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Local fluctuations in solution mixtures

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An extension of the traditional Kirkwood-Buff (KB) theory of solutions is outlined which provides additional fluctuating quantities that can be used to characterize and probe the behavior of solution mixtures. Particle-energy and energy-energy fluctuations for local regions of any multicomponent solution are expressed in terms of experimentally obtainable quantities, thereby supplementing the usual particle-particle fluctuations provided by the established KB inversion approach. The expressions are then used to analyze experimental data for pure water over a range of temperatures and pressures, a variety of pure liquids, and three binary solution mixtures – methanol and water, benzene and methanol, and aqueous sodium chloride. In addition to providing information on local properties of solutions it is argued that the particle-energy and energy-energy fluctuations can also be used to test and refine solute and solvent force fields for use in computer simulation studies.

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INTRODUCTION

Kirkwood-Buff (KB) theory, more generally known as the Fluctuation Theory (FT) of solutions, has provided a wealth of data concerning the properties of solution mixtures.¹⁻⁵ Specific examples include studies of preferential solvation in binary solutions,^{3,6-8} transfer free energies and the solubility of solutes,⁹⁻¹¹ surface tension and free energy changes due to the addition of additives,^{12,13} cosolvent effects on both small solutes and proteins,¹⁴⁻¹⁸ and the investigation of protein-protein interactions.¹⁹ The approach has also been used as a basis for the generation of improved force fields for computer simulation.^{20,21} In all these examples KB theory provides a rigorous statistical mechanical formalism used to provide a link between thermodynamic data concerning the system of interest, and integrals over the underlying molecular distributions corresponding to local regions within the system.

The primary quantities of interest which help to characterize and quantify the above effects are the KB integrals (KBIs) between the different species present in solution. The KBIs (G_{ij} 's) can be expressed in terms of either radial distribution functions (g_{ij}) between species i and j , or as particle-particle fluctuations corresponding to local regions within the system of interest,¹

$$G_{ij} = G_{ji} = 4\pi \int_0^{\infty} [g_{ij}(r) - 1] r^2 dr$$

$$= V \left[\frac{\langle \delta N_i \delta N_j \rangle}{\langle N_i \rangle \langle N_j \rangle} - \frac{\delta_{ij}}{\langle N_i \rangle} \right], \quad (1)$$

where δ_{ij} is the Kroenecker delta function, and $\delta N_i = N_i - \langle N_i \rangle$ is the deviation in the number of i particles from the average number of i particles in the fixed volume (V) for each member of the grand canonical ensemble. Combinations

of the KBIs and number densities then provide expressions for thermodynamic properties – such as chemical potential derivatives, partial molar volumes, and isothermal compressibilities – in essentially any ensemble with the same average properties as the open system. Alternatively, given an appropriate set of experimental data as a function of composition one can invert the whole procedure and extract the experimental KBIs,²² thereby providing information concerning the local distribution of species in solution. KB theory is particularly attractive in this regard as the expressions are exact, they can be applied to any stable solution mixture involving any type of molecule at any composition, and the resulting KBIs can be obtained relatively easily from computer simulation data.

The vast majority of experimental data analyzed by the KB inversion procedure involve binary or ternary systems at constant pressure (P) and temperature (T) where the results are presented in terms of local particle-particle correlations. Far less attention has been paid to the study of local particle-energy and energy-energy fluctuations in mixtures which naturally arise for thermodynamic temperature derivatives such as the thermal expansion and constant pressure (or volume) heat capacities. The main studies of relevance to the present work include the development of expressions for the partial molar energies and constant volume heat capacity in terms of molecular distribution functions provided by Buff and Brout,²³ and a series of papers by Debenedetti outlining the calculation of partial molar energies (and thereby enthalpies) from computer simulation.²⁴⁻²⁶ However, to our knowledge, the corresponding local fluctuating quantities for mixtures have not been extracted from available experimental data. This is the major aim of this study.

In the following sections we outline the theory behind a general fluctuation description of solutions. The current approach is somewhat different from previous approaches,^{23,24} but is used here as it provides a simple formulation of the inversion process {experimental data} \rightarrow {fluctuating properties} for multicomponent systems. The overall approach

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is then illustrated using available experimental data for a variety of solutions and solution mixtures, including salt solutions.

THEORY

The basic aim is to develop expressions for properties of local regions within solution mixtures by reference to the equations of the grand canonical ensemble. Hence, the angular brackets used here signify an ensemble average in the grand canonical ensemble unless stated otherwise. The resulting expressions, involving fluctuations in the energy and number of particles, can then be related to local (μVT) regions within systems corresponding to a variety of different ensembles possessing the same average properties, although the NPT ensemble will be the one of primary concern.

