Local and global properties of mixtures in one-dimensional systems. II. Exact results for the Kirkwood–Buff integrals

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The Kirkwood–Buff integrals for two-component mixtures in one-dimensional systems are calculated directly. The results are applied to square-well particles and found to agree with those obtained by the inversion of the Kirkwood–Buff theory of solutions.

I. INTRODUCTION

In Part I of this series, one of us has studied both the global and the local properties of mixtures of simple particles in one-dimensional system. This work has been part of a more general advocacy in favor of the study of local properties of liquid mixtures. Instead of the traditional study of mixtures based on the global properties, such as excess Gibbs energy, entropy, volume, etc., we have advocated a shift in the paradigm towards focusing on the local properties of the same mixtures, such as affinities between two species (embodied in the Kirkwood–Buff integrals), and derived quantities such as local composition, preferential solvation, and solvation thermodynamic quantities.

The local properties, though equivalent to and derivable from the global properties, offer a host of new information on the local environments of each molecular species in the mixture. This information is not conspicuous from the global properties. Therefore, the study of the local quantities offer a new and more detailed and interesting view of mixtures.

In this paper we have recalculated the Kirkwood–Buff integrals (KBI) directly for two-component mixtures of particles interacting via square-well (SW) potential.

In the next section, we outline the derivation of the pair correlation functions for two-component systems in 1D system, for arbitrary nearest-neighbor interactions. In section III we present a sample of results for mixtures of SW particles. It is shown that the results are in quantitative agreement with those obtained in Part I, which were based on the partition function method and the inversion of the Kirkwood–Buff (KB) theory of solution. We have also calculated the limiting values of the KBI when one of the species has a vanishing mole fraction, which we could not have done from the partition function methods.

Another question examined both numerically and theoretically is the deviations from symmetrical ideal solutions and its relation with the stability of the mixtures. It is shown that no miscibility gap can occur in such mixtures.

II. THEORETICAL BACKGROUND

It is known that the correlation and thermodynamic properties of any one-dimensional homogeneous system in equilibrium can be derived exactly, provided that every particle interacts only with its nearest neighbors. The aim of this section is to present a self-contained summary of the exact solution. Although the scheme extends to any number of components, here we focus on the two-component case.

A. Correlation functions

Let us consider a binary one-dimensional fluid mixture at temperature $T$, pressure $P$, and number densities $\rho_\alpha$ ($\alpha = A, B$). The particles are assumed to interact only between nearest neighbors via interaction potentials $U_{\alpha\beta}(R)$. Before considering the pair correlation functions $g_{\alpha\beta}(R)$, it is convenient to introduce some probability distributions.

Given a particle of species $\alpha$ at a certain position, let $p^{(\ell)}_{\alpha\beta}(R)dR$ be the conditional probability of finding as its $\ell$th neighbor in some direction a particle of species $\beta$ at a distance between $R$ and $R + dR$. If $\ell \geq 2$ it is obvious that the $(\ell - 1)$th neighbor of $\alpha$ in the same direction (being located at some point $R'$ between 0 and $R$) is also a first neighbor of $\beta$. Therefore, the following recurrence condition holds

$$p^{(\ell)}_{\alpha\beta}(R) = \sum_{\gamma = A, B} \int_0^R dR' p^{(\ell - 1)}_{\alpha\gamma}(R') p^{(1)}_{\gamma\beta}(R - R'),$$

where $p^{(1)}_{\alpha\beta}(R)$ is the nearest-neighbor probability distribution function. On physical grounds, the ratio $p^{(1)}_{\alpha\alpha}(R)/p^{(1)}_{\alpha\beta}(R)$ must become the same for $\alpha = A$ as for $\alpha = B$ in the limit of large $R$, i.e.,

$$\lim_{R \to \infty} \frac{p^{(1)}_{\alpha\alpha}(R)}{p^{(1)}_{\alpha\beta}(R)} = \lim_{R \to \infty} \frac{p^{(1)}_{\beta\beta}(R)}{p^{(1)}_{\beta\alpha}(R)}.$$  \hspace{1cm} (2.2)

