# The Kirkwood–Buff integrals for one-component liquids

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The Kirkwood–Buff integrals (KBIs) for one-component systems are calculated from either the pair correlation functions or from experimental macroscopic quantities. As in the case of mixtures, the KBIs provide important information on the local densities around a molecule. In the low density limit ( $\rho \rightarrow 0$ ) one can extract from the KBI some information on the strength of the intermolecular forces. No such information may be extracted from the KBIs at higher densities. We used experimental data on densities and isothermal compressibilities to calculate the KBIs for various liquids ranging from inert molecules, to hydrocarbons, alcohols, and liquid water. © 2008 American Institute of Physics. [DOI: 10.1063/1.2938859]

# I. INTRODUCTION

Recently, I have advocated in favor of a new way of studying, analyzing, and interpreting liquid mixtures.<sup>1–3</sup> The traditional approach is based on the study of the excess thermodynamic quantities such as excess free energy, excess entropy, enthalpy, volume, etc.<sup>4–6</sup> These quantities convey macroscopic information, and therefore were referred to as *global* properties of the mixtures.

The new approach is based on the so-called Kirkwood– Buff integrals (KBIs). These quantities probe into the immediate surroundings of the molecules, and therefore are referred to as the *local* properties of the mixtures. For mixtures, the KBIs provide a rich and interesting information on the local densities, local composition, and preferential solvation around a single molecule in the mixtures. In addition, the solvation thermodynamic quantities provide information on the strength of the interaction of a molecule with its environment, the effect of a molecule on the "structure" of the solvent,<sup>1,7</sup> etc. In one-component systems, the repertoire of information that is conveyed by the KBI is much more restricted. Nevertheless, it is of interest to have the values of the KBIs for pure liquids as references to the corresponding values in mixtures.

Nowadays, it is common to refer to the quantities

$$G_{\alpha\beta} = \int_{V} [g_{\alpha\beta}(R) - 1] d\overline{R}$$
(1.1)

as the Kirkwood–Buff integrals. They were used in the original "Kirkwood–Buff theory of solution" published in 1951.<sup>8</sup> However, the same integrals were introduced much earlier by Ornstein and Zernike<sup>9</sup> in connection with the fluctuations in the number of particles in an open system of *one*-component. In this article, we study these integrals for one-component systems, we shall use the term KBI, although a more appropriate term, for a one-component system, might be the Ornstein-Zernike integrals.

The KBI for either a one-component or for mixtures may be interpreted (and misinterpreted) in several ways. We shall discuss this in the next section. In Sec. III, we shall examine the KBI for a variety of systems, ranging from hard spheres and Lennard–Jones particles, to hydrocarbons, alcohols, and water. Some concluding remarks are presented in Sec. IV.

# II. DEFINITION AND INTERPRETATION OF THE KB INTEGRALS

The KBI for a one-component system is defined by

$$G_O = \int_V [g_O(R) - 1] d\overline{R}, \qquad (2.1)$$

where  $g_O(R)$  is the pair correlation function or the radial distribution function defined in an open system (or in the grand canonical ensemble), and the integration is extended over the entire macroscopic volume of the system V. Note that R in g(R) is the intermolecular distance, whereas  $d\overline{R}$  is an element of volume dxdydz.

The KBI is related to two macroscopic quantities by the following equations:

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} - 1 = \rho G_O = k_B T \rho \kappa_T - 1, \qquad (2.2)$$

where  $k_B$  is the Boltzmann constant, T is the absolute temperature,  $\rho$  is the average number density N/V in the system, and  $\kappa_T$  is the isothermal compressibility of the system.

On the left hand side of Eq. (2.2), we have the fluctuations in the number of particles in the open system. On the right hand side (rhs) we have a connection with macroscopic measurable quantities. This side of the equation is known as the compressibility equation.<sup>10-12</sup>

It should be emphasized that Eq. (2.2) is valid only when  $G_O$  is defined as in Eq. (2.1) in an *open* system (hence the subscript O). Failing to recognize this fact has been a notorious pitfall. To see this we first write the KBI, defined in the

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same way as in Eq. (2.1), but in a *closed* system (hence the subscript C).

$$G_C = \int_V [g_C(R) - 1] d\overline{R}.$$
 (2.3)

The two quantities  $G_O$  and  $G_C$  looks deceivingly similar (and identical if we remove the subscripts C and O) but, in fact, they are quite different. The difference between the two can be demonstrated even for ideal gas (see Appendix A). For any liquid, and at any density, the closure condition, i.e., the fixed number of particles in the system, imposes the normalization condition on  $G_C$ ,<sup>1,10,11</sup>

$$G_C = \int_V [g_C(R) - 1] d\bar{R} = -1/\rho.$$
(2.4)

Clearly, this condition arises from the fact that the total number of particles N in the system is *conserved*, i.e.,

$$N = \rho \int_{V} d\overline{R} = \rho \int_{V} g_{C}(R) d\overline{R} + 1.$$
(2.5)

On the rhs of Eq. (2.5) the counting of the total number of particles is done in two steps: First, count the number of particles around a selected particle, then add the selected particle to get N. As was pointed out by Munster,<sup>11</sup> if one uses the same notation for  $g_C(R)$  and  $g_O(R)$ , and substitute the integral in Eq. (2.4) into the compressibility equation [Eq. (2.2)], one gets the *absurd* result  $\kappa_T=0$ . Clearly, this result can be avoided by using different notations for the pair correlation functions in the closed and open systems.

