Determination of Cubic Equation of State Parameters for Pure Fluids from First Principle Solvation Calculations

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A new method for estimation of parameters in cubic equations of state from ab initio solvation calculations is presented. In this method, the temperature-dependent interaction parameter a(T) is determined from the attractive component of solvation free energy, whereas the volume parameter b is assumed to be that of solvation cavity. This method requires only element-specific parameters, i.e., atomic radius and dispersion coefficient, and nine universal parameters for electrostatic and hydrogen-bonding interactions. The equations of state (EOS) parameters so determined allow the description of the complete fluid phase diagram, including the critical point. We have examined this method using the Peng–Robinson EOS for 392 compounds and achieved an accuracy of 43% in vapor pressure, 17% in liquid density, 5.4% in critical temperature, 11% in critical pressure, and 4% in critical volume. This method is, in principle, applicable to any chemical species and is especially useful for those whose experimental data are not available.
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Introduction

The cubic equations of state (EOS), such as the Peng-Robinson EOS (PR EOS)[1] and Soave–Redlich–Kwong EOS (SRK EOS),[2] have proven to be a powerful tool for describing the properties of pure components and mixtures, including the vapor pressure,[3–11] critical properties,[7,12] phase equilibrium,[13–21] etc. In general, a cubic EOS has two compound-specific parameters: one temperature-dependent interaction parameter $a(T)$ and one volume parameter b. For pure compounds, their values are typically determined from the critical properties (T_c, P_c) and the acentric factor ω of pure substances. However, for some species there exist substantial inconsistency in the reported values of critical properties. For example, the critical temperature ranges from 629 to 664.3 K and the critical pressure from 3.85 to 4.60 MPa for the cyclohexanone.[22,23] In addition, critical properties are not always available experimentally, for example, for newly synthesized compounds and for heavy organics that would decompose before reaching the critical point. It is therefore desirable to have a method for describing the phase behaviors without the need of critical properties.

There have been efforts made to replace the use experimental critical properties with other properties. For example, Coniglio et al.[3,4] proposed a modified cubic EOS (PR-type with volume translated correction) which requires input of only one boiling point. Kontogeorgis et al.[7] proposed a method to predict the critical properties from one experimental vapor pressure datum and the van der Waals surface area. There are also group contribution models[24–27] available. Such methods, when applicable, are very accurate, however, at the cost of having a large number of parameters and requiring special care for isomers and/or compounds containing multiple functional groups.[28]

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In this work, we propose a method to determine the two parameters in most cubic EOS (the PR EOS is used as an example in this work) from first principle solvation calculations, in which the electrostatic interactions between a solute molecule and the solvent, treated as a dielectric continuum, are determined. It can be shown that such an energy of interaction is related to the interaction parameter $a(T)$ in the EOS; therefore, the calculated value can be used to estimate $a(T)$. Furthermore, the volume parameter b can be well approximated by the volume of cavity used in the same solvation calculations. Therefore, this method makes it possible to obtain fluid properties, such as liquid density and critical properties (T_c, P_c, V_c), and vapor–liquid equilibrium from PR EOS without input of any experimental data.

Theory

The solvation free energy $\Delta G^{*\mathrm{sol}}$, as defined by Ben-Naim,[29] is the work needed for transferring of a molecule (solute) from an ideal gas phase to a solution (solvent) under constant temperature T and pressure P. Such a free energy is commonly computed from a hypothetical two-step process: first, creating a cavity to size of the solute (the corresponding work is referred to as the cavity formation free energy $\Delta G^{*\mathrm{cav}}$), and then placing the solute into the cavity (corresponding work referred to as the charging free energy $\Delta G^{*\mathrm{chg}}$), that is,

$$\Delta G^{*\mathrm{sol}} = \Delta G^{*\mathrm{chg}} + \Delta G^{*\mathrm{cav}} \tag{1}$$

This free energy can be determined from a given EOS by[30] (see Appendix A for details)

$$\frac{\Delta G^{*\mathrm{sol}}(T,V)}{RT} = (z-1) + \int_{V=\infty}^{V} \frac{(1-z)}{V}\,dV \tag{2}$$

where V is the molar volume of the fluid at T and P; R is the universal gas constant; and $z = PV/RT$ is the compressibility factor. In the PR EOS, the temperature and volume dependence of compressibility factor is

$$z(T,V) = \frac{V}{V-b} - \frac{a(T)}{RT}\frac{V}{V(V+b)+b(V-b)} \tag{3}$$

where $a(T)$ is a temperature-dependent parameter and b is a constant corresponding to the molecular volume of the chemical substance. Using Eq. 3 in Eq. 2, we have the solvation free energy expressed in terms of $a(T)$ and b as

$$\begin{aligned}\frac{\Delta G^{*\mathrm{sol}}(T,V)}{RT} &= \left(\ln\frac{V}{V-b} + \frac{b}{V-b}\right)\\ &\quad + \frac{a(T)}{RT}\left[\frac{1}{2b\sqrt{2}}\ln\frac{V+b(1-\sqrt{2})}{V+b(1+\sqrt{2})} - \frac{V}{V^2+2bV-b^2}\right]\end{aligned} \tag{4}$$

