Two-fluid theory and thermodynamic properties of liquid mixtures: General theory

(statistical thermodynamics/fluids/phase equilibria/nonrandomness/molecular size ratio)

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ABSTRACT The two-fluid theory of binary mixtures postulates that the extensive thermodynamic properties of a binary mixture may be expressed by the contributions of two hypothetical fluids that mix ideally. This postulate, coupled with an expression for the partition function of the hypothetical fluid, permits evaluation of the properties of binary liquid mixtures by using only two adjustable binary parameters. Particular attention is given to the problem of nonrandomness in mixtures. A quantitative description of nonrandomness is achieved by combining the two-fluid concept with a hypothesis for ensemble averaging of a distribution of near-neighbor pairs.

The goal of a molecular theory of fluids and fluid mixtures is to calculate their equilibrium macroscopic properties from quantum and statistical mechanics. Upon application to real systems, however, severe mathematical difficulties arise, and approximate treatments are necessary. Quantum mechanics provides only partial information about intermolecular forces between complex molecules; therefore, semiempirical potential energy functions are required. Statistical mechanics, on the other hand, can be applied with high accuracy only to crystals and to gases at low pressure; only approximate methods are available for dense fluids.

Therefore, interest in approximate theories remains strong, especially among those who would like to utilize theoretical results as a basis for engineering applications. Our aim is to calculate thermodynamic excess functions for binary mixtures; we present here an approximate approach toward that end: the two-fluid theory.

In this paper we discuss the general theory. In subsequent papers we present results for binary mixtures of hard spheres (1) and we extend our model to a real mixture and show that the two-fluid theory leads to the concept of local compositions which are needed to attain a satisfactory description of thermodynamic properties (2).

Local compositions are related to bulk compositions by relationships similar to those postulated by Wilson (3) and incorporated (with minor changes) in many successful empirical models widely used in engineering applications (e.g., NRTL, UNIQUAC, UNIFAC, etc.). A derivation of local compositions has been presented recently by Kemeny and Rasmussen (4) who used arguments distinctly different from those used here.

A major motivation for development of our two-fluid theory is to avoid calculation of the combinatorial factor for binary liquid mixtures. We achieve this desirable goal by using a free-volume partition function coupled with a reasonable and clearly defined assumption concerning the ensemble average for calculating the effect of composition on the mixture's free volume and potential energy, as discussed in Section 4.

1. Basic postulate of the two-fluid theory

The basic postulate of the two-fluid theory is that the thermodynamic properties of a binary mixture may be expressed by the contributions of two hypothetical fluids that mix ideally. According to this postulate, for a binary mixture at temperature T and pressure P , containing $N = N_1 + N_2$ molecules, the Gibbs energy G is given by

$$G = N_1 g^{(1)} + N_2 g^{(2)} + kT(N_1 \ln x_1 + N_2 \ln x_2) \quad [1.1]$$

where $g^{(1)}$ and $g^{(2)}$ represent the Gibbs energies per molecule of two hypothetical fluids at the same temperature T and pressure P , k is Boltzmann's constant, and x is the mole fraction. All other equilibrium properties of binary mixtures can be derived from Eq. 1.1 by applying standard thermodynamic relationships. For example, the enthalpy H , the entropy S , and the volume V , are given by

$$H = N_1 h^{(1)} + N_2 h^{(2)} \quad [1.2]$$

$$S = N_1 s^{(1)} + N_2 s^{(2)} - k(N_1 \ln x_1 + N_2 \ln x_2), \quad [1.3]$$

and

$$V = N_1 v^{(1)} + N_2 v^{(2)} \quad [1.4]$$

where temperature and pressure are constant.

Let M be any extensive property of a binary mixture and let m_i stand for property M (per molecule) for pure component i at the temperature and the pressure of the mixture. For the excess property M^E , we have

$$M^E = N_1(m^{(1)} - m_1) + N_2(m^{(2)} - m_2). \quad [1.5]$$

Eq. 1.5 indicates that, to calculate excess thermodynamic properties, we must develop models for evaluating both pure-component and hypothetical-fluid properties.