In our previous and subsequent discussions we continually refer to the concept of local fluctuations within the solution mixture of interest. Hence, it is important to be clear exactly what is meant by the term “local”. Clearly, Eq. (1) does not appear to represent a property characterizing a local region in the solution. However, the integration to infinity actually represents the extent of the open system. In the case of closed systems, one can consider finite microscopic regions within the solution to represent the open system of interest, the extent of which is dictated by the requirement that all g_{ij} are unity at large distances. The fluctuations observed within this microscopic region are the “local” fluctuations of interest here. This is illustrated in Fig. 1. It should be noted, however, that the extent of this microscopic region is generally unknown. For the majority of solutions under ambient conditions the local region may merely extend over a few nanometers. Alternatively, for solutions approaching a critical point the extent of the region will become macroscopic in size and therefore may no longer be considered as “local”. As the majority of solutions fall into the former category, and to help distinguish the present fluctuations from the bulk system fluctuations, we have used “local” to describe the fluctuations provided by the current analysis.

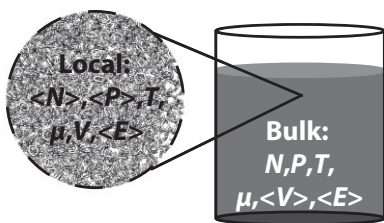


FIG. 1. Local fluctuations in solution mixtures. The local region of interest is surrounded by the macroscopic bulk solution and therefore has the same intensive thermodynamic parameters (pressure, temperature, molar energy, molar volume, number densities, chemical potentials, etc.) as the bulk solution. Fluctuations in the number of particles and energy occur within the fixed local volume, which can be considered to be under the thermodynamic constraints associated with the grand canonical (μVT) ensemble. The extent of the local region will depend on the pressure, temperature, composition, and the nature of the solution components. However, the exact size of this region is irrelevant as long as it is large enough that the region displays the same intensive properties as the bulk solution – typically 3–5 solvation shells.

In the grand canonical ensemble the average number of i molecules ($\langle N_i \rangle$) is a function of the set of chemical potentials ($\{\beta\mu\}$), the volume, and the temperature ($\beta = 1/RT$), where R is the Gas constant. Hence, one can write the following differential for these independent variables,

$$d\langle N_i \rangle = \left(\frac{\partial \langle N_i \rangle}{\partial V} \right)_{\{\beta\mu\}, \beta} dV + \left(\frac{\partial \langle N_i \rangle}{\partial \beta} \right)_{\{\beta\mu\}, V} d\beta + \sum_j \left(\frac{\partial \langle N_i \rangle}{\partial \beta \mu_j} \right)_{\{\beta\mu\}', V, \beta} d\beta \mu_j, \quad (2)$$

where the summation is over all j components in the mixture and the prime in the subscript indicates that all $\beta\mu$ except for the one of interest are held constant. The above thermodynamic derivatives can be related to their corresponding fluctuating quantities using the equations for a classical grand canonical ensemble,²⁷

$$PV = RT \ln \Xi(\{\beta\mu\}, V, \beta), \\ d(PV) = SdT + PdV + \sum_i N_i d\mu_i, \\ \Xi(\{\beta\mu\}, V, \beta) = \sum_{\{N\}=0}^{\infty} e^{\beta\mu \cdot N} Q(\{N\}, V, \beta), \quad (3)$$

where Q is the classical canonical partition function provided by

$$Q(\{N\}, V, \beta) = \left[\prod_i \frac{1}{N_i!} \left(\frac{q_i^{\text{int}}}{h^3} \right)^{N_i} \right] \iint_{-\infty}^{+\infty} e^{-\beta E'} \{dp\} \{dq\}, \quad (4)$$

and $\{dp\}$ and $\{dq\}$ are the generalized momenta and coordinates associated with the molecules, respectively. The internal partition function (q_i^{int}) of molecule i contains the contribution from all the intramolecular degrees of freedom, which are assumed to be decoupled from the intermolecular degrees of freedom. Using the above equations one can show that the required derivatives are given by the following expressions.^{23,24}

$$\left(\frac{\partial \langle N_i \rangle}{\partial \beta \mu_j} \right)_{\{\beta\mu\}', V, \beta} = \langle \delta N_i \delta N_j \rangle = \langle N_i \rangle (\delta_{ij} + N_{ij}), \\ \left(\frac{\partial \langle N_i \rangle}{\partial V} \right)_{\{\beta\mu\}, \beta} = \frac{\langle N_i \rangle}{V} = \rho_i, \\ \left(\frac{\partial \langle N_i \rangle}{\partial \beta} \right)_{\{\beta\mu\}, V} = -\langle \delta N_i \delta E \rangle. \quad (5)$$

Here, E is the total internal energy for each member of the ensemble and includes any intramolecular contributions from the internal partition function. Hence, combining Eqs. (2) and (5) one finds that,

$$d \ln \rho_i = -F_{\mu,i} d\beta + \sum_j (\delta_{ij} + N_{ij}) d\beta \mu_j, \quad (6)$$

for any species in any multicomponent mixture and where we have defined the energy-number fluctuations by

$$F_{\mu,i} = \frac{\langle \delta N_i \delta E \rangle}{\langle N_i \rangle}. \quad (7)$$