Because the cavity formation term is dominated by the solute-solvent repulsion (hard-core interactions), we have

$$\frac{\Delta G^{*\mathrm{cav}}(T,V)}{RT} = \left(\ln\frac{V}{V-b} + \frac{b}{V-b}\right) \tag{5}$$

Consequently, the (attractive) charging term is

$$\begin{aligned}\frac{\Delta G^{*\mathrm{chg}}(T,V)}{RT} &= \frac{a(T)}{RT}\\ &\quad \times \left[\frac{1}{2b\sqrt{2}}\ln\frac{V+b(1-\sqrt{2})}{V+b(1+\sqrt{2})} - \frac{V}{V^2+2bV-b^2}\right]\end{aligned} \tag{6}$$

In the liquid phase, the molar volume V can be well approximated with the molecular volume parameter b. Therefore,

$$\frac{\Delta G^{*\mathrm{chg}}(T,b)}{RT} = C\frac{a(T)}{bRT} \tag{7}$$

with $C = \frac{1}{2\sqrt{2}}\ln\frac{2-\sqrt{2}}{2+\sqrt{2}} - \frac{1}{2}$ being a constant (note that this constant depends only on the EOS used). If we approximate b to be the volume of cavity for the solute solvation, Eq. 7 provides a means to determine parameter $a(T)$ from the computation of charging free energy in the liquid phase.

Among the many approaches to determine the charging free energy,[31–35] we choose here the implicit solvation quantum mechanical calculations.[32,36–38] Of particular interest here is the Conductor-like Screening Model (COSMO), pioneered by Klamt and others.[35,38–42] In this method, a solute is initially placed in a conductor so that it is perfectly screened. The screening charges are then removed so that the environment is restored to the real liquid state. Based on such a process, Lin et al.[40] determined the charging free energy from the sum of four contributions, i.e.,

$$\Delta G^{*\mathrm{chg}} = \Delta G^{*\mathrm{is}} + \Delta G^{*\mathrm{cc}} + \Delta G^{*\mathrm{res}} + \Delta G^{*\mathrm{dsp}} \tag{8}$$

The ideal solvation term is the difference in energy when the solute is in the ideal gas and in the conductor state

$$\Delta G^{*\mathrm{is}} = E^{\mathrm{COSMO}} - E^{\mathrm{IG}} = E(q^*) + E_{\mathrm{diel}}(q^*) - E(0) \tag{9}$$

in which $E(q^*)$ is the total electronic energy of the solute within an external field arising from the screening charges q^* located at the cavity surface (thus, $E^{\mathrm{IG}} = E(0)$); and $E_{\mathrm{diel}}(q^*) = \frac{1}{2}\sum_v \phi_v q_v^*$ is the dielectric energy; q_v^* is the screening charge at some position v on the cavity surface; ϕ_v is the electrostatic potential due to the solute at position v. Note that the values of q_v^*, ϕ_v, $E(q^*)$, $E_{\mathrm{diel}}(q^*)$ are obtained from ab initio COSMO solvation calculations.[38]

In the COSMO-based methods,[40,43–46] the work related to the removal of screening charges is determined from consideration of the electrostatic interactions between surface segments (each possesses certain amount of screening charges) when brought in contact. A fundamental assumption in these methods is that the segment pairs in contact are independent from one another (i.e., no interactions between any segment pairs). For this purpose, a charge averaging process was suggested[47]:

$$\sigma_m = \frac{\sum_n \sigma_n^* \frac{r_n^2 r_{\mathrm{eff}}^2}{r_n^2 + r_{\mathrm{eff}}^2}\exp\left(-\frac{f_{\mathrm{decay}} d_{mn}^2}{r_n^2 + r_{\mathrm{eff}}^2}\right)}{\sum_n \frac{r_n^2 r_{\mathrm{eff}}^2}{r_n^2 + r_{\mathrm{eff}}^2}\exp\left(-\frac{f_{\mathrm{decay}} d_{mn}^2}{r_n^2 + r_{\mathrm{eff}}^2}\right)} \tag{10}$$

where d_{mn} is the distance between segments m and n, f_{decay} is an empirical parameter (set to 3.57) used to adjust the strength of correlation between segments m and n, $r_n = \sqrt{a_n/\pi}$ is the radius of segment n, and $r_{\text{eff}} = \sqrt{a_{\text{eff}}/\pi}$ ($a_{\text{eff}} = 7.50$ Å^2) is the radius of a standard surface segment. As a result, it is necessary to consider the energy shift associated with the charge averaging process:

$$\Delta G^{*\text{cc}} = f_{\text{pol}}^{1/2}[E_{\text{diel}}(q) - E_{\text{diel}}(q^*)] \tag{11}$$

where the polarization factor f_{pol} was determined to be 0.6916.[40]

