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Concentration fluctuations in fluid mixtures. II.

Robert M. Mazo,^{1,a)} Enrico Matteoli,² and Paul E. Smith³¹*Department of Chemistry and Institute of Theoretical Science, University of Oregon, Eugene, Oregon 97405, USA*²*CNR-Istituto Processi Chimico-Fisici, Via Moruzzi 1, 56124 Pisa, Italy*³*Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, USA*

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The method developed in a previous paper [R. Mazo, *J. Chem. Phys.* **129**, 154101 (2008)] for extracting information on the size of relative fluctuations in multicomponent systems is tested on ten binary systems and one ternary system. For the binary systems, it is found that the approximation works well for mole fractions in the range of 0.15–0.85 in most cases. For the ternary case, the method inherently yields less information and is valid only over a more restricted range for the case studied (chloroform-methanol-acetone). It is found that the predicted ratio of number fluctuations is approximately equal to the ratio of molar volumes of the components.

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I. INTRODUCTION

In a previous paper,¹ one of us introduced a method for deducing information on the fluctuations of particle numbers, eventually from thermodynamic data, using Kirkwood–Buff theory.² Two systems for which data were available, urea-water and 2,2,2-trifluoroethanol-water, were analyzed using the method in order to illustrate its applicability. This paper is hereafter referred to as I. Indeed, the method is an approximate one; it is not universally applicable, but it does contain an internal check, so that one is not left guessing about the validity of the results. In the following we shall call the method by the name *principle component approximation* (PCA for short). Our PCA is not identical to the PCA used by statisticians but is closely related to it, as noted in I.

The purpose of this paper is twofold. First, we want to add a few theoretical comments concerning details of the method. The second and the main object of the paper is to apply the method to 11 additional systems. These comprise two electrolyte solutions, a ternary mixture, and eight non-electrolyte binary systems including both polar and nonpolar molecules, and large and small molecules. We hope in this way to investigate the extent of applicability of the method, which was tested in I in only two examples, both aqueous.

II. THEORY

Kirkwood–Buff theory expresses the thermodynamic properties of solutions in terms of certain integrals,

$$G_{ij} = \int (g_{ij}(r) - 1) d^3r, \quad (1)$$

and numbers, $B_{ij} = c_i c_j G_{ij} + c_j \delta_{ij}$. The G_{ij} are called Kirkwood–Buff integrals (KBIs). The g_{ij} are spherically averaged pair correlation functions. These expressions can be inverted to give the B_{ij} in terms of thermodynamic functions.³ Kirkwood and Buff showed that $VB_{ij} = \langle \Delta N_i \Delta N_j \rangle$,

the covariance matrix of the fluctuations of the particle numbers, ΔN_i , of the various species in the solution, defined as in Refs. 1 and 2.

The result of I was the demonstration that, when some of the eigenvalues of \mathbf{B} are much larger than the others, the description of the system can be condensed with little loss in accuracy and new information obtained. In effect, although the ΔN_i are fluctuating quantities, there are certain ratios of the ΔN_i which have fixed relationships. The method leads to a reduction in dimensionality of fluctuation space.

We outline the procedure proposed in I which we call the PCA. Write the \mathbf{B} matrix in dyadic form,

$$\mathbf{B} = \sum_{\alpha} \mathbf{u}^{\alpha} \mathbf{u}^{\alpha T} \lambda_{\alpha}, \quad (2)$$

where the λ_{α} are the eigenvalues and the \mathbf{u}^{α} the corresponding eigenvectors of \mathbf{B} . The T means transposed. Note that we label the eigenvectors by Greek letters as superscripts; components of these vectors will be denoted by Latin subscripts. This is a change from the notation of I, made to avoid confusion. (To avoid more confusion we state explicitly that the placing of sub- and superscripts has nothing to do with the co- or contravariant nature of the vectors.) If we discard the small eigenvalue contributions to the sum in Eq. (2) (the meaning of the term “small eigenvalue” is explained in detail in I), we get a new matrix,

$$\mathbf{b} = \sum_{\text{large}} \lambda_{\alpha} \mathbf{u}^{\alpha} \mathbf{u}^{\alpha T}. \quad (3)$$

This matrix has rank at most $n-r$, where n is the number of components of the solution, and r is the number of small eigenvalues of \mathbf{B} . Consequently it can be described by a smaller number of independent variations or eigenmodes; this implies strong couplings between the fluctuations of various components, especially in two component, and to a lesser extent in three component, solutions.