The F_μ 's are intensive quantities that represent correlations between the energy and the number of i particles in the region of interest. The $N_{ij} = \rho_j G_{ij}$ quantities can be considered as either particle number fluctuations for the same local region, or as an excess coordination number, i.e., the change in the number of j particles resulting from the introduction of an i particle to the reference volume compared to the number of j particles observed in the same volume of the bulk solution. If the temperature is kept constant the above set of equations reduce to a series of simultaneous equations which, after taking the appropriate derivatives, generate the expressions obtained from the traditional KB theory approach for solution mixtures.²⁸

A more convenient form of Eq. (6) for the analysis of experimental data can be obtained by defining an excess internal energy (ε) for each member of the ensemble such that,

$$\varepsilon = E - \sum_j N_j E_j^0, \quad (8)$$

where E_j^0 is a convenient reference energy per particle. For completely miscible mixtures it is natural to take this reference energy as the average molar internal energy in the pure liquid j at the temperature and average pressure of interest. However, for solid solutes it may be more convenient to use the internal energy of the solute at infinite dilution in the primary solvent. In either case one can write,

$$d \ln \rho_i = -F_i d\beta + \sum_j (\delta_{ij} + N_{ij})(d\beta \mu_j - E_j^0 d\beta), \quad (9)$$

where

$$F_i = \frac{\langle \delta N_i \delta \varepsilon \rangle}{\langle N_i \rangle}. \quad (10)$$

Equation (9) represents a series of source equations which can be used to obtain expressions for various properties of solution mixtures in terms of number-number, number-energy, and energy-energy correlations characterizing local microscopic regions within the solution of interest.

Taking derivatives with respect to T with P and $\{N\}$ constant one obtains the following expression:

$$\begin{aligned} RT^2 \alpha_P &= RT^2 \left(\frac{\partial \ln V}{\partial T} \right)_{P, \{N\}} \\ &= -F_i + \sum_j (\delta_{ij} + N_{ij})(\bar{H}_j - E_j^0), \end{aligned} \quad (11)$$

where \bar{H}_j is the partial molar enthalpy of species j and α_P is the thermal expansion coefficient. Some rearrangement provides an expression (inversion formula) for each F_i in terms of observable experimental quantities,

$$F_i = PRT\kappa_T - RT^2 \alpha_P + \sum_j (\delta_{ij} + N_{ij}) \bar{U}_j^{ex}, \quad (12)$$

and κ_T is the isothermal compressibility provided by Eq. (9),

$$RT\kappa_T = -RT \left(\frac{\partial \ln V}{\partial P} \right)_{T, \{N\}} = \sum_j (\delta_{ij} + N_{ij}) \bar{V}_j, \quad (13)$$

with \bar{V}_j indicating the partial molar volume of j , and we have used the fact that $\bar{H}_j = \bar{U}_j + P\bar{V}_j$ and $\bar{U}_j^{ex} = \bar{U}_j - E_j^0$. The

required excess partial molar energies \bar{U}_j^{ex} can be obtained from the relevant experimental enthalpy of mixing and density data. The contributions to F_i and \bar{U}_j^{ex} from the intramolecular degrees of freedom will cancel in Eq. (12), even when the intramolecular energy levels corresponding to the mixture are different from those in the reference states.

Before leaving this section we note that the thermal expansion coefficient can also be expressed in terms of all the F 's by multiplying Eq. (12) by the volume fraction ($\phi_i = \rho_i \bar{V}_i$), summing over all i , and then using Eq. (13) to provide,

$$RT^2 \alpha_P = \frac{RT\kappa_T}{V_m} (U_m^{ex} + P V_m) - \sum_i \phi_i F_i, \quad (14)$$

where U_m^{ex} is the excess molar internal energy of mixing and V_m is the molar volume. The above expression will be used later. It also provides a route to the excess energy of mixing from a single simulation when the thermal expansion is known, although this issue will not be considered here.

The constant pressure heat capacity can be used to provide information on the local energy fluctuations. Given the thermodynamic relationship,

$$C_P = \left(\frac{\partial H}{\partial T} \right)_{P, \{N\}} = \left(\frac{\partial U}{\partial T} \right)_{P, \{N\}} + PV\alpha_P, \quad (15)$$

and the derivative of the average energy obtained by treating $U = \langle E \rangle$ as a function of the chemical potentials, volume and β in a similar manner to before (see Eq. (2)), and to the approach of Buff and Brout,²³ one finds,

$$RT^2 \left(\frac{\partial U_m}{\partial T} \right)_P = RT^2 U_m \alpha_P + \frac{\langle (\delta E)^2 \rangle}{\langle N \rangle} - \sum_i x_i F_{\mu, i} \bar{H}_i. \quad (16)$$

Manipulation of Eq. (16) indicates that the local excess energy fluctuations can be written in terms of experimentally obtainable properties as

$$\begin{aligned} \Delta_m &= \frac{\langle (\delta \varepsilon)^2 \rangle}{\langle N \rangle} = RT^2 C_{P, m} \\ &\quad + \sum_i x_i (F_i - RT^2 \alpha_P) (\bar{U}_i^{ex} + P \bar{V}_i), \end{aligned} \quad (17)$$

where the F 's are given by Eq. (12). The value of $\beta^2 \Delta_m$ obtained from the above expression includes contributions of 1/2 from each molecular translational degree of freedom, and additional contributions of 1/2 from each classical intramolecular potential and kinetic quadratic degree of freedom.

