Thermodynamic equations of state from molecular solvation

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Abstract

A general expression of the canonical partition function for mixture fluids in terms of solvation free energy is presented. Following the same approach as set forth in generalized van der Waals theory, we show that the physical assumptions made in existing thermodynamic models from the perspective of molecular solvation can be prevailed. For example, the temperature dependence on the coordination number, i.e. the number of solvent molecules surrounding the solute, has an impact not only on the temperature dependence of the solvation free energy but on the non-linear solvent reaction field response as well. More importantly, the new formulation provides a unified scheme for deriving the commonly used equations of state (EOS) and newly developed COSMO-type liquid activity coefficient models. We show that from this new formulation it is possible to develop a new class of thermodynamic models that behave like existing EOS and liquid models in the low and high-density limits, respectively.

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1. Introduction

The information on the interrelationship between temperature, pressure, volume and material compositions are important for chemical engineers in the design, development and control of chemical processes [1]. Thermodynamic models are intended to provide such relations. However, existing models usually have limited capabilities [2]. For example, while equations of state (EOS) models such as the Peng–Robinson [3] or Redlich–Kwong [4] EOS are very accurate for pure fluids over a wide range of conditions, their accuracy deteriorates for mixture fluids, especially in the high pressure limit. Excess Gibbs free energy based activity coefficient models such as UNIQUAC [5], NRTL [6] and Wilson [7] are accurate for liquid mixtures but are not applicable in the vapor phase nor to pure substances. Additionally, existing thermodynamic models usually require input of physical parameters (e.g., critical temperature and pressure are needed for most EOS) that must be obtained from experiments, or interaction parameters that can only be obtained from correlation to experimental phase equilibrium data.

Many efforts are made in order to extend the range of applicability of existing thermodynamic models. One very successful

approach is the combined usage of EOS and activity coefficient models [8–15]. Here the excess Gibbs free energy from an EOS model in the limit of infinite pressure [8,13] or zero pressure for the liquid phase [9–12,14] is set to that from an activity coefficient model. This can be regarded as an extension either of an EOS to liquid mixtures or of an activity coefficient model to the vapor phase at the cost of introducing additional parameters from other models.

Another route, known as the generalized van der Waals (GVDW) theory [16–22], is focused on the formulation of a generalized partition function, from which both the EOS and activity coefficient equations can be derived. It has been shown [20] that, under different approximations, most of the commonly used EOS and activity coefficient model can be derived from a single generalized van der Waals partition function. Based on statistical mechanics, the generalized van der Waals theory is a very promising tool to achieve a unified model for thermodynamic modeling. More importantly, it provides a clear physical meaning of the parameters in the existing models, and thus opens up the opportunity to obtain them from first principles calculations, i.e., obtaining the model parameters from quantum mechanical calculations [23–32].

This work is an extension of the generalized van der Waals theory by introducing the ideas of molecular solvation. Solvation theory [33], also based on statistical mechanics, offers a very different perspective to thermodynamic modeling. Rather than

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treating each molecule equally important, in solvation theory one focuses on the interaction between a solute molecule and the solvent molecules surrounding it. The advantage of this is that the solvent as a whole can be approximated as a single dielectric medium. Thus the interplay between the solute and the solvent interactions can be determined from classical electrostatic and quantum mechanical theories [34–36].

The main purpose of this paper is to establish the theoretical foundation of the GVDW partition function from molecular solvation. We show that EOS and recently proposed activity coefficient models based on solvation can be successfully derived from this partition function. This new formulation allows for the understanding of assumptions and limitations in existing models from a molecular solvation perspective. Furthermore, it allows for the development of new thermodynamic models that would satisfy the theoretical boundary conditions both in the low and high-density limit. A simple cubic type EOS is derived to illustrate the realization of these ideas.

2. The generalized van der Waals partition function and solvation free energy

The generalized van der Waals partition function Q for a mixture of volume V at temperature T is [20]

$$Q(N_1, N_2, \dots, V, T) = \prod_i \left[\frac{1}{N_i!} \left(\frac{q_i}{\Lambda_i^3} \right)^{N_i} \right] \times Z(N_1, N_2, \dots, V, T) \quad (1)$$

where N_i is the number of molecules of species i ; $q = q_r q_v q_e$ the product of the rotational, vibrational and electronic partition functions of a single molecule; Λ is the de Broglie wavelength. The configuration integral Z is expressed as

$$Z(N_1, N_2, \dots, V, T) = Z^{\text{HC}}(N_1, N_2, \dots, V, T = \infty) \times \exp \left(\frac{-N\Phi(N_1, N_2, \dots, V, T)}{2kT} \right) \quad (2)$$

where Z^{HC} is the configuration integral due to the hard-core interactions and is related to the free volume in the mixture ($Z^{\text{HC}} = V_f^N$). The mean potential Φ is the temperature integration of the configuration energy E^{CONF}

$$\Phi = \frac{-2kT}{N} \int_{T=\infty}^T \frac{E^{\text{CONF}}}{kT^2} dT \quad (3)$$

with E^{CONF} defined as the energy difference between the real mixture and an ideal gas under the same condition.