The restoring term accounts for changing from the corrected screening state to the actual solvent, and is obtained as a summation over the segment activity coefficients[46]

$$\frac{\Delta G^{*\text{res}}}{RT} = n \sum_{s}^{n\text{hb,hb}} \sum_{\sigma_m} p^{\text{s}}(\sigma_m^{\text{s}}) \, \ln \Gamma^{\text{s}}(\sigma_m^{\text{s}}) \tag{12}$$

where n is the number of surface segments from the solute, which is the ratio of the surface area to the area of standard surface segment ($= A_s/a_{\text{eff}}$); $p(\sigma)$, called the sigma profile, is the probability of finding a segment of charge density $\sigma = q/a$, and is established from the screening charges q distributed over the solvation cavity surface. To better describe hydrogen-bonding species, $p(\sigma)$ is separated into the hydrogen bonding and non-hydrogen bonding components, i.e., $p(\sigma) = p^{\text{nhb}}(\sigma) + p^{\text{hb}}(\sigma)$; $p^{\text{hb}}(\sigma)$ is the sigma profile only for hydrogen-bonding atoms, which are defined to be oxygen, nitrogen, fluorine, and the hydrogen atoms connected to O, N, and F; and $\Gamma(\sigma)$ is the segment activity coefficient obtained from

$$\ln \Gamma^{t}(\sigma_m') = -\ln\left\{ \sum_{s}^{n\text{hb,hb}} \sum_{\sigma_n} p^{\text{s}}(\sigma_n^{\text{s}}) \times \exp\left[\frac{-\Delta W(\sigma_m^{\text{t}}, \sigma_n^{\text{s}}) + \ln \Gamma^{\text{s}}(\sigma_n^{\text{s}})}{kT}\right]\right\} \tag{13}$$

where the superscript "t" and "s" can be either hb or nhb, representing the property for a hydrogen bonding or non-hydrogen bonding segment. Equation 13 allows to solve for $\Gamma(\sigma)$ provided that the segment interaction ΔW is given. We use the following form:

$$\Delta W(\sigma_m^{\text{t}}, \sigma_n^{\text{s}}) = f_{\text{pol}} \frac{0.3 a_{\text{eff}}^{3/2}}{2\varepsilon_0} (\sigma_m^{\text{t}} + \sigma_n^{\text{s}})^2 - c_{\text{hb}}(\sigma_m^{\text{t}}, \sigma_n^{\text{s}})(\sigma_m^{\text{t}} - \sigma_n^{\text{s}})^2 \tag{14}$$

where ε_0 is the permittivity of vacuum; $c_{\text{hb}}(\sigma_m^{\text{t}}, \sigma_n^{\text{s}})$ is the following temperature-independent parameter:

$$c_{\text{hb}}(\sigma_m^{\text{t}}, \sigma_n^{\text{s}}) = \begin{cases} c_{\text{hb}} & \text{if s} = \text{t} = \text{hb, and } \sigma_m^{\text{t}} \cdot \sigma_n^{\text{s}} < 0 \\ 0 & \text{otherwise} \end{cases} \tag{15}$$

The first term on the right-hand side of Eq. 14 considers the electrostatic interactions between two charged segments m and n, whereas the second term considers the stabilization due to the formation of hydrogen-bonding after removal of the screening charges σ_{m} and σ_{n}. The value of c_{hb} is obtained during the parameter optimization.

The dispersion solvation free energy is considered to be proportional to the exposed surface area of the solute and is determined from the sum of contributions from all the atoms contained in the solute.

$$\Delta G^{*\text{dsp}} = \sum_k S_k(A_{\text{dsp},k}T + B_{\text{dsp},k}) + \text{Ring} + \text{HB} \tag{16}$$

where S_k is the exposed surface area of atom type k, $A_{\text{dsp},k}$, and $B_{\text{dsp},k}$ are the dispersion coefficients for atom type k and are obtained from the regression of experimental vapor pressure data of a set of compounds. The last two terms in Eq. 16 are empirical corrections for hydrogen-bonding and ring-contained compounds. They are introduced to improve the model accuracy. The expressions for these additional correction terms are

$$\text{Ring} = N_{\text{AIR}}(A_{\text{dsp,Ring}}T + B_{\text{dsp,Ring}}) \tag{17}$$

$$\text{HB} = \frac{1}{N_{\text{HBH}}}\left[\frac{A_{\text{dsp,HB}}}{1 + \exp(C_{\text{dsp,HB}}T + B_{\text{dsp,HB}})}\right] \tag{18}$$

where N_{HBH} and N_{AIR} are the number of hydrogen bond acceptor (hydrogen atom connects with oxygen, nitrogen, and fluoride atom) and atoms involved in the ring structure, respectively. Equation 18 is formulated this way such that the hydrogen-bonding correction would be zero at high temperatures.

Equations 8–18 provides a way to determine the charging free energy $\Delta G^{*\text{chg}}$ which can be used in Eq. 7 for evaluation of $a(T)$.