This relation will be used later on. The total probability density of finding a particle of species $\beta$, given that a
particle of species $\alpha$ is at the origin, is
\[
p_{\alpha\beta}(R) = \sum_{\ell=1}^{\infty} p_{\alpha\beta}^{(\ell)}(R).
\] (2.3)

The convolution structure of Eq. (2.1) suggests the introduction of the Laplace transforms
\[
\tilde{p}_{\alpha\beta}^{(\ell)}(s) = \int_{0}^{\infty} dR e^{-sR} p_{\alpha\beta}^{(\ell)}(R),
\]
\[
\tilde{p}_{\alpha\beta}(s) = \int_{0}^{\infty} dR e^{-sR} p_{\alpha\beta}(R),
\]
so that Eq. (2.1) becomes
\[
\tilde{p}_{\alpha\beta}(s) = \sum_{\gamma=A,B} \tilde{p}_{\alpha\gamma}^{(-1)}(s) \tilde{p}_{\gamma\beta}(s).
\] (2.5)

Equation (2.5) allows us to express $\tilde{p}_{\alpha\beta}(s)$ in terms of the nearest-neighbor distribution as
\[
\tilde{p}_{\alpha\beta}(s) = \left[\tilde{p}(1)(s)\right]^{-\ell},
\] (2.6)
where $\tilde{p}(s)$ is the $2 \times 2$ matrix of elements $\tilde{p}_{\alpha\beta}(s)$. From Eqs. (2.5) and (2.6) we get
\[
\tilde{p}(s) = \sum_{\ell=1}^{\infty} \left[\tilde{p}(1)(s)\right]^{\ell}
= \tilde{p}(1)(s) \cdot \left[1 - \tilde{p}(1)(s)\right]^{-1},
\] (2.7)
where $\tilde{p}(s)$ is the $2 \times 2$ matrix of elements $\tilde{p}_{\alpha\beta}(s)$ and $1$ is the $2 \times 2$ unity matrix.

Now, notice that the pair correlation function $g_{\alpha\beta}(R)$ and the probability density $p_{\alpha\beta}(R)$ are simply related by $p_{\alpha\beta}(R) = \rho_{\beta} g_{\alpha\beta}(R)$ or, equivalently in Laplace space,
\[
\tilde{p}_{\alpha\beta}(s) = \rho_{\beta} \tilde{g}_{\alpha\beta}(s),
\] (2.8)
where
\[
\tilde{g}_{\alpha\beta}(s) = \int_{0}^{\infty} dR e^{-sR} g_{\alpha\beta}(R)
\] (2.9)
is the Laplace transform of $g_{\alpha\beta}(R)$. Therefore, thanks to the one-dimensional nature of the model and the restriction to nearest-neighbor interactions, the knowledge of the nearest-neighbor distributions $p_{\alpha\beta}^{(1)}(R)$ suffices to obtain the pair correlation functions $g_{\alpha\beta}(R)$. More explicitly, from Eqs. (2.7) and (2.8) the Laplace transforms $\tilde{g}_{\alpha\beta}(s)$ are found to be
\[
\tilde{g}_{AA}(s) = \frac{1}{\rho_T} Q_{AA}(s) [1 - Q_{BB}(s)] + Q_{AB}^2(s),
\] (2.10)
\[
\tilde{g}_{BB}(s) = \frac{1}{\rho_T} Q_{BB}(s) [1 - Q_{AA}(s)] + Q_{AB}^2(s),
\] (2.11)
where $\rho_T = \rho_A + \rho_B$ is the total number density, $x_\alpha = \rho_\alpha / \rho_T$ is the mole fraction of species $\alpha$, and we have called
\[
Q_{\alpha\beta}(s) \equiv \sqrt{\frac{2\pi s R_{\alpha\beta}(s)}{x_\alpha x_\beta}},
\] (2.12)
\[
D(s) \equiv [1 - Q_{AA}(s)][1 - Q_{BB}(s)] - Q_{AB}^2(s).
\] (2.13)
The KBI in the one-dimensional case are defined by
\[
G_{\alpha\beta} = 2 \int_{0}^{\infty} dR [g_{\alpha\beta}(R) - 1].
\] (2.15)