The chemical potential of species i can be readily obtained from the generalized partition function

$$\begin{aligned} \mu_i &= -kT \left(\frac{\partial \ln Q}{\partial N_i} \right)_{T,V} \\ &= -kT \ln \frac{V q_i^{\text{IG}}}{N_i \Lambda_i^3} - kT \frac{\partial \ln [Z(q_i/q_i^{\text{IG}} V)^{N_i}]}{\partial N_i} \end{aligned} \quad (4)$$

In solvation thermodynamics, the chemical potential is related to the solvation free energy [33,37,38]

$$\begin{aligned} \mu_i(T, P) &= \mu_i^{\text{IG}}(T, P) + \Delta G_i^{\text{sol}}(T, P) - kT \ln \frac{V(T, P)}{V^{\text{IG}}(T, P)} \\ &= -kT \ln \frac{V q_i^{\text{IG}}}{N_i \Lambda_i^3} + \Delta G_i^{\text{sol}} \end{aligned} \quad (5)$$

Comparing Eqs. (4) and (5) we have the solvation free energy of species i as

$$\begin{aligned} \Delta G_i^{\text{sol}} &= -kT \frac{\partial \ln [Z \prod_i (q_i/q_i^{\text{IG}} V)^{N_i}]}{\partial N_i} \Big|_{T,V} \\ &= -kT \left[\ln \frac{q_i}{q_i^{\text{IG}}} + \frac{\partial \ln (Z^{\text{HC}}/V^N)}{\partial N_i} \right. \\ &\quad \left. + \frac{\partial}{\partial N_i} \int_{T=\infty}^T \frac{E^{\text{CONF}}}{kT^2} dT \right] \end{aligned} \quad (6)$$

Therefore, we may define the total solvation free energy ΔG^{sol} of the mixture to be

$$\Delta G^{\text{sol}} = \sum_i N_i \Delta G_i^{\text{sol}} = -kT \ln \left[Z \prod_i \left(\frac{q_i}{q_i^{\text{IG}} V} \right)^{N_i} \right] \quad (7)$$

(Note that the relation $\Delta G_i^{\text{sol}} = \partial \Delta G^{\text{sol}} / \partial N_i|_{T,V}$ is used to derive the above equation.) Thus the total solvation free energy of a mixture is the natural logarithm of the volume normalized configuration integral, and the GVDW partition function (Eq. (1)) becomes

$$\begin{aligned} Q(N_1, N_2, \dots, V, T) &= \prod_i \left[\frac{1}{N_i!} \left(\frac{q_i^{\text{IG}}}{\Lambda_i^3} \right)^{N_i} \right] V^N \\ &\quad \times \exp \left(-\frac{\Delta G^{\text{sol}}}{kT} \right) \end{aligned} \quad (8)$$

The solvation free energy of a solute molecule i can be determined through a conceptual process [38] as illustrated in Fig. 1. First the charges (Coulomb and attractive van der Waals interactions) on the solute are “turned-off”. The “hard” solute particle is then inserted into the solvent. The work associated with this process is equivalent to that of creating a cavity to accommodate the solute, and is called the cavity formation free energy ΔG_i^{cav} . Once the hard solute is inside the cavity, the charges on the solute are gradually “turned-on” (charging) to its original state. The work associated with the latter charging process is referred to as the charging free energy ΔG_i^{chg} .