As stated in I, the \mathbf{b} matrix is of little interest in itself. It is an approximation to the \mathbf{B} matrix which we assume we

^{a)}Electronic mail: mazo@uoregon.edu.

already have in hand. The interesting information lies in the eigenvectors of \mathbf{B} . The PCA proceeds by providing a rationale for neglecting one or more of these eigenvectors, thus reducing the dimensionality of the space. The computation of \mathbf{b} is merely a check on the validity of the PCA for the system being studied.

The existence of small eigenvalues is a necessary, but not sufficient condition. To appreciate this, consider the toy model for a binary system with a \mathbf{B} matrix,

$$\mathbf{S} = \begin{pmatrix} 1 & \varepsilon \\ \varepsilon & f\varepsilon \end{pmatrix}. \quad (4)$$

This should be imagined to be the \mathbf{B} matrix for a binary system very dilute (ε small) in component 2, scaled so that its largest matrix element is unity. f is an arbitrary constant. Of course it is easy to compute the eigenvalues and eigenvectors of \mathbf{S} directly, but it is more enlightening to carry out the calculation to first order in ε only. The two eigenvalues are of order unity and order ε , respectively, as one can see immediately from elementary perturbation theory. Carrying out the procedure of I, we find for the relative error of the reconstituted matrix s_{ij} the following results, presented in matrix form:

$$s = \begin{pmatrix} 1 & \varepsilon + O(\varepsilon^2) \\ \varepsilon + O(\varepsilon^2) & O(\varepsilon^2) \end{pmatrix}. \quad (5)$$

In other words, the relative error in the 2,2 matrix element is of the same order as the matrix element itself. This occurs because the matrix \mathbf{S} is almost singular for small ε . The same conclusion holds, *mutatis mutandis*, if component 1 is the dilute one. Since small ε in this example is a metaphor for small concentration in the real physical systems we want to treat, what we learn from this example is that the method of I is not likely to give reliable results for very dilute solutions. Indeed, detailed calculations bear this out as we shall see in the section to follow.

The last methodological point we wish to make here concerns three component systems. In I we pointed out that when there were two large and one small eigenvalues, the fluctuations form a one parameter family,

$$\Delta N_1 : \Delta N_2 : \Delta N_3 = a^1 + \gamma a^2 : b^1 + \gamma b^2 : c^1 + \gamma c^2. \quad (6)$$

Here the ΔN 's are the particle number fluctuations as in I, $\text{col}(a^v, b^v, c^v)$ is the v th eigenvector normalized to unity, and γ is an arbitrary parameter. γ may be eliminated as follows. $(\mathbf{u}^1, \mathbf{u}^2, \mathbf{u}^3)$ form an orthonormal triad of vectors. By our neglect of the small eigenvalue, we are forcing $(\Delta N_1, \Delta N_2, \Delta N_3)$ to lie in the \mathbf{u}^1 - \mathbf{u}^2 plane and hence be normal to \mathbf{u}^3 . Consequently

$$\Delta N_1 a^3 + \Delta N_2 b^3 + \Delta N_3 c^3 = 0 \quad (7a)$$

or

$$\Delta N_3 / \Delta N_2 = -[b_3 + a_3(\Delta N_1 / \Delta N_2)] / c_3. \quad (7b)$$

Although the ratio of the fluctuations is not determined uniquely as is the case in a binary system, a relation between the two pairs of fluctuations is determined. Equations (6) and

(7b) are consistent as can be seen by the more tedious elimination of γ from Eq. (7).

