1.5	4.1	1.4	0.6	1.8	6.5
Propane	2.8	5.1	2.0	3.2	3.5	1.1	0.5	0.9	5.7
n-Butane	3.0	5.7	2.6	0.7	4.8	1.0	0.9	1.5	4.6
n-Pentane	2.6	6.3	2.2	3.2	3.0	1.3	1.0	0.9	4.6
n-Hexane	3.1	5.2	3.1	4.0	2.0	2.1	0.6	1.7	6.4
n-Heptane	2.4	4.5	2.6	4.1	2.6	2.1	0.9	2.6	7.1
n-Octane	1.1	8.4	3.1	2.7	4.7	1.8	1.5	2.3	6.4
n-Nonane	4.2	11.4	3.9	1.3	2.6	2.0	3.4	7.8	5.4
n-Decane	2.6	7.7	4.5	1.2	5.0	3.1	2.4	3.2	9.2
Acetic Acid	30.2	27.6	2.0	20.9	16.6	1.9	1.4	71.0	32.3
Methyl Ether	3.3	6.2	3.1	3.0	6.2	2.0	2.4	6.0	7.5
Ethyl Ether	5.3	4.9	3.5	1.0	4.9	2.0	0.7	2.5	5.2
Methanol	4.3	12.1	4.3	2.7	3.6	2.2	3.6	5.2	14.3
Ethanol	2.3	7.3	5.4	3.6	2.1	1.8	1.4	2.6	7.7
n-Propanol	4.4	5.0	7.3	2.3	1.4	1.6	---	---	---
Ammonia	4.8	7.3	1.0	1.4	1.5	1.8	0.7	3.5	13.9
Carbon Monoxide	3.1	3.7	1.5	3.9	3.5	0.0	1.4	3.0	6.5
Carbon Dioxide	3.4	5.6	2.6	2.4	3.7	0.6	2.1	1.8	4.7
Sulfur Dioxide	2.9	5.5	2.5	2.6	2.0	0.7	1.6	1.5	4.9
Water	2.9	8.5	2.1	2.2	3.6	2.1	4.1	6.5	24.4
Nitrous Oxide	3.8	4.4	1.9	2.1	2.0	0.4	2.2	4.0	4.7
Hydrogen Chloride	0.6	5.2	1.1	1.1	6.1	1.1	---	---	---
Hydrogen Sulfide	1.8	1.1	1.1	---	---	---	---	---	---
Ethyl Acetate	4.7	1.1	4.6	---	---	---	---	---	---

CORRELATION OF SL EQUATION PARAMETERS

The SL equation parameters correlate with both critical and molecular group-contribution properties in much the same way as the KK equation (Kilpatrick and Chang 1986). The product of the two molecular parameters r and v^* is a molecular volume and correlates linearly with either critical volume or van der Waals volume (Figure 4). Here, the van der Waals volume of a molecule is calculated using the group-contribution technique of Bondi (1968) and requires only a knowledge of molecular structure. The product of r and ϵ^* is a molecular interaction energy and correlates linearly with the group contribution energy of vaporization E_0 (Figure 5). The only satisfactory correlation we could obtain for the single parameter ϵ^* , which is the mer-mer interaction energy, was with the experimental critical temperature T_c (Figure 6). All three linear correlations represented by Figures 4-6 gave correlation coefficients greater than 0.96. With a larger data-base, the parameter correlations could presumably be obtained to higher accuracy with nonlinear functions.

CONCLUSIONS

The KK and SL equations represent potentially more accurate alternatives to the cubic equations for predictions of polar fluid phase equilibria. The parameter values in the two lattice-gas equations correlate well with either critical molar volume and temperature or, their group-contribution analogues, van der Waals volume and energy of vaporization. Thus, with only a knowledge of molecular structure or critical properties, the parameter sets for both models can be