Although the rigorous definition for ΔG_i^{cav} is to consider only repulsive interaction for the solute–solvent pairs while retaining the full interactions among all other molecules in the system (i.e., the solvent–solvent interactions), it is common to assume that only repulsive interactions exist in the whole system when modeling ΔG_i^{cav} [39–42]. This is similar to consideration of the limit of infinite temperature, where repulsive hard-core

Fig. 1. Schematic representation of the solvation process.

interactions dominate

$$\Delta G^{*cav} \approx -kT \ln \left(\frac{Z^{HC}}{V^N} \right) \quad (9)$$

Combining Eqs. (2), (3), (7) and (9) we have the total charging free energy related to the mean potential and the configuration energy as

$$\Delta G^{*chg} \approx -kT \sum_i N_i \ln \frac{q_i}{q_i^{IG}} - kT \int_{T=\infty}^T \frac{E^{CONF}}{kT^2} dT \quad (10)$$

and the GVDW partition function becomes

$$Q(N_1, N_2, \dots, V, T) \approx \prod_i \left[\frac{1}{N_i!} \left(\frac{q_i^{IG}}{\Lambda_i^3} \right)^{N_i} \right] Z^{HC} \times \exp \left(-\frac{\Delta G^{*chg}}{kT} \right) \quad (11)$$

Eqs. (7)–(11) allows for the development of new equations of state from the perspective of molecular solvation.

For systems whose configuration energy is pairwise additive, a more precise separation of the solvation free energy can be

done. Let the species occupation number N_{qp} be the number of species q molecules surrounding a p molecule, the configuration energy of the mixture is

$$E^{CONF} = \frac{1}{2} \sum_p N_p \sum_q N_{qp} E_{qp} \quad (12)$$

with E_{qp} being the interaction energy between two molecules p and q . Taking the partial derivative of Eq. (12) with respect to N_i

$$\frac{\partial E^{CONF}}{\partial N_i} = \frac{1}{2} \sum_p N_{ip} E_{ip} + \frac{1}{2} \sum_p N_p \sum_q \frac{\partial N_{pq}}{\partial N_i} E_{pq} \quad (13)$$

The first term on the right hand side of Eq. (13) corresponds to the interaction between a molecule of species i and the rest of the system and the second term corresponds to the change of species occupation due to the introduction of a molecule i . According to the aforementioned charging process, the cavity formation free energy of a solute molecule i can be obtained by turning off the solute–solvent interaction (first term on the RHS of Eq. (13)) and the solute polarization ($q_i = q_i^{IG}$). With this,

Eq. (6) becomes

$$\Delta G_i^{\text{cav}} \approx -kT \left[\frac{\partial \ln(Z^{\text{HC}}/V^N)}{\partial N_i} + \int_{T=\infty}^T \frac{\sum_{p \neq i} N_p \sum_{q \neq i} \frac{\partial N_{pq}}{\partial N_i} E_{pq}}{2kT^2} dT \right] \quad (14)$$

Thus the charging free energy is

$$\Delta G_i^{\text{chg}} \approx -kT \left[\ln \frac{q_i}{q_i^{\text{IG}}} + \int_{T=\infty}^T \frac{\sum_p N_{ip} E_{ip}}{2kT^2} dT \right] \quad (15)$$

These equations are used in the analysis of EOS models in the next section.

3. Solvation free energy from equations of state

In this section, we first follow Sandler's approach [20] to derive the van der Waals EOS from the generalized van der Waals partition function. This helps illustrate the determination of solvation free energy from the EOS. When compared the results to those from the solvation theory, the consequence of assumptions made in the EOS can be elucidated from the perspective of molecular solvation.

Consider a system having N identical molecules in a volume V at temperature T . Suppose the interactions between molecules are described by a square-well potential with a well-depth ε (this is similar to assuming that interactions occur through surface contacts), the configuration energy of the whole system is

$$E^{\text{CONF}} = \frac{N\varepsilon}{2} N_c \quad (16)$$

where N_c is the coordination number, i.e. the number of neighboring molecules any molecule has (note that $N_c = N_{ii}$ and $\varepsilon = E_{ii}$ using the notation in Eq. (12) for a single component system). If N_c is only a function of density ($\rho = N/V$) such as

$$N_c(\rho) = \frac{CN}{V} \quad (17)$$

and the free volume V_f in the system is $V - Nb$ with b being the hard-core volume of each molecule, the generalized van der Waals partition function becomes

$$Q(N, V, T) = \frac{1}{N!} \left(\frac{q^{\text{IG}}}{\Lambda^3} \right)^N (V - Nb)^N \exp \left(-\frac{CN^2\varepsilon}{2VkT} \right) \quad (18)$$

The pressure of the system is obtained from taking the partial derivative with respect to volume

$$P = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T} = \frac{kT}{\tilde{V} - b} - \frac{a}{\tilde{V}^2} \quad (19)$$

which is the van der Waals equation of state [20] with $a = -C\varepsilon/2$ and $\tilde{V} = V/N$.