III. ANALYSIS OF SELECTED SYSTEMS

We have analyzed 11 selected systems to illustrate what can be learned by applying the principal component method to specific cases. These examples were chosen to explore a number of different solvent-solute molecular characteristics. The data for the two electrolyte solutions come from the analysis of thermodynamic data by the group of Smith. The KBI data for the remaining nine solutions were obtained from previous work from the laboratory of Matteoli or calculated here from the referenced thermodynamic data. We discuss them *seriatim*. Because the data are voluminous, we give in the body of this paper only values of the pertinent computed quantities for concentration values near the lower and upper limits of validity of the approximation, and in the middle. More complete tables have been deposited with the Physics Auxiliary Publication Service (EPAPS).⁴

Ar(1)—Kr(2) at 115K (Ref. 5). This system was chosen because the components are simple, spherical, monatomic fluids with no directional intermolecular forces. The sizes of the component atoms are similar; the Lennard-Jones size parameters are $\sigma=3.40$ and 3.60 Å for Ar and Kr, respectively. Table I shows the results of our calculations for selected values of the concentration.

One can see from the table that in the concentration range $0.15 < x_1 < 0.85$, the eigenvalue ratio is greater than 20. Furthermore, b_{ij}/B_{ij} never differs from unity by more than about ± 0.05 throughout this concentration range. Therefore, we have considerable confidence that the replacement of \mathbf{B} by \mathbf{b} is an adequate approximation. This is an example of what we meant when we stated in Sec. I that the theory contains an internal applicability check.

One finds from the table that $\Delta N_1 / \Delta N_2$ increases in absolute value slowly but steadily from 0.95 at $x_1=0.15$ to 1.05 at 0.85; the sign of this ratio is negative. Thus we may say that, whatever the magnitude of the fluctuations, they occur very highly correlated in essentially a 1–1 ratio, one argon leaving the system for every krypton entering, and vice versa.

The partial molar volumes of Ar and Kr at $x_1=0.5$ are 32.59 and 34.11 cm³, respectively. Consequently $\bar{V}_2 / \bar{V}_1 = 1.05$. In I we made the hypothesis that the fluctuations were such as to keep the volume actually occupied by the molecules almost constant in the sense that $\Delta N_1 \bar{V}_1 + \Delta N_2 \bar{V}_2 = 0$. We shall refer to this as the occupied volume hypothesis (OVH). If it is indeed correct, then we should have

$$\Delta N_1 / \Delta N_2 = -\bar{V}_2 / \bar{V}_1. \quad (8)$$

From the table, it is clear that this condition is very closely fulfilled, within 1%, which is probably within the error of the method. With an eigenvalue ratio of 38 (at $x=0.5$), one might expect a discrepancy of about 2.5%. Thus we conclude that the OVH is approximately valid in this case also.

Carbon tetrachloride(1)—methanol, ethanol, propanol, butanol(2) at 298K (Ref. 6). These are four different binary mixtures, not a five component mixture. These systems were

TABLE I. Selected values of the ratio of the reconstructed to the original Kirkwood–Buff B matrix elements. The last column contains the ratios of actual molar volumes except in the cases of Ar–Kr and H₂O–guanidinium chloride, where partial molar volume ratios are given. See the text for a discussion of this. More complete tables may be found in Ref. 4. (x is x_c in the guanidinium chloride example.)