2. Partition function for pure fluids

The partition function Q is related to the Helmholtz energy by

$$A = G - PV = -kT \ln Q. \quad [2.1]$$

To evaluate Q for a pure fluid, we assume that the contributions to the molecular partition function arising from rotational, vibrational, and electronic degrees of freedom depend on temperature but are independent of total volume V . This assumption is exact for a monatomic fluid like argon and it is a reasonable approximation for small polyatomic fluids, but it is poor for large molecules, especially polymers, as discussed by Flory (5). The rotational and vibrational motions of a large molecule in the high-density liquid phase are different from those in the low-density gas phase at the same temperature. For large

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molecules the internal partition function depends on V as well as on T and therefore it contributes to the equation of state and to thermodynamic excess functions. Because we are concerned here with fluids composed of small molecules without strong specific interactions (e.g., hydrogen bonds), we disregard the effect of density on the internal partition function.

It is well known that dense fluids have short-range order but not long-range order. At high densities, excluded-volume effects result in the formation of a nearest-neighbor cage, identified with the first peak in the radial distribution function. Therefore, in our theory, we assume that each molecule is located in a spherical region (cage, or domain) formed by its nearest neighbors and that the properties of the fluid are essentially determined by its short-range structure.

In a pure fluid, the short-range structure can be defined in terms of two variables as discussed by Kerley (6): the size of the cage, R_i , and the number of nearest neighbors, z_i (coordination number).

The potential energy of a molecule in the field of its neighbors can be expressed as a sum over pair, triplet, and higher order interactions. We assume pairwise additive forces and we assume that the two-body potential is given by

$$\Gamma(r) = \infty \quad r < \sigma \quad [2.2]$$

$$\Gamma(r) = -\epsilon\sigma^3/R_i^3 \quad \sigma \leq r \leq R_i \quad [2.3]$$

$$\Gamma(r) = 0 \quad r > R_i \quad [2.4]$$

where R_i is the radius of a domain, σ is the molecular diameter, and ϵ is a characteristic energy. The attractive potential energy, ϕ_i , of a molecule placed at the center of its domain with z_i neighbors fixed on the surface of the coordination sphere of radius R_i is given by

$$\phi_i = -z_i\epsilon\sigma^3/R_i^3. \quad [2.5]$$

The absence of long-range attraction, expressed by Eq. 2.4, is not realistic for a real fluid. However, since only the short-range structure of the fluid is important for an accurate calculation of ϕ_i , the long-range structure can be approximated.

The canonical partition function, with kinetic energy contributions omitted, is given by

$$Q = \frac{1}{N!} \sum'_{\{N_i\}} \frac{N!}{\prod N_i!} [\prod \omega(N_i)] \exp \left[\frac{1}{2} \epsilon \sigma^3 \beta \sum_i N_i \frac{z_i}{R_i^3} \right] \\ = \sum'_{\{N_i\}} \exp \Psi \{N_i\}. \quad [2.6]$$

Here $\beta = 1/kT$ and Σ' indicates summation over all configurations (a configuration is defined by the set of numbers $\{N_i\}$ subject to the condition

$$\sum_i N_i = N. \quad [2.7]$$

Introducing Stirling's approximation into Eq. 2.6, we obtain

$$\Psi \{N_i\} = \sum_i [\ln \omega(N_i) - N_i \ln N_i + N_i] \\ + \frac{1}{2} \beta \epsilon \sigma^3 \sum_i N_i \frac{z_i}{R_i^3} \quad [2.8]$$

where $\omega(N_i)$ represents the amount of phase space associated with N_i domains which have the short-range coordinates (z_i, R_i) in the range $z_i + \delta z$ and $R_i + \delta R$, respectively.