Equations (12) and (17) contribute to a general theory of local solution behavior in terms of experimentally observable properties. Alternatively, the calculation of the number-number, energy-number, and energy-energy fluctuations, from theory or computer simulation, provides a route to a series of experimental properties. For completion we include the corresponding expression obtained for the constant volume heat capacity previously presented

by Buff and Brout,²³

$$\Delta_m = RT^2 C_{V,m} + \sum_i F_i (x_i \bar{U}_i^{ex} - \phi_i U_m^{ex}) + \frac{V_m}{RT\kappa_T} \left(\sum_i \phi_i F_i \right)^2. \quad (18)$$

The two previous expressions can be shown to satisfy the known thermodynamic relationship, $C_{P,m} - C_{V,m} = TV_m \alpha_p^2 / \kappa_T$ after some algebra and the use of Eq. (14).

Using Eqs. (12) and (17) we have investigated the local fluctuations for a variety of solutions as obtained from the relevant experimental data. These fluctuations can be used to either characterize the properties of solutions, as demonstrated by the traditional KB approach, to help rationalize changes in properties such as the compressibility, thermal expansion, and heat capacities, or as target data for the testing and evaluation of force fields developed for molecular simulation.

METHODS

Pure water was analyzed at six pressures (1, 200, 400, 600, 800, and 1000 bar) over the subset of temperatures between 273 and 1073 K for which a given P , T point was in the liquid region of the water phase diagram.²⁹ Experimental data were analyzed for several n -alcohols (methanol through decanol),^{30–36} linear alkanes (hexane through tetradecane),^{35,37–41} 1-alkenes (hexene through octene),^{35,37} alkylamines (propyl-, butyl-, hexyl-, and octylamine, diethylamine through dibutylamine, and triethylamine through tributylamine),⁴² and aromatics (benzene and methylbenzene through propylbenzene).^{37,43–45} For all liquids, excluding pure water, the T and P were fixed at 298 K and 1 bar, respectively. The molar volume of each liquid was calculated from the molecular weights and densities.³⁵

The general outline for the analysis of solution mixtures is provided in Fig. 2. We have followed a sequential approach whereby the usual KB analysis is performed first to obtain the KBIs, these data are then combined with the thermal expansion and excess partial molar energy data to provide the F 's, and finally the heat capacity data are used to obtain Δ_m values. Experimental data for the methanol + water system at a T of 298 K and P of 1 bar was analyzed over the full composition range. The Redlich-Kister power series equation was used to fit the density data (four parameters),⁴⁶ excess Gibbs energy (G^{ex}) data (three parameters),^{47,48} enthalpy of mixing (H^{ex}) data (four parameters),⁴⁹ α_p data (six parameters),⁵⁰ and C_p data (four parameters).⁵⁰ κ_T was approximated to display ideal behavior. Data for the benzene + methanol system at 308 K and 1 bar were analyzed over the full composition range. G^{ex} was fit using the Wilson equation and the enthalpy of mixing was fit using the Redlich-Kister power series equation with six parameters.^{51,52} All other properties were approximated to be ideal.^{53–56} Aqueous sodium chloride data at 298 K and 1 bar were studied up to 4M NaCl due to a lack of α_p data at higher salt concentrations. The solution V_m was fit to a cubic polynomial.⁵⁷ Experimental activity data were fit to the form $\ln \gamma_{\pm} = -(A\sqrt{m_s}) / (1 + B\sqrt{m_s}) - \ln(1 - Cm_s)$, in

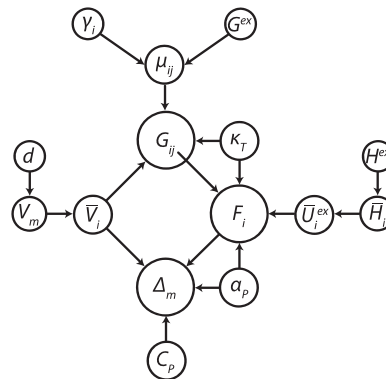


FIG. 2. The general scheme for obtaining local fluctuating properties from the available experimental data. Here d is the solution mass density and the definitions of the other symbols are provided in the main text.

which m_s is the salt molality, γ_{\pm} is the molal salt activity coefficient, and the other symbols are fitting constants.^{16,58} Polynomials were used to model the enthalpy of mixing (cubic),⁵⁹ α_p (quadratic),⁶⁰ C_p (quartic),⁶¹ and κ_T (quadratic).⁶⁰ After a fit to the data for each solution was obtained, the first derivatives of V_m were determined to provide the partial molar volumes for use in the calculation of the KBIs and F 's, while second derivatives of G^{ex} were used for use in the calculation of the KBIs, and first derivatives of the enthalpy of mixing were taken to obtain \bar{H}_i^{ex} . From \bar{H}_i^{ex} , the excess partial molar energies of mixing were calculated according to $\bar{U}_i^{ex} = \bar{H}_i^{ex} - P\bar{V}_i^{ex}$ for use in the calculation of the F 's. The solution α_p , C_p , and κ_T were used directly in the KBI, F_i , and Δ_m calculations.