Obviously, the conservation argument for  $g_C(R)$  in Eq. (2.4) does not apply for  $g_O(R)$ . The microscopic, or the local reason, for the difference in the two integrals can be seen from the following considerations.

We know from both experimental data on the pair correlation functions and from theoretical calculation that the pair correlation function is significantly larger than unity only in a small region of distances. In other words, there exists a correlation length  $R_{corr}$  such that for  $R \ge R_{corr} g(R)$  is practically unity. This fact allows us to deduce *local* information from  $G_O$  (but not from  $G_C$ ). To see this, it is convenient to rewrite the KBI as

$$\int_{V} [g(R) - 1] d\overline{R} = \int_{V_{\text{corr}}} + \int_{V - V_{\text{corr}}}, \qquad (2.6)$$

where  $V_{\text{corr}} = 4 \pi R_{\text{corr}}^3 / 3$  is the correlation volume which is essentially a *microscopic* volume, and  $V - V_{\text{corr}}$  is the *macroscopic* volume V of the system minus  $V_{\text{corr}}$ . It is well known that the pair correlation function in the region  $V - V_{\text{corr}}$  is different in the open and the close systems.<sup>1,10,11</sup> This is shown schematically in Fig. 1.

$$g_O(R \ge R_{\rm corr}) \cong 1, \tag{2.7}$$





FIG. 1. The effect of placing a particle (dark disk) at the center of the correlation sphere (shaded disk) in (a) closed and (b) open systems.

$$g_C(R \ge R_{\text{corr}}) \cong 1 - \frac{k_B T \rho \kappa_T}{N}.$$
 (2.8)

From Eqs. (2.7) and (2.8) it follows that the second integral on the rhs of Eq. (2.6) can be neglected in  $G_O$ , but not in  $G_C$ , hence we have

$$G_{O} = \int_{V} [g_{O}(R) - 1] d\bar{R} = \int_{0}^{\infty} [g_{O}(R) - 1] 4\pi R^{2} dR$$
$$\approx \int_{0}^{R_{\text{corr}}} [g_{O}(R) - 1] 4\pi R^{2} dR, \qquad (2.9)$$

$$G_{C} = \int_{0}^{R_{\text{corr}}} [g_{C}(R) - 1] 4 \pi R^{2} dR - \frac{k_{B} T \rho \kappa_{T}}{\rho'}, \qquad (2.10)$$

where  $\rho = N/V$  and  $\rho' = N/(V - V_{corr})$ . Thus, because of Eq. (2.9),  $G_O$  itself provides local information around a molecule. Furthermore, since in the correlation region  $(R \leq R_{corr})$  the values of  $g_C(R)$  and  $g_O(R)$  are nearly the same, the same local information is also contained in the integral on the rhs of Eq. (2.10). However, in this case this integral is not equal to  $G_c$ . Therefore, we cannot identify the local information conveyed by  $G_O$  with  $G_C$ . Another way of viewing the different behavior of the open and closed systems is shown schematically in Fig. 1. In a closed system with *fixed* density  $\rho = N/V$ , placing one particle at the center of a sphere of radius  $R_{\rm corr}$  will change the density in the region  $R_{corr} \leq R \leq R_M$ , where  $R_M$  is the radius of the macroscopic system, from  $\rho = N/V$  to  $\rho^* = \rho(1 - k_B T \rho \kappa_T/N)$ . This is a result of the conservation of the total number of particles. The same process in an open system does not cause any change in the density  $\rho$ .

Thus, in the open system one can replace the integral over the entire region V by an integral over the correlation region. This makes the KBI  $G_O$  useful in studying local quantities, such as local density, local composition, and local preferential solvation. The same is not true for  $G_C$ , for which the second integral on the rhs of Eq. (2.6) is finite. Therefore, one cannot replace  $G_C$  by the local integral over the correlation sphere. One can obtain the KBI from integration over  $g_C(R)$ , provided one *first* takes the thermodynamic limit  $N \rightarrow \infty V \rightarrow \infty$ , but N/V constant. In which case  $g_C(R)$  becomes equal to  $g_O(R)$ . We shall comment further on the evaluation of the KBI from experimental data in Sec. IV.



FIG. 2. The integrand  $\{\exp[-\beta U(R)]-1\}4\pi R^2$  as a function of R for LJ particles with parameters  $\sigma=2.78$  Å  $\varepsilon/k_B=34.9$  K and at T=273 K. The negative and the positive regions contribute negative and positive values to the integral G in Eq. (3.3).