In terms of the Laplace transform $\tilde{g}_{\alpha\beta}(s)$, Eq. (2.10) can be rewritten as
\[
G_{\alpha\beta} = 2 \lim_{s \to 0} \left[\tilde{g}_{\alpha\beta}(s) - \frac{1}{s}\right].
\] (2.16)

We see that only the nearest-neighbor distribution $p_{\alpha\beta}^{(1)}(R)$ is needed to close the problem. It can be proven that $p_{\alpha\beta}^{(1)}(R)$ is just proportional to the Boltzmann factor $e^{-U_{\alpha\beta}(R)/k_B T}$ times a decaying exponential $e^{-\xi R}$, where the damping coefficient is $\xi = P/k_B T$.

Therefore,
\[
p_{\alpha\beta}^{(1)}(R) = x_\beta K_{\alpha\beta} e^{-U_{\alpha\beta}(R)/k_B T} e^{-\xi R},
\] (2.17)
where the proportionality constants $K_{\alpha\beta} = K_{\beta\alpha}$ (which of course depend on the thermodynamic state of the mixture) will be determined below by applying physical consistency conditions. Taking Laplace transforms in Eq. (2.17) and inserting the result into Eq. (2.13) we get
\[
Q_{\alpha\beta}(s) = \sqrt{x_\alpha x_\beta K_{\alpha\beta} \Omega_{\alpha\beta}(s + \xi)},
\] (2.18)
where
\[
\Omega_{\alpha\beta}(s) = \int_{0}^{\infty} dR e^{-sR} e^{-U_{\alpha\beta}(R)/k_B T}
\] (2.19)
is the Laplace transform of $e^{-U_{\alpha\beta}(R)/k_B T}$.

To recapitulate, given the interaction potentials $U_{\alpha\beta}(R)$ and given a particular thermodynamic state ($P, T, x_A$), the three correlation functions are obtained (in Laplace space) from Eqs. (2.10), (2.12), supplemented by Eqs. (2.14), (2.15), and (2.16).

B. Equation of state

In order to close the exact solution, it only remains to determine the total density $\rho_T$ (equation of state) and the amplitudes $K_{\alpha\beta}$ as functions of $P, T$, and $x_A = 1 - x_B$. As said above, they can be easily obtained by applying
basic physical conditions. First, note that Eq. (2.22) establishes the following relationship

\[ K_{AB}^2 = K_{AA}K_{BB}. \]  

(2.20)

Next, the physical condition \( \lim_{R \to \infty} g_{\alpha \beta}(R) = 1 \) implies that \( \tilde{g}_{\alpha \beta}(s) \to 1/s \) for small \( s \). According to Eqs. (2.10)–(2.12), this is only possible if \( D(0) = 0 \), so that \( D(s) \to D'(s) \) for small \( s \), where \( D'(s) = dD(s)/ds \). Thus, one has

\[ [1 - Q_{AA}(0)][1 - Q_{BB}(0)] - Q_{AB}^2(0) = 0, \]  

(2.21)

\[ \rho_T = \frac{Q_{AB}(0)}{\sqrt{x_Ax_BD'(0)}}, \]  

(2.22)

\[ \rho_T = \frac{Q_{AA}(0)[1 - Q_{BB}(0)] + Q_{AB}^2(0)}{x_AD'(0)}, \]  

(2.23)

\[ \rho_T = \frac{Q_{BB}(0)[1 - Q_{AA}(0)] + Q_{AB}^2(0)}{x_BD'(0)}. \]  

(2.24)

Elimination of \( \rho_T \) between Eqs. (2.22)–(2.24) yields two coupled equations which, together with Eq. (2.21), gives

\[ K_{AA} = \frac{1 - x_BK_{AB}\Omega_{AB}(\xi)}{x_A\Omega_{AA}(\xi)}, \]  

(2.25)

\[ \rho_T(P, T, x_A) = -2x_{\alpha\beta}K_{AB}\Omega_{\alpha\beta}'(\xi) + 2x_Ax_BK_{AB}\Omega_{\alpha\beta}'(\xi), \]  

(2.30)

where \( \Omega_{\alpha\beta}'(s) \) is the first derivative of \( \Omega_{\alpha\beta}(s) \).