RESULTS

One component solutions

The fluctuation quantities for a one component fluid (1) are provided by the following equations where the superscript (o) denotes the pure liquid values,

$$1 + N_{11}^o = \rho_1^o RT \kappa_T^o, \\ F_1^o = PRT \kappa_T^o - RT^2 \alpha_p^o, \\ \Delta_m^o = RT^2 C_{P,m}^o + PV_m^o (PRT \kappa_T^o - 2RT^2 \alpha_p^o), \quad (19)$$

and are in agreement with previous literature values.^{62,63} We have evaluated the corresponding local fluctuating properties for water over a range of temperatures and pressures. The results are shown in Fig. 3. As expected the curves peak in the vicinity of the critical temperature (647 K) and critical pressure (220 bars).⁶⁴ The βF curves are dominated by the thermal expansion term. This also results in all the pressure curves adopting the same value of $\beta F = -0.06$ at ≈ 292 K, in a similar manner to the raw thermal expansion data.^{65,66} The fact that $dF/dP = 0$ at this temperature implies a relationship between the higher local fluctuating moments of the liquid. These moments can be determined,⁶⁷ but this is beyond the scope of the present work.

An analysis of the data concerning simple pure organic liquids at 298 K and 1 bar is presented in Fig. 4. All

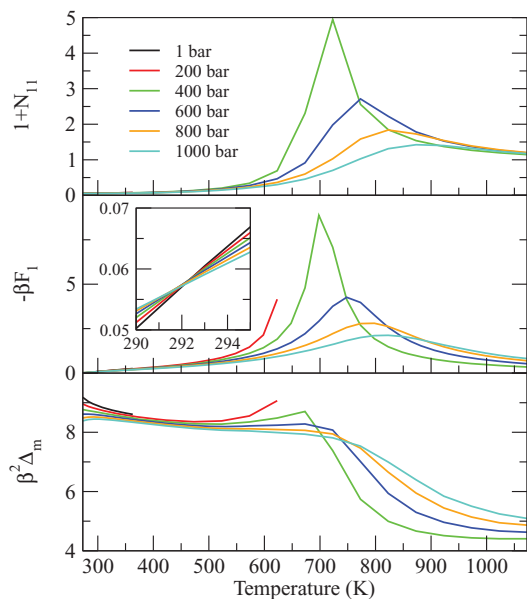


FIG. 3. Local fluctuating properties for pure liquid water over a range of T and P .

liquids studied here displayed a systematic decrease in the number fluctuations (compressibility),²² and a corresponding increase in F and Δ_m values, as the number of carbons is increased. The energy fluctuations display essentially a linear dependence on the number of carbons, which is to be expected from the relationships observed for the heat capacities of hydrocarbons,^{68,69} and the dominating contribution from $C_{P,m}$ at this temperature and pressure.

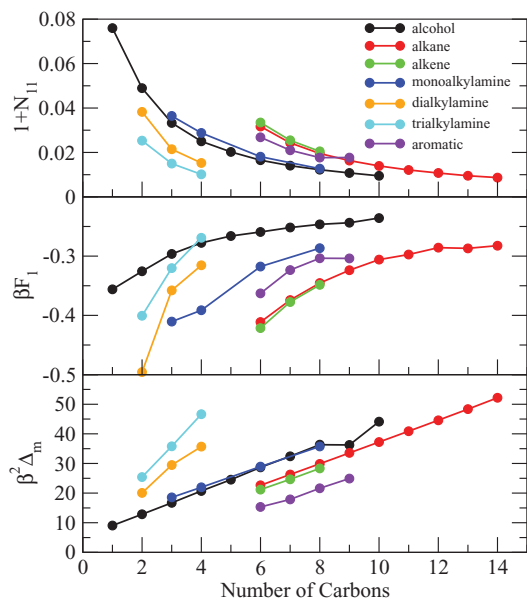


FIG. 4. Local fluctuating properties of pure liquids at 298 K and 1 bar. The number of carbons for the aromatic molecules was taken as the total number of carbons including the ring atoms, while the number of carbons for the di- and trialkyl amines was taken as the number of carbons in a single alkyl chain.

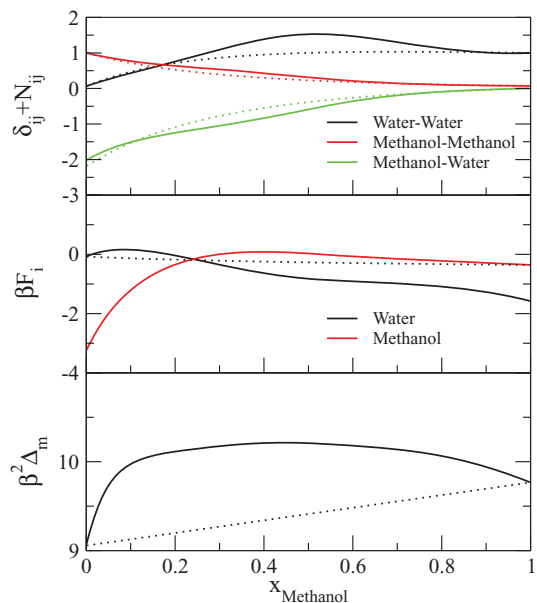


FIG. 5. A fluctuation analysis of water (1) and methanol (2) mixtures at 298 K and 1 bar. The solid lines correspond to the experimental data, while the dotted lines represent the SI solution values.