System	x_2	λ_1/λ_2	b_{11}/B_{11}	b_{22}/B_{22}	b_{12}/B_{12}	$\Delta N_1/\Delta N_2$	V_2/V_1
Ar(1)–Kr(2)	0.15	19.1	0.950	0.951	1.055	–0.993	1.05
	0.50	38.1	0.976	0.972	1.027	–1.041	
	0.85	20.5	0.958	0.949	1.051	–1.051	
CCl ₄ (1)–CH ₃ OH(2)	0.15	92.8	0.937	0.998	1.011	–0.401	0.420
	0.50	265.3	0.979	0.999	1.004	–0.415	
	0.85	137.6	0.961	0.999	1.007	–0.421	
CCl ₄ (1)–C ₂ H ₅ OH(2)	0.15	43.9	0.934	0.993	1.023	–0.569	0.606
	0.50	122.6	0.978	0.997	1.008	–0.596	
	0.85	104.0	0.975	0.996	1.010	–0.609	
CCl ₄ (1)–C ₃ H ₇ OH(2)	0.15	25.8	0.951	0.985	1.029	–0.735	0.775
	0.50	91.4	0.982	0.994	1.012	–0.767	
	0.85	98.4	0.982	0.993	1.011	–0.782	
CCl ₄ (1)–C ₄ H ₉ OH(2)	0.20	34.6	0.966	0.976	1.030	–0.913	0.952
	0.50	89.6	0.988	0.990	1.011	–0.942	
	0.85	86.1	0.988	0.989	1.012	–0.961	
H ₂ O(1)–acetonitrile(2)	0.25	281	0.996	0.764	1.037	–2.943	2.98
	0.50	602.5	1.000	0.986	1.002	–2.953	
	0.85	711.1	1.000	0.988	1.001	–2.967	
C ₈ H ₁₈ (1)–hexadecane(2)	0.15	35.8	0.991	0.921	1.029	–1.754	1.80
	0.50	89.3	0.997	0.965	1.011	–1.804	
	0.85	107.2	0.997	0.969	1.009	–1.842	
C ₈ H ₁₈ (1)–2,2,3-trimethylpentane(2)	0.15	27.2	0.962	0.967	1.038	–0.963	1.02
	0.50	57.3	0.983	0.982	1.018	–1.016	
	0.85	29.0	0.971	0.962	1.036	–1.069	
H ₂ O(1)–guanidiniumchloride(2)	0.156	67.0	0.997	0.938	1.015	–2.106	2.05
	0.27	95.4	0.997	0.952	1.012	–2.087	
	0.351	90.0	0.997	0.952	1.011	–2.087	

chosen to study the effect of molecular size in solutions of otherwise rather similar molecules. We intend to present and discuss the results of all four cases together. The results of our calculations are given in Table I. In all of them, the alcohol moiety fluctuates more than the CCl₄ although $|\Delta N_1/\Delta N_2|$ is rather close to unity in the case of butanol, which has a very similar molar volume to that of CCl₄.

In all four cases the values of the b_{ij}/B_{ij} are quite close to unity. As in the previous case, this means that our approximation is valid. In estimating whether Eq. (9) holds approximately, in these and all the following examples in this paper, we shall use molar volumes of the pure components instead of partial molar volumes. The volume changes on mixing are small relative to the molar volumes themselves, and in any case, the ratio of volumes is to be compared to an approximate ratio of number fluctuations. The greater precision afforded by using partial molar volumes would be in most cases negligible, but widens the range of validity of Eq. (9) as we have verified by a sample calculation. We do not make the manifestly incorrect claim that this is a valid approximation for all solutions, but it is valid for the systems discussed in this paper except for the Ar–Kr and electrolyte examples. This can be verified by consulting the references given to the thermodynamic data from which the B_{ij} were computed in each example. For the Ar–Kr case, the temperature ranges of the coexistence curves of Ar and Kr do not overlap. The

normal boiling point of Ar is 87.3 K; our data are for 115 K. Therefore we have used partial molar volumes instead in this case.

The same reasoning forces us to use partial molar volumes when we present the results on electrolyte solutions later in this section. The molar volumes of the pure solid solute salts are not relevant to our considerations.

One can see from the tables that methanol fluctuates about 2.4 times more than CCl₄, ethanol about 1.7 times as much, propanol about 1.3 times as much, and butanol about the same as CCl₄. Equation (8) is satisfied in all four cases quite closely although not exactly.