Computational Details

The calculation of parameters $a(T)$ and b in PR EOS requires the computation of the solvation charging free energy $\Delta G^{*\text{chg}}$. The computation consists of nine steps. (1) The equilibrium geometry of the molecule in the ideal gas phase is obtained from molecular energy minimization using the quantum chemistry package DMol3[48] implemented in Cerius2.[49] The molecular energy is determined from the density functional theory with nonlocal VWN-BP functional at the DNP (double numeric with polarization functions version 4.0.0 with a real space cutoff set to 5.50 Å) basis set level. The minimum energy of molecule in ideal gas E^{IG} can be found in the output file (extension outmol). (2) The COSMO calculation[38] (solvation calculation for a molecule in the conductor) at the same VWN-BP and DNP level (with default settings for all other parameters) is performed to obtain the energy in conductor E^{COSMO}, and the screening charges q^* on the molecular cavity surface (output file with extension cosmo). The molecular cavity is defined using the default atomic radii (listed in Table 1). The cavity surface area (including the atom exposed surface area S_{k}) and volume are obtained in the same calculation. (Note that there is a relatively comprehensive COSMO file databank maintained by Liu's group[50] at Virginia Tech[51] and can be used directly here.) (3) The volume of the cavity (multiplied by Avogadro's number) is taken as parameter b. (4) The ideal solvation free energy $\Delta G^{*\text{is}}$ is calculated using Eq. 9. (5) Perform screening charge averaging using Eq. 10 and determine the

Table 1. Parameters and Their Values for Use in the Calculation of the Charging Free Energy Described in Eqs. 8–18

Universal Parameters	
Parameter	Value
a_{eff} (Å^2)	7.5000
c_{hb} (kJ/mol/Å^4/e^2)	6127.1445
f_{pol}	0.6916
f_{decay}	3.5700
$A_{\mathrm{dsp,HB}}$ (J/mol/K/Å^2)	−7920.6974
$B_{\mathrm{dsp,HB}}$ (J/mol/Å^2)	−10.9984
$C_{\mathrm{dsp,HB}}$ (J/mol/K^2/Å^2)	0.0288
$A_{\mathrm{dsp,Ring}}$ (J/mol/K/Å^2)	−2.2597
$B_{\mathrm{dsp,Ring}}$ (J/mol/Å^2)	−678.7522

Atom Specific Parameters			
Atom Type	R_{i} (Å)	$A_{\mathrm{dsp,i}}$ (J/mol/K/Å^2)	$B_{\mathrm{dsp,i}}$ (J/mol/Å^2)
H	1.30	0.3064	−344.1410
C	2.00	0.3064	−344.1410
N	1.83	0.5654	−719.5852
O	1.72	0.5375	−573.3108
F	1.72	0.3573	−236.0765
Cl	2.05	0.3950	−485.5521

energy shift correction with Eq. 11. (6) Generation of the sigma profiles $p^{\mathrm{hb}}(\sigma)$ and $p^{\mathrm{nhb}}(\sigma)$. (The details of this step can be found elsewhere.[40,46]) (7) For each given temperature, determine the restoring free energy from Eqs. 12 and 13. (8) For each given temperature, determine the dispersion contribution from Eq. 16. (9) Finally, parameter $a(T)$ is calculated from the sum of solvation contributions according to Eq. 7. It should be noted here that steps 1–6 needs to be done only once for each chemical substance, whereas steps 7–9 must be done at each temperature.

Once we have $a(T)$ and b for PR EOS, the calculation of vapor pressure and liquid phase density is done following the standard procedures, e.g., in the book by Sandler.[52] A procedure for calculation of critical properties is described in Appendix B.

Parameter Optimization

In the model proposed above (Eqs. 8–18), there are a total of nine universal parameters (a_{eff}, c_{hb}, $A_{\mathrm{dsp,HB}}$, $B_{\mathrm{dsp,HB}}$, $C_{\mathrm{dsp,HB}}$, $A_{\mathrm{dsp,Ring}}$, $B_{\mathrm{dsp,Ring}}$, f_{pol}, and f_{decay}), three element specific parameters for each atom (R_{i}, $A_{\mathrm{dsp,i}}$, $B_{\mathrm{dsp,i}}$), all of which are not system specific. Nine ($a_{\mathrm{eff}} = 7.5$ Å, $f_{\mathrm{pol}} = 0.6916$, $f_{\mathrm{decay}} = 3.57$, and R_{i}) of the total 27 ($9 + 6 \times 3$) parameters are taken from previous work. The remaining 18 parameters are optimized using experimental vapor pressure data with the following objective function:

$$\mathrm{rms} = \left[\frac{1}{M}\sum_{j}^{M}\left(\ln P^{\mathrm{vap}}_{\mathrm{calc},j} - \ln P^{\mathrm{vap}}_{\mathrm{expt},j}\right)^2\right]^{1/2} \tag{19}$$

where M is the total number of points, $P^{\mathrm{vap}}_{\mathrm{calc},j}$ and $P^{\mathrm{vap}}_{\mathrm{expt},j}$ are the vapor pressures of pure compounds from calculation and experiment, respectively. Experimental data are taken from the DIPPR database.[53] For each compound, experimental vapor pressures at three different temperatures between the normal boiling point T_{b} and the critical point T_{c} are used.