Following van Kampen (7), we define the function $f(N_i/\Delta)$

by

$$\ln \omega(N_i) = N_i \ln N_i - N_i + \Delta f(N_i/\Delta) \quad [2.9]$$

$$f(N_i/\Delta) = 3 \frac{N_i}{\Delta} \left(\ln(\sigma \alpha^{1/3}) + \ln \left[\left(\frac{\Delta}{\alpha N_i \sigma^3} \right)^{1/3} - 1 \right] \right) \quad [2.10]$$

where Δ is the many-body Cartesian space corresponding to the short-range coordinate space defined by δz and δR , and α is a geometric factor equal to $\pi/(6 \cdot 0.64) = \pi/3.84$ (see equation 1.3 in ref. 1). Insertion of Eq. 2.10 into Eq. 2.9 allows $\omega(N_i)$ to satisfy the general features discussed by van Kampen. Moreover, the particular form of Eq. 2.10 was selected to meet the limiting behavior of a fluid of hard spheres, at least in the range of liquid densities, by utilizing the simplest expression compatible with the theoretical significance of $\omega(N_i)$.

We now must find the maximum term in Eq. 2.6 or the absolute maximum of Eq. 2.8. This absolute maximum is among the points in which Ψ is stationary with respect to variations in N_i , subject to Eq. 2.7. These points obey the set of equations

$$\frac{\partial \ln \omega(N_i)}{\partial N_i} - \ln N_i + \frac{1}{2} \beta \epsilon \sigma^3 \frac{z_i}{R_i^3} = \lambda_N \quad [2.11]$$

where λ_N is a Lagrangian multiplier, adjusted to satisfy Eq. 2.7.

One solution of Eqs. 2.11 is easily obtained by postulating a homogeneous density and, as a consequence, independence of the ratio z_i/R_i^3 on the particular domain, so that

$$\frac{N_i}{\Delta} = \frac{N}{V} \quad [2.12]$$

$$\frac{z_i}{R_i^3} = \left\langle \frac{z}{R^3} \right\rangle \quad [2.13]$$

In this way, all Eqs. 2.11 are satisfied, provided that λ_N is taken to be

$$\lambda_N = \ln \alpha + 3 \ln \sigma + 3 \ln(\bar{v}^{1/3} - 1) \\ - \frac{\bar{v}^{1/3}}{\bar{v}^{1/3} - 1} + \frac{1}{2} \beta \epsilon \sigma^3 \left\langle \frac{z}{R^3} \right\rangle \quad [2.14]$$

where reduced volume $\bar{v} = \langle R \rangle^3 / \sigma^3$. Furthermore, let us expand $F(z_i, R_i) = z_i/R_i^3$ in a Taylor series about $z_i = \langle z \rangle$ and $R_i = \langle R \rangle$. Taking into account Eq. 2.13 and averaging over all configurations, we obtain

$$\left\langle \frac{z}{R^3} \right\rangle = \frac{\langle z \rangle}{\langle R \rangle^3} \left[1 - 3 \left(\frac{\hat{O}}{\langle R \rangle} \right)^2 + \dots \right] \quad [2.15]$$

where $\hat{O}^2 = \langle R^2 \rangle - \langle R \rangle^2$. In our model we assume that fluctuations in R_i are small so that we can set equal to zero all quantities $\langle (R_i - \langle R \rangle)^k \rangle$ where $k = 1, 2, 3, \dots$. Then Eq. 2.14 becomes

$$\lambda_N = \ln \alpha + 3 \ln \sigma + 3 \ln(\bar{v}^{1/3} - 1) \\ - \frac{\bar{v}^{1/3}}{\bar{v}^{1/3} - 1} + \frac{1}{2} \beta \epsilon \sigma^3 \frac{\langle z \rangle}{\langle R \rangle^3}. \quad [2.16]$$