Binary solutions

One natural application of the above theory is to deepen our understanding of the local microstructure of binary mixtures. For a binary mixture of a solvent (1) and solute (2) one finds the following expressions apply:

$$\mu_{22} = \beta \left(\frac{\partial \mu_2}{\partial \ln m_2} \right)_{T,P} = x_1 \beta \left(\frac{\partial \mu_2}{\partial \ln x_2} \right)_{T,P},$$

$$1 + N_{11} = \rho_1 RT \kappa_T + \rho_1 \frac{\phi_2 \bar{V}_2}{\mu_{22}},$$

$$1 + N_{22} = \rho_2 RT \kappa_T + \frac{\phi_1^2}{\mu_{22}},$$

$$N_{12} = \rho_2 RT \kappa_T - \frac{\phi_1 \phi_2}{\mu_{22}},$$

$$F_i = \bar{U}_i^{ex} + PRT \kappa_T - RT^2 \alpha_P + N_{i1} \bar{U}_1^{ex} + N_{i2} \bar{U}_2^{ex},$$

$$\Delta_m = RT^2 C_{P,m} - RT^2 \alpha_P (U_m^{ex} + P V_m) + x_1 F_1 \bar{U}_1^{ex} + x_2 F_2 \bar{U}_2^{ex} + P V_m (\phi_1 F_1 + \phi_2 F_2), \quad (20)$$

where m_i and x_i are the molality and mole fraction of i , respectively. The first four expressions correspond to the traditional KB inversion approach. The N 's and F 's can be eliminated from the last two expressions if desired, but we retain them here for simplicity. Figures 5–7 display the results from a fluctuation analysis of three binary solutions. It is known that the KBIs for solutions under ambient conditions are most sensitive to the solution activities, relatively insensitive to the partial molar volumes, and essentially unaffected by the precise value of the isothermal compressibility.⁶ The F values presented here were sensitive to the partial molar enthalpies (energies), with a significant but relatively constant contribution from the thermal expansion coefficient, and an essentially negligible contribution from the compressibility term.

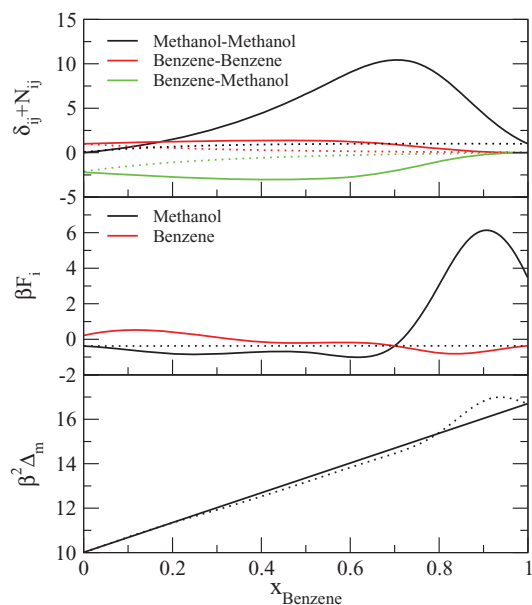


FIG. 6. A fluctuation analysis of methanol (1) and benzene (2) mixtures at 308 K and 1 bar. The solid lines correspond to the experimental data, while the dotted lines represent the SI solution values.

The results from an analysis of methanol and water mixtures at 298 K and 1 bar are presented in Fig. 5. A KB analysis of this system has already been presented.^{6,70} At this temperature and pressure the experimentally extracted F 's closely mirror the partial molar excess enthalpies (data not shown). The F 's and Δ_m functions display nontrivial variations with mole fraction. Hence, they provide insights into the behavior of solution mixtures which can be used to characterize the solution in terms of local fluctuating properties. However, to obtain a deeper insight into these variations with composition

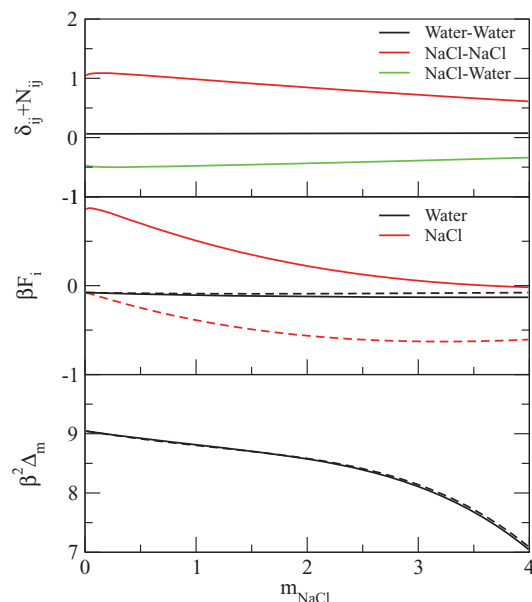


FIG. 7. A fluctuation analysis of water (1) and sodium chloride (2) mixtures at 298 K and 1 bar. The solid lines correspond to the experimental data using the crystal reference state, while the dashed lines correspond to the experimental data using the infinitely dilute salt reference state.

one probably requires a similar analysis of computer simulation data.