H₂O(1)–acetonitrile(2) at 303K (Ref. 7). This system was chosen as an example of a hydrogen bonding, dipolar molecule interacting with water. Water and acetonitrile are miscible over the entire concentration range. In this case b_{11}/B_{11} is close to unity for x_1 0.1, while b_{12}/B_{12} and b_{22}/B_{22} are only close to unity for $x_1 \geq 0.25$. This contrasts with the cases previously discussed, where the approximation held for all three ratios over a wider range.

In the range $0.25 \leq x_1 \leq 0.95$, $\Delta N_1/\Delta N_2$ is quite close to –3 over the entire range. The ratio of molar volumes is 2.98. Again, the assumption that the fluctuations are such as to keep the total volume occupied by molecules in a given volume constant is a very good approximation.

Octane(1)-hexadecane(2) at 298K (Ref. 8). This system was chosen as an example of two chemically very similar species of different sizes. In this case, the b 's are again excellent approximations to the B 's for $0.15 \leq x_1 \leq 0.85$. However, the value of $\Delta N_1/\Delta N_2$ decreases steadily from -1.75 to -1.84 . This is a relatively small change over this range but it is larger than in third case, above. The details are shown in Table I. It should be emphasized that there is nothing in our development that requires, or even implies, that $\Delta N_1/\Delta N_2$ be constant as a function of concentration. It is our auxiliary approximation that the partial molar volume ratio be equal to the molar volume ratio which implies this, and we do not assert that this hypothesis be rigorously true. For this binary mixture, the ratio of molar volumes is 1.8.

Octane(1)-2,2,4 trimethylpentane(2) (Ref. 8). This system was chosen in order to have a sample system of chemical isomers. The molar volumes are almost the same, the ratio being 1.02. Hence, if we are to be guided by experience up to now, we should expect b_{ij}/B_{ij} to be close to unity for $0.15 \leq x_1 \leq 0.85$ and $\Delta N_1/\Delta N_2$ to be approximately constant over this range. Indeed, this is the case, as shown in Table I $\Delta N_1/\Delta N_2$ varies from -0.96 to -1.07 over this range. The ratio of molar volumes is 1.02. Our expectations are borne out.

Acetone(1)-chloroform(2)-methanol(3) at 323K (Ref. 9). We close our description of selected nonelectrolyte solutions with one example of a ternary solution. The three components are miscible in all proportions at the temperature of the experiments.

In contrast to the binary solution examples we have presented, this ternary solution exhibits a more limited range of validity of the approximation we study here. When at least one of the components is dilute, say $x < 0.1$, we have a similar situation to that described in Sec. II. Think of the system displayed in the usual composition triangle. Then, in the region around the edges of the triangle, our approximation is invalid. As one proceeds concentrically toward the center, there is a region where no one or no pair of the eigenvalues of the B matrix dominates. So our considerations are invalid here also. Proceeding further toward the center, one finds that this system is a case of two large and one small eigenvalue. The region where all of the b_{ij}/B_{ij} are close to unity ($\pm 10\%$) (based on neglecting the small eigenvalue) is shown in Fig. 1. It should be realized that the edges of this region are not terribly well defined. They depend on how strict one wants to be in deciding whether a number is sufficiently close to unity.

The constant molecular volume hypothesis, $\bar{V}_1\Delta N_1 + \bar{V}_2\Delta N_2 + \bar{V}_3\Delta N_3 = 0$, together with Eq. (7b) leads to equations similar to Eq. (8),

$$\frac{\bar{V}_1}{\bar{V}_3} = \frac{a}{c}, \quad \frac{\bar{V}_2}{\bar{V}_3} = \frac{b}{c}. \quad (9)$$

We have again taken the molar volumes of the pure components as surrogates for their partial molar volumes and computed the expected volume ratios on the basis of the a , b , c coefficients obtained in the course of the eigenvalue analysis.

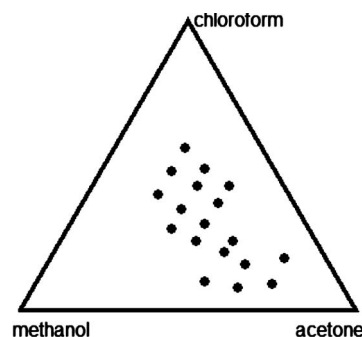


FIG. 1. Ternary triangular diagram for the system acetone, chloroform-methanol, showing the region in which the PCA adequately reconstructs the B matrix. The points shown should be interpreted as showing the general region of validity.; the boundaries are fuzzy, depending on the definition of "adequate."