The parameterization proceeded as follows. First, linear alkanes (from ethane to dodecane) were used to optimize A_{dsp} and B_{dsp} for C and H atoms. Once the parameters were optimized, these optimized parameters were fixed in the further optimization of other parameters. Second, compounds that contain only C, H, and O atoms (6 aldehydes, 11 ketones, 6 ethers, and 8 esters without branches) were used to determine the dispersion parameters for O. Third, 14 linear alcohols [from 1-propanol (C3) to 1-octadecanol (C18) except 1-undecanol (C11) and 1-tridecanol (C13)] were used to optimized c_{hb} first and then the same set compounds were also used to determine the dispersion H-bond correction parameters ($A_{\mathrm{dsp,HB}}$, $B_{\mathrm{dsp,HB}}$, and $C_{\mathrm{dsp,HB}}$). Next, compounds containing C, H, O, and N atoms (3 nitros and 3 nitriles) were used to optimize the dispersion parameters of *N*. Next, the dispersion correction parameters ($A_{\mathrm{dsp,Ring}}$ and $B_{\mathrm{dsp,Ring}}$) for ring structure involved in molecule was obtained from the optimization of 49 cycloalkane and aromatic compounds containing C and H atoms. Finally, The dispersion parameters of chlorine and fluorine were then found using the data of four chlorine containing alkyl halides (chloroethane, 1-chloropropane, 1-chlorobutane, and 1-chloropentane) and six fluorine containing alkyl halides (ethylfluoride, hexafluoroethane, carbontetrafluoride, octafluorocyclobutane, fluorobenzene, hexafluorobenzene), respectively. All the optimized parameters are listed in Table 1.

Results and Discussion

The root mean square (rms) deviation in describing vapor pressures from the proposed method for a total of 392 compounds (a complete list of these compounds is available as Supplementary Material) from boiling point to critical point is listed in Table 2 and shown in Figure 1. The overall rms deviation in ln P^{vap} (from Eq. 19) is 0.3597, or 43% error in P^{vap}. The proposed method is usually less accurate for the first member in a homologous family, such as methanol, ammonia, methylchloride, nitromethane, and methylflouride. In addition, it has been reported previously that the implicit

Table 2. The Accuracy of the Predicted Vapor Pressure for Different Classes of Compounds Between the Boiling Point to Near Critical Point

Compound Type	No. of Compounds	Root Mean Square Deviation in ln *P*
Alkane	38	0.1431
Alkene	9	0.0795
Alkyne	7	0.0488
Aldehyde	8	0.2507
Ketone	21	0.1204
Ether	13	0.2019
Alcohol	32	0.1830
Ester	22	0.2701
Acid	10	0.3832
Amine	22	0.8830
Nitro	5	0.4270
Nitrile	5	0.9697
Aromatic	40	0.2314
Cl Containing	24	0.5395
F Containing	8	1.6918
Multifunctional	128	0.3872
Overall	392	0.3597

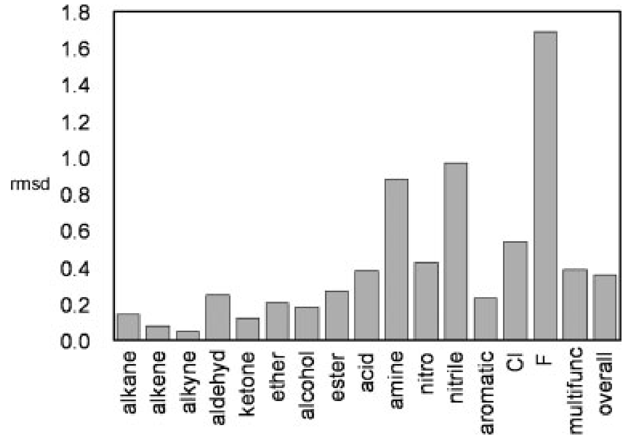

Figure 1. Root mean square deviation (Eq. 19) of the predicted vapor pressure for different classes of compounds.

solvation methods may have difficulty with amines and cyano groups.[40,45,54,55] These reasons accounts for the relatively poor performance observed in fluorine, amine, and nitrile group containing species.

The method proposed here allows one to predict the critical properties. Figure 2 compares the predicted and experimental critical properties for the 392 chemical species considered in this work. The critical volumes predicted from the proposed method (Figure 2a) are in excellent agreement with those from experiment, with the average absolute relative deviation being 4%. It has been observed previously that the critical volume is highly correlated with the molecular size.[7] We also found (results not shown here) that there is an excellent linear correlation between the value of parameter b determined from the solvation cavity and that from T_c and P_c in the PR EOS. These results show that the atomic radii (Table 1) used in establishing the solvation cavity are adequate for describing the volume parameter b.