When λ_N is given by Eq. 2.16, the corresponding stationary value of Ψ is

$$\Psi_s = N \ln \alpha + 3N [\ln \sigma + \ln(\bar{v}^{1/3} - 1)] + \frac{z}{2} N \beta \frac{\epsilon}{\bar{v}} \quad [2.17]$$

where $z \equiv \langle z \rangle$ is the average value of the coordination number, which can be set equal to 10 for a liquid far removed from critical

conditions. Therefore, we may write

$$Q = \exp \Psi_s. \quad [2.18]$$

Introducing Eqs. 2.18 and 2.17 into Eq. 2.1 gives the configurational Helmholtz energy of a pure liquid

$$\frac{A}{NkT} = 0.201 - 3 \ln \sigma - 3 \ln(\bar{v}^{1/3} - 1) - \frac{z}{2} \frac{\epsilon}{kT}. \quad [2.19]$$

From Eq. 2.19, the equation of state is

$$\frac{P}{kT\rho} = \frac{\bar{v}^{1/3}}{\bar{v}^{1/3} - 1} - \frac{z}{2} \frac{\epsilon}{kT\bar{v}}. \quad [2.20]$$

This result is equivalent to that of Flory (5) for monomeric molecules. The main features of our theory are the following. (a) The domains are not considered to be rigid and uniform, in contrast to the cells in the quasi-lattice theories; in our theory, the concept of a distribution of domain types accounts for the liquid entropy. (b) The structure of a dense fluid is mainly determined by repulsive forces (hard-sphere potential) acting between a molecule and its nearest neighbors. (c) The attractive forces may be considered as a perturbation, and the hard-sphere potential determines the short-range structure of the fluid through parameters z and R .

3. Partition function for binary mixtures using the two-fluid theory

The basic postulate of the two-fluid theory for a binary mixture is that the partition function for a binary mixture is given by

$$Q = \frac{N!}{N_1! N_2!} Q^{(1)} Q^{(2)} \quad [3.1]$$

where $Q^{(1)}$ and $Q^{(2)}$ represent, respectively, the partition functions for N_1 domains of hypothetical fluid 1 and for N_2 domains of hypothetical fluid 2.

As for pure fluids, the domains of the hypothetical fluids are characterized by the size and the number of nearest neighbors. However, for hypothetical fluids, these variables depend upon the composition of the mixture. Therefore, for a hypothetical fluid, the short-range structure can be expressed in terms of three variables: the size of the domain, the number of nearest neighbors, and a variable that accounts for the composition of the real mixture.

As for pure fluids, we assume that fluctuations in the coordination number and in the size of the domains are small for each hypothetical fluid. This assumption leads us to consider the distribution of the coordination numbers to be unimodal and the same for all hypothetical fluids. Simply, we assume that the coordination number is a constant ($\langle z^{(1)} \rangle = \langle z^{(2)} \rangle = z$) which we set equal to 10, as for pure fluids.

From the previous assumption it follows that for each hypothetical fluid we can define $z + 1$ classes of domains, each characterized by the index j which varies between zero and z . For each hypothetical fluid, the average potential energy for domains of class j is given by

$$\phi_j^{(1)} = -z \left\{ \epsilon_{21} \sigma_{21}^3 + \frac{j}{z} (\epsilon_{11} \sigma_{11}^3 - \epsilon_{21} \sigma_{21}^3) \right\} / \langle R^{(1)} \rangle^3 \quad [3.2]$$

and

$$\phi_j^{(2)} = -z \left\{ \epsilon_{12} \sigma_{12}^3 + \frac{j}{z} (\epsilon_{22} \sigma_{22}^3 - \epsilon_{12} \sigma_{12}^3) \right\} / \langle R^{(2)} \rangle^3. \quad [3.3]$$