Equations (2.23)–(2.28) and (2.29) complete the full determination of \( \tilde{g}_{\alpha \beta}(s) \) and the equation of state for any choice of the nearest-neighbor interaction potentials \( U_{\alpha \beta}(x) \) and of the thermodynamic state \( (P, T, x_A) \).

C. Kirkwood–Buff integrals

The KBI \( G_{\alpha \beta} \) can be derived, according to Eq. (2.16), by expanding \( s\tilde{g}_{\alpha \beta}(s) \) in powers of \( s \) as \( s\tilde{g}_{\alpha \beta}(s) = 1 + \frac{1}{2}G_{\alpha \beta}s + \cdots \) and identifying the linear term. After some algebra one gets

\[ G_{AB} = \rho_T J + 2\frac{\Omega_{AB}'(\xi)}{\Omega_{AB}(\xi)} \]  

(2.31)

\[ G_{AA} = \rho_T J - 2x_BK_{BB}\Omega_{AB}'(\xi) + 2\frac{1}{\rho_TX_A}, \]  

(2.32)

\[ K_{BB} = \frac{1 - x_AK_{AB}\Omega_{AB}(\xi)}{x_B\Omega_{BB}(\xi)}. \]  

(2.26)

Insertion of Eqs. (2.20) and (2.21) into Eq. (2.20) allows one to obtain a quadratic equation for \( K_{AB} \) whose physical root is

\[ K_{AB} = \frac{1}{\Omega_{AB}(\xi)} \left[ 1 - \frac{\sqrt{1 - 4x_Ax_B(1 - R)}}{2x_Ax_B(1 - R)} \right], \]  

(2.27)

where we have called

\[ R \equiv \frac{\Omega_{AA}(\xi)\Omega_{BB}(\xi)}{\Omega_{AB}(\xi)}. \]  

(2.28)

It is interesting to note that, since \( K_{\alpha \beta} \) and \( \Omega_{\alpha \beta} \) are positive definite, Eq. (2.25) and (2.26) imply that \( x_AK_{AB}\Omega_{AB}(\xi) < 1 \) for \( \alpha = A, B \), i.e.,

\[ K_{AB}\Omega_{AB}(\xi) < \min \left( \frac{1}{x_A}, \frac{1}{x_B} \right) \leq 2. \]  

(2.29)

Finally, the density \( \rho_T \) is obtained from either of Eqs. (2.23)–(2.24). The result is

\[ G_{BB} = \rho_T J - 2x_AK_{AA}\Omega_{AA}'(\xi) + 2\frac{2}{\rho_TX_B}, \]  

(2.33)

where

\[ J = x_A^2K_{AA}\Omega_{AA}'(\xi) + x_B^2K_{BB}\Omega_{BB}'(\xi) + 2x_Ax_BK_{AB}\Omega_{AB}'(\xi) - 2x_Ax_BK_{AB}\Omega_{AA}'(\xi)\Omega_{BB}'(\xi) - [\Omega_{AB}'(\xi)]^2. \]  

(2.34)

The knowledge of the KBI allows us to obtain the (reduced) isothermal compressibility

\[ \chi = k_B T \left( \frac{\partial \rho_T}{\partial P} \right)_{T,x_A} \]  

(2.35)

by means of

\[ \chi = \frac{1}{1 + \rho_TX_Ax_B\Delta_{AB}} \left[ 1 + \rho_T (x_AG_{AA} + x_BG_{BB}) + \rho_T^2x_Ax_B (G_{AA}G_{BB} - G_{AB}^2) \right], \]  

(2.36)
\[ \Delta_{AB} \equiv G_{AA} + G_{BB} - 2G_{AB}. \] (2.37)

It can be checked that the resulting expression of \( \chi \) (which, due to its length, will be omitted here) coincides with the one obtained as \( \chi = \left( \partial \rho_T / \partial \xi \right)_{T,x_A} \) from Eq. (2.30). This confirms the exact character of the solution.