The volume ratios are adequately reproduced (to within $\sim 5\%$).

Because the data on which these remarks are based are inherently voluminous, we present here only a small sample, in Table II. For the bulk of the data see Ref. 4.

H₂O(1)-NaCl(2) (Refs. 10 and 11) and *H₂O(1)-guanidinium chloride(2)* (Ref. 12) at 298K. So far, all of our examples, both here and in I, have been nonelectrolyte solutions. For electrolyte solutions, Kirkwood-Buff theory, on which the present paper is based, must be applied with care. This occurs because electroneutrality requires that the B matrix be singular. There are several ways to do take care of this complication. The simplest way for our purposes is to base the stoichiometry on the total ion concentration rather than on the salt concentration. Quantities based on total ion concentration will be denoted by the subscript c .

We initially chose NaCl because it is a prototypical electrolyte for which much data are available. However, it has a limited solubility in water at room temperature, about $6M$ or a mole fraction of approximately 0.1. This is the mole fraction of salt. The mole fraction of total ions, the most useful concentration unit for our analysis, is roughly double this. Unfortunately, even at $5.3M$, the highest concentration for which we have data, B_{12} is not reproduced well; $b_{1c}/B_{1c} = -1.54$, even though the eigenvalue ratio is of reasonable size, 13.9. This is because of the small mole fraction. Therefore, one cannot draw any reliable conclusions from this example. It does appear that $\Delta N_1/\Delta N_c$ is leveling off at a value close to unity, but, because we are at the very limits of the validity of our approximation, this is not reliable. Thus aqueous NaCl is a cautionary example rather than an illustrative one.

Guanidinium chloride also has a solubility of approximately $6M$ at room temperature. We have data up to $7.2M$ at 300 K. Its total ion mole fraction at this concentration is, however, about 0.35 essentially because guanidinium ion is a larger and heavier particle than is chloride ion. Thus, based on our experience with the nonelectrolyte solutions, we might expect our approximation to be invalid for NaCl but valid from about $4M$ to $7M$ for guanidinium chloride. At $4M$, the total ion mole fraction is $x_c = 0.17$.

Some data for concentrations greater than $4M$ are shown in Table I. One can see that $\Delta N_1/\Delta N_c$ is approximately 2.1

TABLE II. The reconstruction of the \mathbf{B} matrix for case 6, the ternary mixture acetone (1)-chloroform (2)- methanol (3). a , b , and c are the coefficients defined in Eqs. (7). These values were computed by the methods in Sec. II using data from Ref. 9.

x_1	x_2	b_{11}/B_{11}	b_{22}/B_{22}	b_{33}/B_{33}	b_{12}/B_{12}	b_{13}/B_{13}	b_{23}/B_{23}	a	b	c
0.2	0.56	0.95	0.97	0.997	1.074	1.079	1.014	-0.655	-0.674	-0.341
0.2	0.64	0.948	0.964	0.994	1.065	1.407	1.024	-0.656	-0.672	-0.344
0.3	0.42	0.964	0.967	0.997	1.067	1.038	1.016	-0.639	-0.688	-0.345
0.3	0.49	0.962	0.966	0.996	1.057	1.077	1.022	-0.64	-0.685	-0.347
0.3	0.56	0.961	0.963	0.992	1.051	1.251	1.036	-0.64	-0.682	-0.353
0.4	0.3	0.971	0.963	0.997	1.063	1.025	1.02	-0.627	-0.698	-0.345
0.4	0.36	0.969	0.963	0.996	1.055	1.042	1.024	-0.63	-0.695	-0.347
0.4	0.42	0.968	0.963	0.994	1.049	1.079	1.033	-0.631	-0.692	-0.351
0.4	0.48	0.967	0.961	0.989	1.045	1.206	1.054	-0.63	-0.688	-0.362
0.5	0.2	0.974	0.954	0.997	1.064	1.02	1.029	-0.616	-0.709	-0.343
0.5	0.3	0.972	0.96	0.995	1.049	1.046	1.037	-0.622	-0.701	-0.349
0.5	0.4	0.971	0.961	0.985	1.041	1.184	1.079	-0.621	-0.691	-0.37
0.6	0.000	1.000	0.004	1.000	1.005	1.000	1.003	-0.004	-1.000	-0.002
0.6	0.24	0.973	0.955	0.992	1.047	1.053	1.061	-0.615	-0.705	-0.352
0.6	0.32	0.974	0.959	0.979	1.039	1.183	1.123	-0.611	-0.693	-0.382
0.7	0.18	0.973	0.948	0.989	1.049	1.064	1.111	-0.605	-0.711	-0.358