It is useful to examine the description of solvation free energy in the van der Waals EOS. From Eq. (15), we have the charging

free energy of any molecule as half of the total interaction energy (εN_c) associated with this molecule (assuming $q_i = q_i^{\text{IG}}$)

$$\Delta G_i^{\text{chg}} = \frac{N_c(\rho)\varepsilon}{2} \quad (20)$$

This is in accordance with the result from the linear response theory [43] in which one assumes that the dielectric response of solvent is linearly proportional to the external field with the proportional constant being the dielectric constant. Thus the solute–solvent interaction is linearly proportional to a charging factor λ , i.e. $N_c\varepsilon(\lambda) = N_c\varepsilon\lambda$. The charging free energy is obtained from the charging process of gradually varying λ from 0 to 1.

$$\Delta G_i^{\text{chg}} = \int_0^1 N_c\varepsilon\lambda d\lambda = \frac{N_c\varepsilon}{2} \quad (21)$$

Thus degree of polarization of a solvent following the van der Waals EOS would be linearly proportional to the strength of an external electrostatic field (e.g. the solute) as prescribed in the linear response theory.

In van der Waals EOS ΔG_i^{chg} (Eq. (20)) is only a function of density but not temperature. More sophisticated EOS models such as the Redlich–Kwong EOS considers the temperature dependence of N_c

$$N_c(\rho, T) = \frac{C}{\sqrt{T}} \ln \left(1 + \frac{Nb}{V} \right) \quad (22)$$

which leads to the following expression for the charging free energy

$$\Delta G_i^{\text{chg}} = \frac{2}{3} \frac{N_c(\rho, T)\varepsilon}{2} \quad (23)$$

There are two interesting points to make here. First, the dependence of ΔG_i^{chg} on temperature and density from EOS can be compared to that from the theory of dielectric polarization. For many systems the charging free energy of a solute is proportional to the solvent dielectric constant ε as $\Delta G_i^{\text{chg}} \propto (\varepsilon - 1)/(\varepsilon + x)$ [44] where x is a constant between 0 (ion solvation [45]) and 1 (rigid dipole solvation [46]). The solvent dielectric constant is related to the solvent polarizability α and dipole moment μ through the Clausius–Mossotti equation [47] and Debye equation for molar polarization

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{\rho}{3\varepsilon_0} \left(\alpha + \frac{\mu^2}{3kT} \right) \quad (24)$$

where ε_0 is the permittivity of vacuum. The first term on the right hand side of Eq. (24) is the contribution from electron polarization (induced dipole) and the second term is that from the permanent dipole. Thus from the theory of dielectric polarization the dielectric constant, and hence ΔG_i^{chg} , is linearly proportional to the solvent density. This is in agreement with Eq. (20) from the VDW EOS and Eq. (23) from the RK EOS at the low density limit. Furthermore, from Eq. (24) ΔG_i^{chg} is temperature independent for non-polar solvents ($\mu = 0$) and is inversely proportional to temperature for polar solvents. Thus the temperature independent assumption of N_c in the VDW EOS (Eq. (17)) is in agreement with the theory of dielectrics for non-polar systems; whereas the inverse square-root dependence on

T in RK EOS (Eq. (22)) seems to be a compromise in order to describe both polar and non-polar systems.

A second interesting observation is that by introducing temperature effects to the solvation free energy, the Redlich–Kwong model considers only 66% of the ideal (linear) solvent polarization. This is equivalent to a non-linear response ($N_c \varepsilon(\lambda) = N_c \varepsilon \lambda^2$) of the solvent molecules in the charging process

$$\Delta G_i^{\text{chg}} = \int_0^1 N_c \varepsilon \lambda^2 d\lambda = \frac{N_c \varepsilon}{3} \quad (25)$$

Here we observe that the non-linear solvent response is a consequence of the temperature dependence of N_c . In general if $N_c \propto T^n$, ΔG^{chg} would reduce to $1/(1-n)$ of the ideal value, corresponding to a non-linear charge process proportional to $\lambda^{(1-2n)}$ [$n=0$ for vdW EOS and $-1/2$ for RK EOS]. In general non-linear response takes place in polar systems where multiple types of solvent polarization (permanent dipole orientation, electron cloud polarization, etc.) may take place. This again shows that the Redlich–Kwong model would behave better for polar systems.