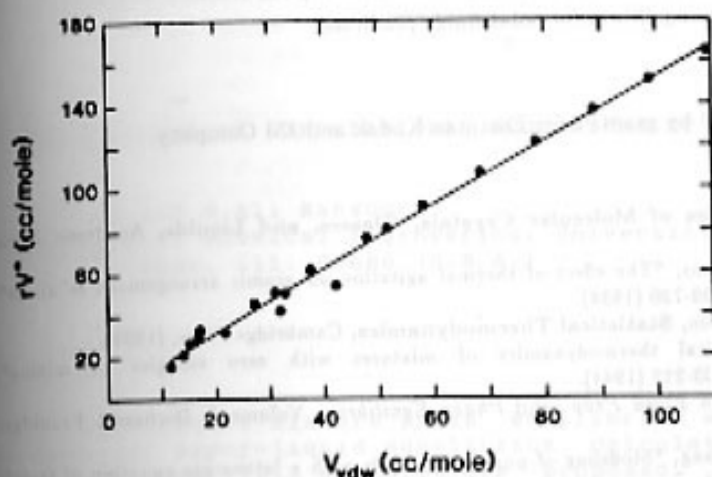


Figure 4.
Correlation of molecular volume rv^* in SI equation with van der Waals volume (Bondi 1968). Line is least squares fit with correlation coefficient of 0.994:
 $rv^* = 1.5061V_{vdw} + 2.1634$,
 rv^* and V_{vdw} in units of cm^3/mole .

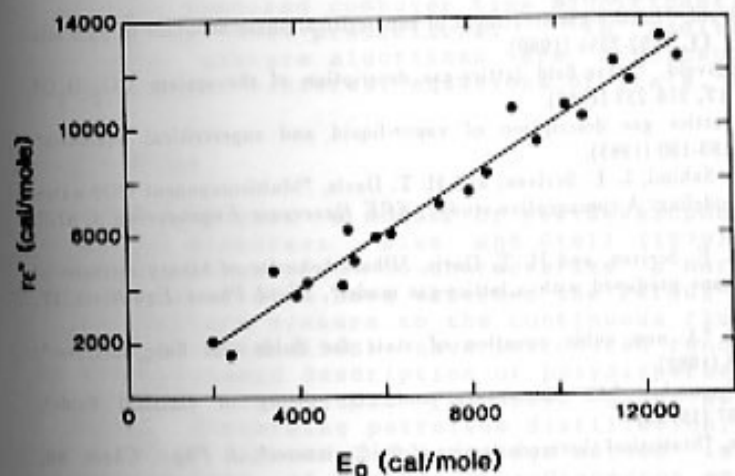


Figure 5.
Correlation of molecular interaction energy with group-contribution energy of vaporization (Bondi 1968). Line is least squares fit with correlation coefficient of 0.960:
 $rc^* = 1.0314E_0 - 43.411$,
 rc^* and E_0 in units of cal/mole .

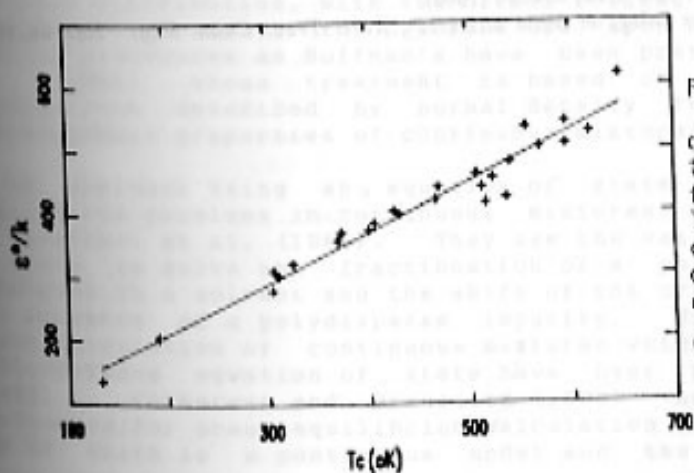


Figure 6.
Correlation of mer-mer characteristic interaction temperature with critical temperature. Line is least squares fit with correlation coefficient of 0.960:
 $c^*/k = 0.8005T_c + 51.0548$,
 c^*/k and T_c in degrees K.

estimated and saturated phase equilibria for polar fluids predicted.

ACKNOWLEDGEMENTS

This work was supported by grants from Eastman Kodak and 3M Company.

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