In contrast to methanol and water mixtures an analysis of methanol and benzene solutions at 308 K and 1 bar indicates a substantial degree of methanol self association at low methanol compositions. This is illustrated in Fig. 6. The F 's no longer closely mimic the partial molar enthalpies, as was the case for methanol and water, primarily due to the relatively large values of the KBIs (see Eq. (20)). The energy-energy fluctuations are essentially the same as the ideal values as, at these temperatures and pressures, the Δ_m term is dominated by the heat capacity contribution and this was taken to be ideal in nature. The large values of F for methanol at low methanol mole fractions coincides with the increased self association of methanol molecules (increase in N_{22}) albeit at a lower benzene mole fraction for the latter.²¹

Many potential applications involve systems where one component (2) is at infinite dilution (∞), as is the case with many biological problems for example. Under these conditions F_1 is given by Eq. (19) and F_2 by the expression,

$$F_2^\infty = PRT\kappa_T^0 - RT^2\alpha_p^0 + \bar{U}_2^{ex,\infty}. \quad (21)$$

Hence, there is a direct link between F_2 and the excess partial molar energy at infinite dilution, i.e., between a local fluctuating property and a thermodynamic derivative of the solution. The value of F_2 at infinite dilution expressed in terms of fluctuations reduces to

$$F_2^\infty = \langle \varepsilon \rangle_2 - \langle \varepsilon \rangle_o = \langle E \rangle_2 - \langle N_1 \rangle_2 E_1^o - E_2^o, \quad (22)$$

where the subscripts 2 and o refer to ensemble averages obtained for regions containing the solute molecule, or for regions in the pure solvent, respectively. For classical pairwise additive potentials this can be expressed as

$$F_2^\infty = \langle E_{22} + E_{21} + E_{11} \rangle_2 - \langle N_1 \rangle_2 E_1^o - E_2^o, \quad (23)$$

where E_{22} is the intramolecular (potential and kinetic) contribution to the energy from the solute, E_{21} is the solute-solvent potential energy, and E_{11} is the solvent-solvent potential and kinetic energy. The E_1^o term represents the total energy that the same number of local solvent molecules would have in bulk solution. Hence, the solute F has been reduced to a series of simple ensemble averages for a region in the vicinity of the solute under these conditions. Furthermore, these averages quantify the energy of the solute and the interaction with the solvent, and how the solute perturbs the solvent-solvent interactions from those observed in bulk solvent, all relative to the solute reference energy.

Salt solutions

The study of electrolyte solutions by fluctuation theory is slightly complicated by the electroneutrality constraints that are often invoked for these solutions.⁷¹ If we consider a salt ($M_{n+}^{z+} X_{n-}^{z-}$) which completely dissociates to provide n_+ cations and n_- anions, and therefore n total ions, one can relate fluctuations involving any indistinguishable ion (I) to that of the cations and anions via

the expressions,

$$\begin{aligned} G_{II} &= \left(\frac{n_+}{n}\right)^2 G_{++} + \left(\frac{n_-}{n}\right)^2 G_{--} + \frac{n_+ n_-}{n^2} (G_{+-} + G_{-+}), \\ G_{I1} &= G_{1I} = \frac{n_+}{n} G_{+1} + \frac{n_-}{n} G_{-1}, \\ F_I &= \frac{n_+}{n} F_+ + \frac{n_-}{n} F_-, \end{aligned} \quad (24)$$

which were obtained from a simple substitution of $N_I = N_+ + N_-$ into Eqs. (1) and (10).⁷² Further imposing the electroneutrality conditions,^{71,73,74}

$$\begin{aligned} z_+ + z_+ \rho_+ G_{++} + z_- \rho_- G_{+-} &= 0, \\ z_- + z_+ \rho_+ G_{+-} + z_- \rho_- G_{--} &= 0, \\ z_+ \rho_+ G_{+1} + z_- \rho_- G_{-1} &= 0, \\ z_+ \rho_+ F_+ + z_- \rho_- F_- &= 0, \\ n_+ z_+ + n_- z_- &= 0, \end{aligned} \quad (25)$$

provides the following relationships:

$$\begin{aligned} G_{II} &= -\frac{1}{\rho_I} + G_{+-}, \\ G_{+-} &= \frac{1}{\rho_+} + G_{++}, \\ \frac{1}{\rho_+} + G_{++} &= \frac{1}{\rho_-} + G_{--}, \\ G_{I1} &= G_{+1} = G_{-1}, \\ F_I &= F_+ = F_-, \end{aligned} \quad (26)$$