Making use of Eqs. (2.30)–(2.33), it is easy to prove that

\[ 1 + \rho_T x_A x_B \Delta_{AB} = 2 \frac{k_A \Omega_{AB}(\xi)}{K_{AB}(\xi)} - 1, \] (2.38)

which, according to Eq. (2.29), is a positive definite quantity. More explicitly, from Eq. (2.27) we have

\[ 1 + \rho_T x_A x_B \Delta_{AB} = \sqrt{1 - 4x_A x_B(1 - R)}. \] (2.39)

Therefore, the denominator in Eq. (2.36) never vanishes and the isothermal compressibility is well defined. This agrees with van Hove’s classical proof that no phase transition can exist in this class of nearest-neighbor one-dimensional models.

Let us now obtain the KBI in the infinite dilution limit \( x_A \to 0 \). In that limit, Eqs. (2.25)–(2.27) and (2.30) become

\[ K_{AA} = \frac{\Omega_{BB}(\xi)}{\Omega_{AB}(\xi)}, \quad K_{BB} = \frac{1}{\Omega_{BB}(\xi)}, \quad K_{AB} = \frac{1}{\Omega_{AB}(\xi)}, \]

\[ \rho_T = -\frac{\Omega_{BB}(\xi)}{\Omega_{AB}(\xi)}. \] (2.40)

Analogously, from Eqs. (2.31)–(2.34) one gets

\[ G_{AB} = -\frac{\Omega_{BB}(\xi)}{\Omega_{BB}(\xi)} + 2 \frac{\Omega_{AB}(\xi)}{\Omega_{BB}(\xi)}, \] (2.42)

\[ G_{AA} = -\frac{\Omega_{BB}(\xi)}{\Omega_{BB}(\xi)} + 2 \frac{\Omega_{AB}(\xi)}{\Omega_{BB}(\xi)} - 2 \frac{\Omega_{AA}(\xi)\Omega_{BB}(\xi)}{\Omega_{AB}(\xi)}, \] (2.43)

\[ G_{BB} = -\frac{\Omega_{BB}(\xi)}{\Omega_{BB}(\xi)} + 2 \frac{\Omega_{AB}(\xi)}{\Omega_{BB}(\xi)}, \] (2.44)

\[ \Delta_{AB} = 2\Omega_{BB}(\xi) \left[ \frac{1}{\Omega_{BB}(\xi)} - \frac{\Omega_{AA}(\xi)}{\Omega_{AB}(\xi)} \right]. \] (2.45)

Note that special care is needed to obtain \( K_{AA} \) and \( G_{AA} \).

### D. Chemical potentials and solvation Gibbs energies

Finally, let us get an explicit expression for the chemical potential. From the KB theory of solution we have

\[
\frac{1}{k_B T} \left( \frac{\partial \mu_A}{\partial x_A} \right)_{P,T} = \frac{1}{x_A} - \frac{\rho_T x_A \Delta_{AB}}{1 + \rho_T x_A x_B \Delta_{AB}}
\]

\[
= \frac{1}{x_A} - \frac{1}{x_B} \frac{\sqrt{1 - 4x_A x_B(1 - R)}}{\sqrt{1 - 4x_A x_B(1 - R)} - 1},
\] (2.46)

where in the last step we have made use of Eq. (2.38). Integration over \( x_A \) yields

\[
\frac{\mu_A}{k_B T} = \text{const} + \ln x_A + \ln \left[ 1 - 2x_B(1 - R) \right] + \frac{1}{2} \sqrt{1 - 4x_A x_B(1 - R)}. \] (2.47)

For pure A (\( x_B = 0 \)), we have

\[
\frac{\mu_A}{k_B T} = \text{const} + \ln 2. \] (2.48)