The overall average absolute errors in critical temperature T_c is found to be 28 K, or an average absolute relative deviation of 5.4%. The three poorly predicted species are methyl chloride, methyl fluoride, and acetonitrile (marked A, B, and C, respectively, on Figure 2b). These are the first member of a homologous family, for which the proposed method is not very accurate as mentioned previously.

The critical pressure can be obtained once T_c and V_c are known because the PR EOS has a constant value of compressibility factor z_c ($= P_cV_c/RT_c$) being 0.307. The average absolute relative deviation in P_c ($= 0.307RT_c/V_c$) is found to be 27%. The large (and systematic) error in predicted P_c is a result of the fact that that value of z_c is indeed different for different chemical species, and is somewhat smaller than 0.307. Thus, we suggest to use $z_c = 0.26$ when calculating P_c (i.e., $P_c = 0.26RT_c/V_c$). In such a case the average absolute relative deviation in P_c reduces to 11% (Figure 2c). [Note that the use of $z_c = 0.26$ is recommended for calculation of P_c only and is not used in any other property calculations (e.g. the vapor pressure).] The poorly described compounds are either the first member in a homologous family, i.e., methyl chloride, methyl fluoride, acetonitrile, and ammo-

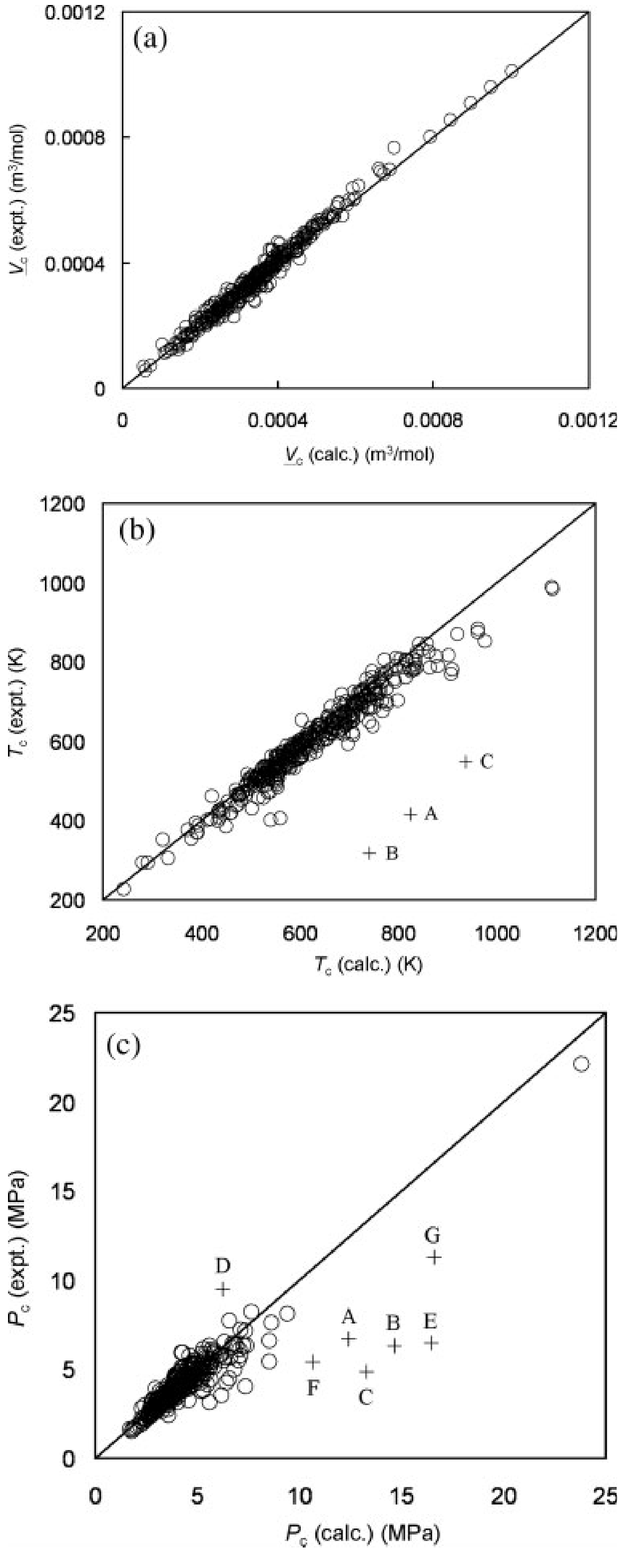

Figure 2. Comparison of the predicted and experimental critical volume (a), critical temperature (b), and critical pressure (c).

In (b) and (c), the marked species are methyl chloride (A), methyl fluoride (B), acetonitrile (C), 1,3-propylene glycol (D), hydrogen fluoride (E), hydrogen cyanide (F), and ammonia (G).