To each class of hypothetical fluid 1, we can assign the occu-

pation number $n_j^{(1)}$ which represents the number of domains of hypothetical fluid 1 (characterized by a central molecule of type 1) surrounded by j molecules of the same type and $(z - j)$ molecules of the other component. For hypothetical fluid 2, we define the occupation number by $n_j^{(2)}$. In our model, each occupation number represents an ensemble of domains. The occupation numbers of the two hypothetical fluids are subject to the conditions:

$$\sum_{j=0}^z n_j^{(1)} = N_1 \quad [3.4]$$

and

$$\sum_{j=0}^z n_j^{(2)} = N_2. \quad [3.5]$$

From Eqs. 3.4 and 3.5 we can define the frequencies of a particular class of domains for each hypothetical fluid by

$$f_j^{(1)} = n_j^{(1)} / N_1 \quad [3.6]$$

and

$$f_j^{(2)} = n_j^{(2)} / N_2. \quad [3.7]$$

Following the procedure given in Section 2, the canonical partition functions for the two hypothetical fluids (the kinetic energy part omitted) are

$$Q^{(1)} = \exp \Psi_s^{(1)} \quad [3.8]$$

and

$$Q^{(2)} = \exp \Psi_s^{(2)} \quad [3.9]$$

where

$$\Psi_s^{(1)} = N_1 \ln \alpha + 3N_1 [\ln \langle \sigma^{(1)} \rangle + \ln(\bar{v}^{(1)1/3} - 1)] - \frac{1}{2} N_1 \beta \langle \phi^{(1)} \rangle \quad [3.10]$$

$$\Psi_s^{(2)} = N_2 \ln \alpha + 3N_2 [\ln \langle \sigma^{(2)} \rangle + \ln(\bar{v}^{(2)1/3} - 1)] - \frac{1}{2} N_2 \beta \langle \phi^{(2)} \rangle. \quad [3.11]$$

The average free energies $\langle \phi^{(1)} \rangle$ and $\langle \phi^{(2)} \rangle$ are related to the average energies $\langle \phi^{(1)} \rangle$ and $\langle \phi^{(2)} \rangle$ by standard thermodynamics:

$$\langle \phi^{(1)} \rangle = \frac{1}{\beta} \int_0^\beta \langle \phi^{(1)} \rangle d\beta \quad [3.12]$$

and

$$\langle \phi^{(2)} \rangle = \frac{1}{\beta} \int_0^\beta \langle \phi^{(2)} \rangle d\beta \quad [3.13]$$

where

$$\langle \phi^{(1)} \rangle = \sum_{j=0}^z f_j^{(1)} \phi_j^{(1)} \quad [3.14]$$

and

$$\langle \phi^{(2)} \rangle = \sum_{j=0}^z f_j^{(2)} \phi_j^{(2)}. \quad [3.15]$$

In deriving Eqs. 3.10 and 3.11, the reduced volume for each hypothetical fluid was considered to be independent of the

class of domains. Furthermore, we assumed that

$$\langle \ln \sigma^{(1)} \rangle \approx \ln \langle \sigma^{(1)} \rangle \quad [3.16]$$

and

$$\langle \ln \sigma^{(2)} \rangle \approx \ln \langle \sigma^{(2)} \rangle \quad [3.17]$$

where

$$\langle \sigma^{(1)} \rangle = \sum_{j=0}^z f_j^{(1)} \sigma_j^{(1)} \quad [3.18]$$

and

$$\langle \sigma^{(2)} \rangle = \sum_{j=0}^z f_j^{(2)} \sigma_j^{(2)}. \quad [3.19]$$

Numerical calculations indicate that Eqs. 3.16 and 3.17 are good approximations, provided that the ratio between the hard-sphere diameters of the two pure components is not greater than about 2; in this case the difference between the two averages is <1%. For $\sigma_{22}/\sigma_{11} = 3$, the difference is about 5%.