The solvation Gibbs energy of A in pure A may be obtained from (2.47) as

\[
\Delta \mu_A^* \equiv \mu_A - k_B T \ln(\rho_A \Lambda_A), \] (2.49)

where \( \Lambda_A = h/\sqrt{2\pi m_A k_B T} \) is the momentum partition function of A in one-dimensional systems. Similarly,

\[
\Delta \mu_A^{sp} \equiv \mu_A^* - k_B T \ln(\rho_A^* \Lambda_A), \] (2.50)

where \( \rho_A^* \) is the density of pure A at the same \( T \) and \( P \) as the mixture. Taking the limit \( x_B \to 0 \) in Eqs. (2.25) and (2.30) one has

\[
\frac{\rho_A^*}{\rho_A} = -\frac{\Omega_{AA}(\xi)}{\Omega_{AA}(\xi)}. \] (2.51)

The excess solvation Gibbs energy relative to the solvation Gibbs energy in pure A is defined as

\[
\Delta \Delta \mu_A^* = \Delta \mu_A^* - \Delta \mu_A^{sp}. \] (2.52)

This quantity may be calculated from (2.47)–(2.52) with the result

\[
\frac{\Delta \Delta \mu_A^*}{k_B T} = \ln \left[ \frac{1}{2} - x_B(1 - R) + \frac{1}{2} \sqrt{1 - 4x_A x_B(1 - R)} \right] + \ln \frac{\rho_A^*}{\rho_A}. \] (2.53)
III. A SAMPLE OF RESULTS

Let us start considering a binary system composed of (additive) hard rods of different diameters (lengths) $\sigma_{AA}$, $\sigma_{BB}$, and $\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2$. The Laplace function $\Omega_{\alpha\beta}(s)$ defined by Eq. (2.19) is

$$\Omega_{\alpha\beta}(s) = \frac{e^{-s\sigma_{\alpha\beta}}}{s}. \quad (3.1)$$

In this case the parameter defined in Eq. (2.28) is $R = 1$ and thus the limit $R \rightarrow 1$ must be taken in Eq. (2.27) with the result $K_{AB} = 1/\Omega_{AB}(\xi)$. The general scheme of section II can be used to obtain the KBI explicitly:

$$G_{AB} = -\frac{\sigma_{AA} + \sigma_{BB} + \xi\sigma_{AA}\sigma_{BB}}{1 + (x_A\sigma_{AA} + x_B\sigma_{BB})}, \quad (3.2)$$

$$G_{AA} = G_{AB} + \sigma_{BB} - \sigma_{AA}, \quad (3.3)$$

$$G_{BB} = G_{AB} + \sigma_{AA} - \sigma_{BB}, \quad (3.4)$$

so that $\Delta_{AB} = 0$. Figure 1 shows the values of $G_{\alpha\beta}$ for a diameter ratio $\sigma_{BB}/\sigma_{AA} = 2$ and a thermodynamic state $P\sigma_{AA}/k_B T = 1$. These results are in perfect agreement with those calculated in Part I.

Having established that the programs give the correct results for hard rods, we next present results for a mixture of particles’ interaction via SW potential of the form

$$U_{\alpha\beta}(R) = \begin{cases} \infty, & R < \sigma_{\alpha\beta}, \\ \epsilon_{\alpha\beta}, & \sigma_{\alpha\beta} < R < \sigma_{\alpha\beta} + \delta_{\alpha\beta}, \\ 0, & R \geq \sigma_{\alpha\beta} + \delta_{\alpha\beta}. \end{cases} \quad (3.5)$$

where $\epsilon_{\alpha\beta} < 0$. For this SW potential the Laplace func-
The KBI $G_{AA}$ for SW particles with parameters given in (3.7) and $k_B T / |\epsilon_{AA}| = 1$, $P \sigma / k_B T = 1$. The lines are obtained from the exact expressions presented in Sec. II C, while the circles are the data obtained in Ref. [1].