and indicates that there is only one unique (independent) solute KBI and F value for a salt solution. Hence, in practice it is often easier to treat the solution as a mixture of a solvent and a collection of indistinguishable ions ($2 = I$) in which case the following relationships should be used:

$$\begin{aligned} m_2 &= nm_s \quad \rho_2 = n\rho_s \quad n\bar{V}_2 = \bar{V}, \\ \mu_{22} &= 1 + \left(\frac{\partial \ln \gamma_{\pm}}{\partial \ln m_s}\right)_{T,P} \quad n\bar{U}_2^{ex} = \bar{U}_s^{ex}, \end{aligned} \quad (27)$$

in Eq. (20) to provide the required G_{II} , G_{I1} , and F_I values. Here, the subscript s refers to the traditional salt concentration, volume, or partial molar excess energy, and $\gamma_I = \gamma_{\pm}$ is the mean molal ion activity coefficient.

The results from a fluctuation analysis of NaCl solutions at 298 K and 1 bar are provided in Fig. 7. We have included the results obtained from two different reference states for the salt: namely, the salt crystal and an infinitely dilute solute. The choice of reference state does not significantly affect the values of F for water or the energy-energy fluctuations, while the ion F value is significantly shifted and displays a slightly different dependence on composition. The trend in the ion F with composition is the same for both reference states and indicates a decrease in the ion-energy correlation with increasing ion concentration. The local energy-energy fluctuation displays a similar decrease with salt concentration.

Ideal solutions

Ideal solutions represent interesting reference states for comparison to real solutions. Symmetrical ideal (SI) solutions are defined by the fact that $\mu_i = RT \ln x_i$ and $\bar{U}_i^{ex} = 0$ for all i species. The local fluctuations exhibited by symmetric ideal solution mixtures involving any number of n_c components are then given by^{4,75}

$$\begin{aligned} G_{ij}^{SI} &= RT \kappa_T^{SI} - V_i^o - V_j^o + S_{n_c} \quad S_{n_c} = \sum_{k=1}^{n_c} \rho_k (V_k^o)^2, \\ F_i^{SI} &= PRT \kappa_T^{SI} - RT^2 \alpha_P^{SI}, \\ \Delta_m^{SI} &= RT^2 C_{P,m}^{SI} + PV_m^{SI} (PRT \kappa_T^{SI} - 2RT^2 \alpha_P^{SI}), \\ V_m^{SI} &= \sum_{k=1}^{n_c} x_k V_k^o, \\ \kappa_T^{SI} &= \sum_{k=1}^{n_c} \phi_k \kappa_{T,k}^o, \\ \alpha_P^{SI} &= \sum_{k=1}^{n_c} \phi_k \alpha_{P,k}^o, \\ C_{P,m}^{SI} &= \sum_{k=1}^{n_c} x_k C_{P,m,k}^o. \end{aligned} \quad (28)$$

In this case the F values vary with composition, but are the same for each component (as would be expected). The SI results have been included in Figs. 5 and 6 to help indicate deviations from ideal behavior.

Bulk system fluctuations

It is well known that fluctuations in the properties of bulk systems can be related to various experimental properties. For systems at constant $\{N\}$, pressure and temperature the experimental properties are the compressibility, thermal expansion, and constant pressure heat capacity. The appropriate relationships can be obtained directly from the isothermal-isobaric partition function,⁷⁶

$$\begin{aligned} \langle (\delta V)^2 \rangle_{NPT} &= VRT \kappa_T, \\ \langle \delta V \delta(E + PV) \rangle_{NPT} &= VRT^2 \alpha_P, \\ \langle (\delta(E + PV))^2 \rangle_{NPT} &= RT^2 C_P. \end{aligned} \quad (29)$$

These relationships are different from the ones presented here as they represent fluctuations in the properties of *bulk closed systems* and not *local open regions* within these systems. It is interesting to note that the local fluctuation relationships (Eqs. (13) and (14) and (17)) can be generated from the corresponding bulk expressions by use of the transformations,

$$\delta V \rightarrow -\sum_i \bar{V}_i \delta N_i \quad \delta(E + PV) \rightarrow \delta E - \sum_i \bar{H}_i \delta N_i, \quad (30)$$

followed by some algebra and a subsequent transformation of E to ε using Eq. (8).

CONCLUSIONS

We have outlined a method for extracting information concerning local energy-particle and energy-energy fluctuations in solution mixtures from experimental data. The resulting local fluctuations can be used to help characterize the properties of solution mixtures in much the same way as the traditional KB/FT approach. Another possible use of the experimentally derived fluctuations is for the evaluation and development of accurate force fields for molecular simulation, where the fluctuating quantities serve as additional experimental data for the parametrization procedure.^{20,21} In addition, the same type of approach can be applied to understand the effects of temperature on chemical equilibria in terms of energy-particle and energy-energy fluctuations. Studies along these lines will be published separately.^{67,77}

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