The partition function of a binary mixture is now given by

$$Q = \frac{N!}{N_1!N_2!} \exp \Psi_s^{(1)} \exp \Psi_s^{(2)} \quad [3.20]$$

where $\Psi_s^{(1)}$ and $\Psi_s^{(2)}$ are given by Eqs. 3.10 and 3.11, respectively. To use Eq. 3.20, we require a distribution law for $f_j^{(1)}$ and $f_j^{(2)}$. According to our assumptions, $f_j^{(1)}$ and $f_j^{(2)}$ follow a discrete distribution.

4. Distribution law for classes of domains of hypothetical fluids

To obtain a distribution law for $f_j^{(1)}$ and $f_j^{(2)}$ we can follow two approximations.

First Approximation. We postulate an infinite reservoir containing molecules 1 and 2 in the ratio N_1/N_2 at temperature T of the real mixture but at a pressure so low that the fluid can be considered an ideal gas mixture. We suppose that the properties of a domain of hypothetical fluid 1 (the same arguments hold for hypothetical fluid 2) can be described in terms of the configurations that are obtained when we extract from the reservoir z molecules, one at a time. This operation represents a sequence of z independent trials. Let j be the number of occurrences of molecules 1 in the sequence of z trials, in each of which the probability of its occurrence is a constant equal to $p_1 \equiv f(x_1)$. Therefore, we have

$$f_j^{(1)} \text{ (1st approx.)} = C_z^j (p_1)^j (q_1)^{(z-j)} \quad [4.1]$$

where

$$q_1 = 1 - p_1 \quad [4.2]$$

and

$$C_z^j = \frac{z!}{j!(z-j)!} \quad [4.3]$$

Eq. 4.1 satisfies, by definition, the condition

$$\sum_{j=0}^z f_j^{(1)} \text{ (1st approx.)} = 1. \quad [4.4]$$

For hypothetical fluid 2, we have

$$f_j^{(2)} \text{ (1st approx.)} = C_z^j (p_2)^j (q_2)^{(z-j)} \quad [4.5]$$

where the symbols have definitions analogous to those in Eq. 4.1. For p_1 and p_2 , we suggest

$$p_1 = x_1/[x_1 + x_2(\sigma_{22}/\sigma_{11})^m] \quad [4.6]$$

and

$$p_2 = x_2/[x_2 + x_1(\sigma_{11}/\sigma_{22})^m]. \quad [4.7]$$

When $m = 0$ or $\sigma_{11} = \sigma_{22}$, this approximation gives the *semi-random approximation* discussed by Rowlinson (8). Values of m different from zero allow weighting of thermodynamic properties to depend on differences in molecular size.

Second Approximation. In this approximation we maintain all the arguments discussed in the previous paragraph. However, we also assume that the central molecule of the domain is not "blind"; we assume that the central molecule can guide the choice of its nearest neighbors by promoting a particular class of domains. In other words, we assign to each class a statistical weight defined by

$$W_j^{(1)} = \exp(-\beta \phi_j^{(1)}). \quad [4.8]$$

Therefore, in this approximation, for hypothetical fluid 1,

$$f_j^{(1)} \text{ (2nd approx.)} = (1/\Omega^{(1)}) C_z^j (p_1)^j (q_1)^{(z-j)} W_j^{(1)} \quad [4.9]$$

where $1/\Omega^{(1)}$ is a normalization factor defined by

$$\Omega^{(1)} = \sum_{j=0}^z C_z^j (p_1)^j (q_1)^{(z-j)} W_j^{(1)}. \quad [4.10]$$

Similarly, for hypothetical fluid 2, we have

$$f_j^{(2)} \text{ (2nd approx.)} = (1/\Omega^{(2)}) C_z^j (p_2)^j (q_2)^{(z-j)} W_j^{(2)} \quad [4.11]$$

and

$$\Omega^{(2)} = \sum_{j=0}^z C_z^j (p_2)^j (q_2)^{(z-j)} W_j^{(2)}. \quad [4.12]$$

We call this approximation the "nonrandom" approximation. We show in ref. 2 that application of this approximation to real mixtures leads to "local compositions" similar to those assumed by Wilson (3).

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