In most cubic EOS the free volume V_f is estimated as $V - Nb$ which leads to the expression of cavity formation free energy (Eq. (14))

$$\frac{\Delta G_i^{\text{cav}}}{kT} = -\ln(1 - \rho b) + (z - 1) \quad (26)$$

with the compressibility factor $z = PV/NkT$. When the Carnhan–Starling (CS) model [48]

$$V_f = V \exp \left[\frac{-\rho b(4 - 3\rho b)}{(1 - \rho b)^2} \right] \quad (27)$$

is used, a more accurate cavity formation free energy can be obtained for hard spheres

$$\frac{\Delta G_i^{\text{cav}}}{kT} = \frac{\rho b[4 - 3\rho b]}{(1 - \rho b)^2} + (z - 1) \quad (28)$$

It is interesting to note that the scaled-particle theory (SPT) [41] adapted in many solvation models for calculation of the cavity formation free energy takes the form

$$\frac{\Delta G_i^{\text{cav}}}{kT} = -\ln(1 - \rho b) + \frac{3}{2} \frac{\rho b(4 - \rho b)}{(1 - \rho b)^2} + z\rho b \quad (29)$$

where the first term on the right hand side of Eq. (29) comes from the work required to introduce a point solute, the second term corresponds to the surface work (creating the surface of the cavity), and the last term to the volume work (creating the cavity of size b). Interestingly, the initial work of forming an infinitely small cavity appears to be ignored in the CS model. Since the CS model is known to be accurate for hard spheres, the discrepancy might be compensated by the different formulation for the surface and volume work. In contrast, most cubic EOS models do contain the initial work of creating a cavity but the surface and volume work ($z - 1$) appears to be oversimplified. Since the compressibility factor z is much smaller than unity for liquids, this work could erroneously become negative in the high-density limit. This may be a reason for the deteriorated accuracy of such EOS models in the liquid phase.

In the above analysis we see that, at least for square-well systems, the main challenge in developing a more accurate EOS model is the behavior of the coordination number (N_c) with temperature and density. Although the solvation free energy from cubic EOS models does contain the essential features of those from solvation theory, there are few discrepancies among different models which may be the source of error of EOS models, especially for high-density systems where solvation effects are most significant.

4. Solvation free energy from activity coefficient models

In the section, we examine the solvation free energy from liquid models. We will focus on the charging free energy part here as it is the main difference among various models.

The physical picture of mixtures in most activity coefficient models is that molecules are in contact with one another in the liquid phase with an effective (or average) contact area of a_{eff} . A molecule of area A would have A/a_{eff} surface segments, each in contact with its neighboring molecules. Thus, A/a_{eff} is also the coordination number. To describe the potential energy of the system, it is assumed that the interaction occurs only through contacting surface segments (square-well fluids). Surface segments of a molecule can be classified into one of the known segment types. (This is done by using the surface charge density in the COSMO-type models [49–53]. Nonetheless this is quite similar to dissecting a molecule into functional groups in group contribution models such as UNIFAC [54–56].) Thus the energy of a mixture system can be determined by knowing the energy of any two surface segments in contact and the type and amount of the contacting segment pairs. Consequently, the interaction between molecules of a mixture is simplified to that between surface segments.

Consider that a mixture contains N_i molecules of species i whose surface area is A_i . For each molecule i , there are n_k^i type k surface segments, i.e.,

$$\sum_k n_k^i = \frac{A_i}{a_{\text{eff}}} \quad (30)$$

The total number of type k segments is the sum of contributions from all molecules in the system

$$n_k = \sum_i N_i n_k^i \quad (31)$$

and the total number of segments is

$$n_t = \sum_k n_k \quad (32)$$

Analogous to Eq. (12), the configuration energy of the system is determined from the interactions of all paired segments

$$E^{\text{CONF}} = \frac{1}{2} \sum_k n_k \sum_l n_{lk} e_{kl} \quad (33)$$

where e_{kl} is the interaction energy between a segment of type k and a segment of type l , and n_{lk} is the average number (or probability) of type l segments in contact with one type k segment.

[Note that n_{lk} is equivalent to the species occupation number used for molecular species.]