over this range of concentration. The partial molar volume ratio \bar{V}_c/\bar{V}_1 over this concentration range increases slightly but steadily by about 5%, ranging from 2.0 at the lower end to 2.1 at the upper. Again, the hypothesis of constant molecular volume is correct to a good approximation.

IV. DISCUSSION AND CONCLUSIONS

One might ask, why not just calculate $(\langle \Delta N_1^2 \rangle / \langle \Delta N_2^2 \rangle)^{1/2} = (B_{11}/B_{22})^{1/2}$? It would be much simpler than our procedure and is always valid. If one is satisfied with this ratio of averages, this is a reasonable thing to do. Our procedure, however, shows when the ratio of the ΔN 's (the actual fluctuating values, not just their root-mean-square values) can give definite values in spite of fluctuations of the numerator and denominator separately. We believe that this is useful and interesting information.

A referee has pointed out that the result for binary solutions can be interpreted as finding the ratio of the most probable values of ΔN_1 and ΔN_2 subject to the side condition that $\Delta N_1^2 + \Delta N_2^2 = \text{const}$. This is an interesting mathematical side-light and is easily verified by the method of Lagrange multipliers. The maximization problem leads to the same eigenvalue equation considered here. On the other hand, why impose the condition $\Delta N_1^2 + \Delta N_2^2 = \text{const}$? The eigenvectors \mathbf{u}^α have a fixed, although arbitrary, magnitude, but the vector $(\Delta N_1, \Delta N_2)$ does not. It is only the PCA which enables us to diminish the dimensionality of the space of fluctuations.

In I we made the hypothesis of conservation of molecular volume in the sense that $\sum \Delta N_i \bar{V}_i = 0$, called here the OVH, based on two examples. This hypothesis has an intuitive appeal, but it is clear that it cannot be rigorously true. To see this, square this equation.,

$$V^{-2} \sum_{i,j} \langle \Delta N_i \Delta N_j \rangle \bar{V}_i \bar{V}_j = 0 \quad (10)$$

or

$$V^{-1} \sum_{i,j} B_{ij} \bar{V}_i \bar{V}_j = 0. \quad (11)$$

This is the variance of the ratio of the fluctuation in the occupied volume to the total volume. The formulas of Kirkwood and Buff show that the left hand side of Eq. (11) is actually $\rho kT/N$, and not zero; κ is the compressibility and ρ the overall number density. This follows from Eqs. (13) and (14) of Ref. 2 and the determinantal relationship $\delta_{ij}|B| = \sum_k B_{ik}|B|_{kj}$. It is intuitively clear that there should be some sort of compressibility correction. For when the compressibility is large, as in a gas, there is much empty volume and nothing to force correlations in fluctuations. On the other hand, when the compressibility is small, there is not much free volume and correlations of the several components are enforced by hard core constraints.