The thermodynamic variables are $T$, $P$, and $x_A$. In all the calculations we choose $k_B T / |\epsilon_{AA}| = 1$ and $P \sigma / k_B T = 1$ to compare the present results with those of Part I.

Figures 2–4 show the values of $G_{AA}$, $G_{BB}$, and $G_{AB}$ for these systems for various values of $\epsilon$ ranging from $\epsilon = -0.001$ to $\epsilon = -1$, and from $\epsilon = -1$ to $\epsilon = -11$. Figure 5 shows the values of $\Delta_{AB} = G_{AA} + G_{BB} - 2G_{AB}$ in the entire range of composition. In all the cases the agreement with the results of Part I is quantitative.

The KBI in the infinite dilution limit ($x_A \to 0$), as obtained from Eqs. (2.42)–(2.44), are plotted in Fig. 6 as functions of $-\epsilon$ for the same system as that of Figs. 2–5. We observe that both $G_{AB}$ and $G_{BB}$ are hardly sensitive to the value of $\epsilon$. In contrast, the solute-solute KBI, $G_{AA}$, is strongly influenced by the solvent-solvent potential depth, increasing both for small and for large values of $|\epsilon|$. A careful inspection of the explicit expressions (2.42)–(2.44) in the limit $|\epsilon| \to \infty$ shows that, while
FIG. 6: The KBI $G_{\alpha\beta}$ in the infinite dilution limit ($x_A \to 0$) for SW particles with parameters given in \ref{3.7} and $k_BT/|\epsilon_{AA}| = 1$, $P\sigma/k_BT = 1$. $G_{AB}$ and $G_{BB}$ tend to the same constant value, $G_{AA}$ diverges as $G_{AA} \sim \exp\left([|\epsilon_{BB}| - 2|\epsilon_{AB}|]/k_BT\right)$. This phenomenon might be relevant to the study of hydrophobic interactions, as discussed in Ref. 9.

**IV. DISCUSSION AND CONCLUSION**

In Part I we calculated all the KBI in an indirect way.\footnote{A. Ben-Naim, J. Chem. Phys. 128, 084510 (2008); Erratum: A. Ben-Naim, J. Chem. Phys. 130, 159901 (2009).} We first calculated the excess functions from the partition function of the system, then we used the inversion of the KB theory\footnote{A. Ben-Naim, *Molecular Theory of Solutions* (Oxford University Press, Oxford, 2006).} to calculate the KBI. This lengthy procedure might have introduced accumulated errors. Some readers of Part I have expressed doubts regarding the reliability of the results calculated along this procedure. In fact some have also claimed that there might be a miscibility gap which we might have missed by this indirect and lengthy calculations.

In this paper we have repeated the calculations of the KBI directly, from the same program that was designed to calculate the pair correlation functions in mixtures of two components in 1D system.

The agreement between the two methods was satisfying, it also lent credibility to the inversion procedure and encouraged us to extend the calculations of the KBI for aqueous like mixtures.\footnote{J. G. Kirkwood and F. P. Buff, J. Chem. Phys. 19, 774 (1951).} We hope to report on that in the near future.

Regarding the question of miscibility gap we have shown that the inequality

$$1 + \rho_T x_A x_B \Delta_{AB} > 0$$

always holds in these mixtures, as shown by Eq. \ref{2.39}.

From the KB theory\footnote{Z. W. Salsburg, R. W. Zwanzig, and J. G. Kirkwood, J. Chem. Phys. 21, 1098 (1953).} of solution we have the equation

$$\left(\frac{\partial^2 g}{\partial x_A^2}\right)_{P,T} = \frac{1}{x_B} \left(\frac{\partial \mu_A}{\partial x_A}\right)_{P,T} = \frac{k_BT}{x_A x_B (1 + \rho_T x_A x_B \Delta_{AB})},$$

where $g = G/(N_A + N_B)$ is the Gibbs energy of the system per mole of mixture. It follows from \ref{4.1} and \ref{4.2} that $g$ is everywhere a concave (downward) function of $x_A$. Therefore, there exists no region of compositions where the system is not stable, hence no phase transition in such a system.

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