In many local composition models (e.g. Wilson, UNIQUAC, UNIFAC) n_{lk} is assumed to be

$$n_{lk} = x_l \Lambda_{kl} \quad (34)$$

where $x_l = n_l/n_t$ is the fraction of segment type l ; $\Lambda_{kl} = \exp(-e_{kl}/2kT)$ is the energy parameter of segment pair $k-l$. It is useful to define the probability n_k^{cnt} of one segment k getting in contact with any other segment

$$n_k^{\text{cnt}} = \sum_l n_{lk} = \sum_l x_l \Lambda_{lk} \quad (35)$$

Substituting Eqs. (34) and (35) into Eq. (33), we have

$$\frac{E^{\text{CONF}}}{kT^2} = \sum_k n_k n_k^{\text{cnt}} \frac{\partial \ln \sum_l x_l \Lambda_{lk}}{\partial T} \quad (36)$$

In the liquid phase it is reasonable to assume that each segment is in contact with another segment, i.e., $n_k^{\text{cnt}} = 1$. With this assumption, the charging free energy of the mixture is obtained from Eq. (10) (assuming $q_i = q_i^{\text{IG}}$)

$$\Delta G^{\text{chg}} = \sum_k n_k \Delta g_k^{\text{chg}} = -kT \sum_k n_k \ln \sum_l x_l \Lambda_{lk} \quad (37)$$

[Note that there is an inconsistency in the temperature dependence of n_k^{cnt} while deriving Eqs. (36) and (37). This is an intrinsic problem in many local composition models and has been pointed out previously by Flemr [57].] The segment charging free energy can be obtained from taking the partial derivative of Eq. (37) with respect to n_k

$$\frac{\Delta g_k^{\text{chg}}}{kT} = \ln \Gamma_k = 1 - \ln \sum_l x_l \Lambda_{lk} - \sum_l \frac{x_l \Lambda_{lk}}{\sum_m x_m \Lambda_{ml}} \quad (38)$$

where $\Gamma_k = \exp(\Delta g_k^{\text{chg}}/kT)$ is a charging free energy parameter for segment k and will be referred to as the segment activity coefficient (SAC). This is similar to the Wilson [7] and UNIQUAC [5] expressions for (the residual part of the) activity coefficient. The charging free energy of molecule i is

$$\Delta G_i^{\text{chg}} = \sum_k n_k^i \Delta g_k^{\text{chg}} = kT \sum_k n_k^i \ln \Gamma_k \quad (39)$$

Therefore the molecular charging free energy is determined from the sum of contributions from the surface segments. In the case where there is only one type of surface segment (e.g. pure liquid), Eq. (38) gives the segment charging free energy as $\ln \Gamma = \varepsilon/2kT$ and the molecular charging free energy is

$$\Delta G_i^{\text{chg}} = \frac{\varepsilon N_c}{2} \quad (40)$$

with $N_c = \sum_k n_k^i$ being the coordination number. Thus the charging free energy is half of the interaction energy between a solute and its neighbors. This is identical to the results from the van der Waals EOS (Eq. (20)).

There is another class of liquid activity coefficient models that is developed based on different assumptions for the local

composition. The COSMO-type models [49–53] starts from the assumption for the probability p_{lk} of finding segment pairs $k-l$ formed in the liquid phase

$$p_{lk} = x_k x_l \Gamma_k \Gamma_l \tau_{lk} \quad (41)$$

where $\tau_{lk} = \exp(-e_{lk}/kT)$ is the energy parameter of segment pair $k-l$. Since p_{lk} is the product of the probability of finding segments of type k (x_k) and the probability of segment l in contact with segment k (n_{lk}) we have

$$n_{lk} = x_l \Gamma_k \Gamma_l \tau_{lk} \quad (42)$$

It is noteworthy that, unlike Eq. (34) where the local composition n_{lk} is assumed to be different from the bulk composition x_l by the Boltzmann factor τ_{lk} only, COSMO-type models assume that n_{lk} is also affected by the charging free energies (Γ) of both surfaces in contact. Together with the assumption that in the liquid phase the probability n_k^{cnt} of one segment k getting in contact with any other segment is unity

$$n_k^{\text{cnt}} = \sum_l n_{lk} = \sum_l x_l \Gamma_k \Gamma_l \tau_{lk} = 1 \quad (43)$$

The charging free energy parameter can be obtained as

$$\Gamma_k = \frac{1}{\sum_l x_l \Gamma_l \tau_{lk}} \quad (44)$$

This is the COSMO-RS [49] or COSMO-SAC [53] equation for the segment activity coefficient (SAC). The configuration energy of the mixture can be determined from Eq. (33)

$$\begin{aligned} \frac{E^{\text{CONF}}}{kT^2} &= \frac{1}{2kT^2} \sum_k n_k \sum_l x_l \Gamma_k \Gamma_l \tau_{lk} e_{lk} \\ &= \frac{n_t}{2} \sum_k \sum_l x_k x_l \Gamma_k \Gamma_l \frac{\partial \tau_{lk}}{\partial T} \end{aligned} \quad (45)$$