Consequently the OVH is not rigorous. On the other hand, ρkT is a small number for typical liquids. For example, for methanol at 293 K it is 0.073. Consequently $(\rho kT/N)^{1/2}$ is extremely small for any volume containing more than, say, 10^4 particles. Thus we may expect observed deviations from the OVH when the PCA is valid to be due to numerical roundoff, experimental error, our use of the molar volume of the pure components as a substitute for partial molar volumes, or actual physical effects. Although our examples only show that the OVH holds in the range $0.15 < x < 0.85$ for the binary solutions studies, this is due to the invalidity of the PCA in the dilute solution region, and the OVH may still hold there. Our results are mute on this point. We suspect that the OVH probably holds over most of the rest of the concentration range also.

An easy way of estimating, when the PCA may be expected to hold without actually solving the eigenvalue problem, is to calculate the correlation coefficient of the number variances. The correlation coefficient is defined in mathematical statistics to be

$$\rho_{\Delta N_1 \Delta N_2} = \langle \Delta N_1 \Delta N_2 \rangle / (\langle \Delta N_1 \Delta N_1 \rangle \langle \Delta N_2 \Delta N_2 \rangle)^{1/2}. \quad (12)$$

It is clear that if ΔN_1 and ΔN_2 were strictly proportional, then $|\rho_{\Delta N_1 \Delta N_2}|$ would be unity. So if $|\rho_{\Delta N_1 \Delta N_2}|$ is not close to unity there is little hope that the PCA will be valid. For example, for aqueous NaCl, $|\rho_{\Delta N_1 \Delta N_2}|$ is never greater than 0.865 for the range of concentrations studied. On the other hand, for guanidinium chloride it is greater than 0.95 for concentrations greater than 4M. Similar behavior is visible in the other systems we studied. For example, in the system H₂O-acetonitrile, $|\rho_{\Delta N_1 \Delta N_2}|$ rises to 0.94 at $x_{\text{water}}=0.35$ and is as high as 0.99 at $x_{\text{water}}=0.99$. But even at $x_{\text{water}}=0.35$, b_{22}/B_{22} is only 0.91, not large enough for the PCA to be fully reliable. Although the calculation of the correlation coefficient is simple and gives one a rough indication of what is occurring, it is not a substitute for the full spectral analysis and inspection of the resulting b 's.

In this work we have investigated a number of binary systems and one ternary system to determine how general the PCA is. For binary systems it has turned out to be more general than we had expected. For the nonelectrolyte systems studied, the approximation held for range of concentrations usually ranging from about 0.15 to 0.85 mol fraction. In some cases, the validity range was smaller, *viz* the water-acetonitrile case just mentioned. Also, in the NaCl-water case the available concentration range was too small, $x_{\text{NaCl}} < 0.15$. One reason for the failure of the approximation in the low concentration range was discussed in Sec. II. On the whole, one can say that the PCA is widely, although not universally, applicable. For the single ternary system studied, the region of validity of the PCA is similarly restricted to the interior part of the ternary composition triangle and even this part is relatively small. Furthermore, even when valid, the approximation does not give as much information as in the binary case.

The PCA, when valid, yields a value of the ratio $\Delta N_1/\Delta N_2$. Although not necessarily implied by the approximation, we found that this ratio was almost constant for each system. Furthermore the constant, in each case, was approximately the negative of the ratio of molar volumes of the components (for binary systems). This led us to the hypothesis that the fluctuation of the several components was such

as to keep the volume occupied by the molecules in the system of volume V constant. The constant value of the ΔN ratio was, in fact, the molar volume ratio (or very close to it). While this hypothesis cannot be rigorously valid, empirically it seems to be a very good approximation. We want to emphasize, however, that the PCA and the OVH are distinct. The PCA does not logically imply the OVH. Conversely, the OVH may be valid where the PCA is not. This question is open since at present we cannot test the OVH without calling upon the PCA.

Our final conclusion is that the PCA is a useful way of approximating the relative fluctuations of components in a binary solution. It does not work well in dilute solutions (at least one component dilute) and gives more restricted information on ternary than on binary solutions. A second conclusion is that the volume actually occupied by molecules within the system during a fluctuation is essentially constant.

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