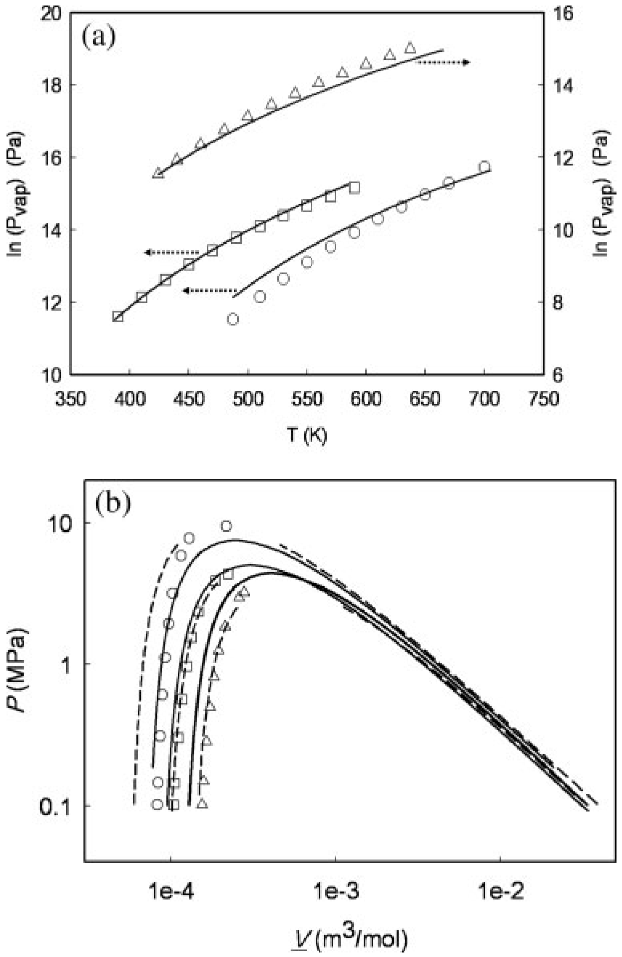

Figure 3. The pressure–temperature (a) and pressure–volume (b) diagrams from the original PR EOS (dashed lines) and the PR EOS with its parameters determined from solvation calculation (solid lines) for cyclooctane, 1,1,2-trichloroethane, and 1,3-propylene glycol.

The experimental data are shown in triangles, squares, circles for the three compounds, respectively.

nia (marked A, B, C, and G, respectively, on Figure 2c) or have a value of z_c that is very different from 0.26, e.g., 1,3-propylene glycol (z_c = 0.342), hydrogen fluoride (z_c = 0.117), and hydrogen cyanide (z_c =0.197) (marked D, E, and F in Figure 2c).

To illustrate that the method proposed here can be used to describe the complete fluid phase diagram, in Figure 3 we present the pressure–volume and pressure–temperature diagrams for three chemical species having very different critical pressures: 1,3-propylene glycol (high P_c = 9.5 MPa), 1,1,2-trichloroethane (medium P_c = 4.83 MPa), cyclooctane (low P_c = 3.57 MPa). The solid and dashed lines are the results from the proposed method and the original PR EOS. The temperature dependence of the vapor pressure (Figure 3a) is well described for these compounds. The deviations of liquid molar volume and the gas molar volume from proposed model are similar to those from original PR EOS (Figure 3b). The average absolute relative deviation in the liquid density for 379 compounds (note that there are no experimental data available in the DIPPR database for 13 of the 392 compounds considered in this work) was found to be 17%. Although the agreement is not perfect, the present model shows how effectively a theoretically based quantum and statistical mechanics model can describe the temperature-dependent parameter *a*(*T*) in PR EOS.

Instead of performing the time consuming QM COSMO calculations, one may also use the free online database (containing COSMO files for 1432 compounds) of Liu and coworkers[50,51] in the proposed model. Figure 4 shows the predicted vapor pressure at normal boiling point (T_b) for 1289 compounds (these are compounds that consists of atoms H, C, O, N, F, or Cl only and whose experimental data at normal boiling point are available in the DIPPR database). The average absolute relative derivation is 42%, slightly more accurate than that (~63%) from the recent work of Wang et al.[56] The poorly predicted compounds are carbon monoxide, ammonia (marked G), flexible compounds which may have intramolecular hydrogen-bonding (maleic acid and malic acid, marked H and K, respectively), and compounds containing many nitro groups (pentaerythritol tetranitrate and tetryl, marked I and J, respectively). The rms deviation in ln P^{vap} (from T_b to T_c) is 0.3834 or 46.73% and the absolute average relative deviations in P_c, T_c, and V_c are 13.5%, 6.7%, and 3.9%, respectively, for these 1289 compounds. The accuracy is similar to that from the previous set of 392 compounds. The results demonstrate the robustness our model and the applicability of the COSMO database.