Note that the total number of surface segments in the mixture is

$$n_t = \sum_k n_k \sum_l n_{lk} = n_t \sum_k \sum_l x_k x_l \Gamma_k \Gamma_l \tau_{lk} \quad (46)$$

Taking the temperature derivative of Eq. (46) we have

$$\begin{aligned} \sum_k \sum_l x_k x_l \Gamma_k \frac{\partial \Gamma_l \tau_{lk}}{\partial T} &= - \sum_k \sum_l x_k x_l \Gamma_l \tau_{lk} \frac{\partial \Gamma_k}{\partial T} \\ &= \frac{1}{2} \sum_k \sum_l x_k x_l \Gamma_k \Gamma_l \frac{\partial \tau_{lk}}{\partial T} \end{aligned} \quad (47)$$

Use Eq. (47) in Eq. (45) we have the configuration energy as

$$\frac{E^{\text{CONF}}}{kT^2} = n_t \sum_k \Gamma_k x_k \sum_l x_l \frac{\partial \Gamma_l \tau_{lk}}{\partial T} = -n_t \sum_k x_k \frac{\partial \ln \Gamma_k}{\partial T} \quad (48)$$

To obtain the last identity in Eq. (48), the temperature derivative of Eq. (44) is used. The total charging free energy can now be obtained from Eq. (10)

$$\Delta G^{\text{chg}} = \sum_k n_k \Delta g_k^{\text{chg}} = kT \sum_k n_k \ln \Gamma_k \quad (49)$$

which indicates that the total charging free energy is the sum of contributions from all segments. In the case where there is only one type of segment, Eq. (44) becomes $\ln \Gamma = \varepsilon/2kT$ and the molecular charging free energy is identical to that obtained in Eq. (40).

5. New equations of state satisfying conditions in the low and high-density limits

It is clear that the knowledge for the functional dependence (temperature, pressure, composition) of the local composition n_{lk} (or equivalently the coordination number) is the key to a complete formulation of the generalized van der Waals partition function. Here we show that by considering the segment solvation, one can in fact determine the temperature dependence of n_{lk} .

The starting point is to determine the probability p_{lk} of finding segment pairs k – l from the partition function of Eq. (11)

$$\begin{aligned} p_{lk} &= \frac{Q(n_l - 2) \exp(-e_{lk}/kT)}{Q(n_l)} \\ &= \exp\left(\frac{-e_{kl} + \Delta g_k^{\text{chg}} + kT \ln \rho \beta x_k + \Delta g_l^{\text{chg}} + kT \ln \rho \beta x_l}{kT}\right) \\ &= (\rho \beta)^2 x_k x_l \Gamma_k \Gamma_l \tau_{lk} \end{aligned} \quad (50)$$

where β is the effective volume for the segments and $\rho \beta = 1$ for the liquid phase. Eq. (50) is a generalization of Eq. (41) to include the density effect. The probability of finding a segment of type k is $(\rho \beta x_k)$, thus the local composition n_{lk} becomes

$$n_{lk} = \rho \beta x_l \Gamma_k \Gamma_l \tau_{lk} \quad (51)$$

Note that in the low density limit where the charging free energy parameters are unity ($\Delta g^{\text{chg}} = 0$) Eq. (51) reduces to $n_{lk} = \rho \beta x_l \tau_{lk}$ and is the same as obtained from the radial distribution function for square-well fluids [20]. Furthermore in the limit of small segment interactions, $n_{lk} = \rho \beta x_l$ which is the same as that used in the van der Waals EOS (Eq. (17)).

Following the same derivation for Eq. (44) we have the expression for the charging free energy parameter

$$\Gamma_k = \frac{n_k^{\text{cnt}}}{\rho \beta \sum_l x_l \Gamma_l \tau_{kl}} \quad (52)$$

Here the percentage of surface contact n_k^{cnt} could be a function of temperature and density. We expect that at high densities ($\rho \beta = 1$) $n_k^{\text{cnt}} = 1$ and zero densities ($\rho \beta = 0$) $n_k^{\text{cnt}} = 0$ (ideal gas limit). With Eq. (51) the configuration energy becomes

$$\frac{E^{\text{CONF}}}{kT^2} = n_t \sum_k x_k \left(\frac{1}{2} \frac{\partial n_k^{\text{cnt}}}{\partial T} - n_k^{\text{cnt}} \frac{\partial \ln \Gamma_k}{\partial T} \right) \quad (53)$$