Conclusion

The employment of ab initio solvation calculation in determination of cubic EOS parameters for pure substances has led to a new way for describing fluid phase equilibria without input of experimental data such as critical properties. The sol-

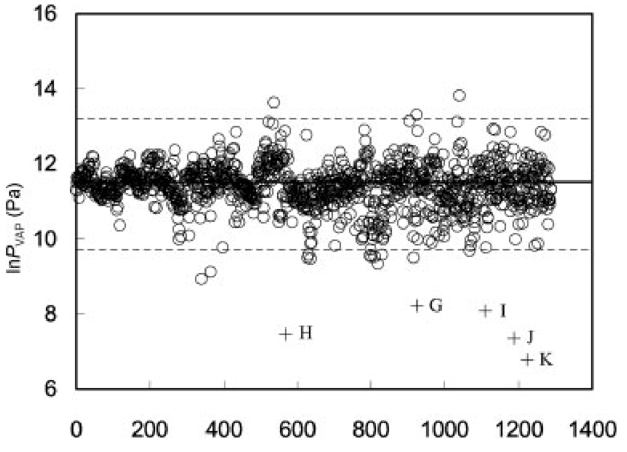

Figure 4. Predicted vapor pressure at normal boiling point for 1289 compounds with the COSMO files from the database of Mullins et al.[50]

The solid line represents 1 atm and the two dashed lines are the maximum error in the work of Wang et al.[56] The marked species are ammonia (G), maleic acid (H), pentaerythritol tetranitrate (I), tetryl (J), and malic acid (K).

vation calculation presented in this work is capable of capturing the correct temperature dependence of the interaction parameter $a(T)$, whereas the solvation cavity is a good estimate for volume parameter b. We show that this method can be used to estimate the vapor pressure and liquid density of chemical species up to the critical point. In addition, the critical properties can be predicted with satisfactory accuracy. Although not shown here, this method can be used to determine other properties such as the normal boiling point, heat of vaporization, etc. This method is in principle applicable to any chemical substances, although less accuracy is expected for small molecules (first member in a homologous family), amine, and nitriles. The extension of this method to mixture fluids should be straightforward and is underway in our lab.

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Appendix A: Solvation Free Energy from an EOS

Lin et al.[30] have shown that the solvation free energy is related to the configuration Helmholtz free energy A^{CONF} as

$$\Delta G^{*\mathrm{sol}} = A^{\mathrm{CONF}} + (z-1)RT \tag{A1}$$

where A^{CONF} is the difference in A between a real system and a ideal gas system at the same volume, temperature (and compositions), i.e., $A^{\mathrm{CONF}}(V,T) = A(V,T) - A^{\mathrm{IG}}(V,T)$. Abbott and Prausnitz[57] showed that A^{CONF} can be determined from the integration of the compressibility factor, that is,

$$A^{\mathrm{CONF}}(V,T) = RT\int_{V=\infty}^{V} \frac{(1-z)}{V}dV \tag{A2}$$

Substituting A^{CONF} in Eq. A1 with Eq. A2, one has

$$\frac{\Delta G^{*\mathrm{sol}}(T,V)}{RT} = (z-1) + \int_{V=\infty}^{V} \frac{(1-z)}{V}dV \tag{A3}$$

Appendix B: Method for Calculation of the Critical Properties

In the P–V diagram, the critical point is the inflection point of $T = T_c$ isotherm,[52] i.e.,

$$\left(\frac{\partial P}{\partial V}\right)_T\bigg|_{T_C,P_C,V_C} = \left(\frac{\partial^2 P}{\partial V^2}\right)_T\bigg|_{T_C,P_C,V_C} = 0 \tag{B1}$$

For the PR EOS, we have

$$\left(\frac{\partial P}{\partial V}\right)_T\bigg|_{T_C,P_C,V_C} = \frac{-RT_C}{(V_C-b)^2} + \frac{2a(V_C+b)}{(V_C^2+2bV_C-b^2)^2} = 0 \tag{B2}$$

and

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T\bigg|_{T_C,P_C,V_C} = \frac{2RT}{(V_C-b)^3} + \frac{2a(V_C^2+2bV_C-b^2) - 8a(V_C^2+2bV_C+b^2)}{(V_C^2+2bV_C-b^2)^3} = 0 \tag{B3}$$

Solving Eqs. B2 and B3, we obtain the critical volume expressed in terms of the volume parameter b,

$$V_C = b[1 + (4+2\sqrt{2})^{1/3} + (4-2\sqrt{2})^{1/3}] \tag{B4}$$

Rewriting Eq. B2, we obtain the expression for energy parameter a at the critical point,

$$a(T_C) = \frac{RT_C}{(V_C-b)^2}\frac{(V_C^2+2bV_C-b^2)^2}{2(V_C+b)} \tag{B5}$$

Thus, the critical temperature T_c can be evaluated numerically, e.g., by the Newton–Rapson method. Once we have T_c and V_c, the critical pressure P_c can be easily calculated from the original PR EOS,

$$P_C = \frac{RT_C}{V_C-b} - \frac{a(T_C)}{V_C(V_C+b)+b(V_C-b)} \tag{B6}$$

or, equivalently,

$$P_C = \frac{z_C RT_C}{V_C} \tag{B7}$$

where $z_c = 0.307$ is a constant in PR EOS. As mentioned in the context, most chemical species have a value of z_c ($= P_cV_c/RT_c$) around 0.26. Therefore, it is recommended that, for better accuracy, $z_c = 0.26$ be used in Eq. B7 for P_c.

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