For consistency, the configuration energy in Eq. (53) must be identical to that from the temperature derivative of Eq. (10)

$$\frac{E^{\text{CONF}}}{kT^2} = - \frac{\partial (\Delta G^{\text{chg}}/kT)}{\partial T} = -n_t \sum_k x_k \frac{\partial \ln \Gamma_k}{\partial T} \quad (54)$$

Therefore we obtain a necessary condition for the temperature derivative of n_k^{cnt}

$$\frac{\partial n_k^{\text{cnt}}}{\partial T} = 2(n_k^{\text{cnt}} - 1) \frac{\partial \ln \Gamma_k}{\partial T} \quad (55)$$

for which the general solution is

$$n_k^{\text{cnt}} = 1 - \Gamma_k^2 f(\rho) \quad (56)$$

where $f(\rho)$ is a universal function of density only. Although we do not know the exact f , we expect that its value to be 0 as $\rho \beta = 1$. Use Eq. (56) in Eq. (52) we obtain a general expression for the charging free energy parameter

$$\Gamma_k = \frac{\sqrt{[\rho \beta \sum_l x_l \Gamma_l \tau_{kl}]^2 + 4f(\rho)} - [\rho \beta \sum_l x_l \Gamma_l \tau_{kl}]}{2f(\rho)} \quad (57)$$

This is the general form for the segment charging free energy (Eq. (44)) which we will refer to as the generalized SAC (GSAC) equation. Once given the function f (which controls the percentage of segment surface coverage) a complete GVDW partition function is obtained. One possible form for f is $f(\rho) = 1 - \rho \beta$, and in this case Eq. (57) becomes

$$\Gamma_k = \frac{\sqrt{[\rho \beta \sum_l x_l \Gamma_l \tau_{kl}]^2 + 4(1 - \rho \beta)} - [\rho \beta \sum_l x_l \Gamma_l \tau_{kl}]}{2(1 - \rho \beta)} \quad (58)$$

It is not difficult to show that Eq. (58) satisfies the boundary conditions in the low and high-density limits [that is $\Gamma_k = 1$ as $\rho \beta \rightarrow 0$ and Eq. (58) reduces to Eq. (44) as $\rho \beta \rightarrow 1$].

As an illustration of obtaining the PVT relation from Eq. (57), we may consider a system having only one type of segment (e.g. a single component system). In such case Eq. (58) becomes

$$\ln \Gamma = \frac{-1}{2} \ln[1 + \rho \beta(\tau - 1)] \quad (59)$$

Assuming the free volume of the system to be $V_f = V - Nb$, the pressure of the system can be obtained from

$$\begin{aligned} P &= kT \left(\frac{\partial \ln Q}{\partial V} \right)_{T,N} = \frac{kT}{\tilde{V} - b} - nkT \frac{\partial \ln \Gamma}{\partial V} \\ &= \frac{kT}{\tilde{V} - b} - \frac{AkT}{2a_{\text{eff}}} \frac{b(\tau - 1)}{\tilde{V}^2 + b\tilde{V}(\tau - 1)} \end{aligned} \quad (60)$$

which is a cubic type EOS. [Note we have used relations $n = NA/a_{\text{eff}}$ and $b = \beta A/a_{\text{eff}}$ when deriving Eq. (60).] Thus we see that a typical EOS can be derived from the GSAC equation provided an appropriate description for the function $f(\rho)$ is given.

6. Conclusions

In this paper, we present a theoretical basis for obtaining the solvation free energy from existing equations of state and activity coefficient models. Making connections between the theories of statistical thermodynamics and solvation can be very rewarding. First of all, it allows one to examine the consequences of assumptions made in the existing models from the perspective

of molecular solvation. For example, we show that the introduction of temperature dependence to the coordination number for polar systems leads to proper solvent polarization behavior. Furthermore, we show that, in addition to EOS models, newly developed COSMO-type activity coefficient models based on molecular solvation can be derived within the same scheme. Therefore, it becomes possible to develop a new class of EOS that would behave like activity coefficient models in the high-density limit. We have demonstrated this by developing a new cubic EOS model.

The present approach opens up many interesting possibilities that are the subjects of our current study. For example, there is no need of special treatment for multicomponent systems. Thus there will be no ambiguity of choosing mixing and combination rules in such new models. More importantly, current success in the quantum mechanics based COSMO-type models proves the reliability of obtaining model parameters from first principle calculations. Therefore the interaction parameters needed in any of the newly developed models can be obtained from quantum mechanical calculations, without resorting to experimental data.

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