The local meaning of the KBI  $(G_O, \text{ but not } G_C)$  is the following:  $\rho 4\pi R^2 dR$  is the average number of particles in a spherical shell of radius R and width dR.  $\rho g_O(R) 4\pi R^2 dR$  is the average number of particles in the same spherical shell, but in the center of which a particle is placed. Therefore,  $\int_0^{R_{\text{corr}}} \rho [g_O(R) - 1] 4\pi R^2 dR$  is the *change* in the average number of particles in the sphere of radius  $R_{\text{corr}}$ , caused by placing a particle at the center of the sphere. Because of the property Eq. (2.7) or (2.9) in the open system, one can replace the upper limit  $R_{\text{corr}}$ , by infinity to obtain the same interpretation for the KBI  $(G_O, \text{ but not } G_C)$ .

Another useful relation between the KBI and the partial molar volume at a *fixed position* is

$$G_0 = -V^*$$
. (2.11)

Note that the *molar* volume  $V_M$  is the change in the volume of the system caused by adding one mole (or one molecule depending on the context of using this term) of particles to the system at constant T and P. The quantity  $V^*$  is the change in the volume of the system caused by placing a particle at a fixed position in the system, keeping T and P constant. The relation between the two volumes is (per particle)<sup>1</sup>

$$V_M = V^* + k_B T \kappa_T. \tag{2.12}$$

From Eq. (2.11) it follows that

$$\rho G_O = \Delta N(R_{\rm corr}) = -\rho V^*. \tag{2.13}$$

Thus, the change in the average number of particles in the correlation volume  $\Delta N(R_{\rm corr})$  caused by placing a particle at the center of the correlation volume is equal to minus the average number of particles occupying the volume  $V^*$  in the liquid having the density  $\rho$ .

Note that  $\rho V^*$  is different from the average number of particles occupying the correlation volume. The relation between the two quantities follows from Eq. (2.9) and (2.13),

$$\rho V_{\rm corr} - \rho V^* = \rho \int_0^{R_{\rm corr}} g_O(R) 4 \pi R^2 dR.$$
 (2.14)

It is sometimes convenient to reinterpret the KBI as follows (we drop the subscript O in the rest of this paper since we shall always refer to  $G_O$ , and not to  $G_C$ ),

$$G = \int_{V} [g(R) - 1] d\bar{R} = \int_{V^{e_{X}}} + \int_{V - V^{e_{X}}}$$
(2.15)

$$= -V^{\text{ex}} + \int_{V-V^{\text{ex}}} [g(R) - 1] d\overline{R} = -V^{\text{ex}} + L, \qquad (2.16)$$

where  $V^{\text{ex}}$  is the excluded volume. This is defined as the region around the center of the particle for which  $g(R) \cong 0$ , hence the integration over this region produce the negative quantity  $-V^{\text{ex}}$ . For spherical particles with hard-core diameter  $\sigma$  this volume is simply

$$V^{\rm ex} = \frac{4\pi\sigma^3}{3}.$$
 (2.17)

Thus, in general G has two contributions: One,  $-V^{ex}$ , which is always negative, and L which may be either positive or negative depending on the strength of the correlation function in the region  $V_{corr} - V^{ex}$ . It is tempting to interpret the two parts of G in Eq. (2.16) as arising from the repulsive and attractive parts of the potential function, respectively. This is true only in very special cases of ideal gases (see Sec. III A), but it is not true, in general. While  $-V^{ex}$  results only from the repulsive parts of the pair potential, the remaining part L is a result of both the repulsive and the attractive parts of the pair potential. We shall see in the next section that for hard spheres (HSs) particles both parts of the KBI are negative, and obviously both results from the repulsive part of the pair potential. For real molecules at liquid densities, there is no way of extracting information on the attractive part of the pair potential from the KBI.

#### III. EXAMPLES

In this section, we present values of the KBI as defined in Eq. (2.1), but we shall omit the subscript O. We shall start with ideal gases, then simple Lennard-Jones particles, then water and some other liquids.

#### A. Ideal gas

Ideal gas (i.g.) behavior can be realized by either systems of hypothetical, *strictly noninteracting* particles or by real particles but at the limit of low densities  $\rho \rightarrow 0$ . Both of these give the same equation of state,

$$P = \rho k_B T. \tag{3.1}$$

However, the two systems produce different KBIs. For the hypothetical ideal gas, all intermolecular interactions are by definition zero, hence, the pair correlation function is unity, and therefore



FIG. 3. g(R) and  $G(R_M)$  for hard spheres at low densities ( $\rho=0.1$ ) [Eq. (3.8)].

Note that this equality is not true for the KBI defined in a

closed system (see Appendix A).

#### B. Real gases at low densities

For the *real* ideal gas, i.e., system of interacting particles but at  $\rho \rightarrow 0$ , we have the limiting value of the KBI,

$$G(\text{real i.g.}) = \lim_{\rho \to 0} G = \int_{V} \{ \exp[-\beta U(R)] - 1 \} d\bar{R}.$$
 (3.3)

This limit follows from the well known expression for the pair correlation function at  $\rho \rightarrow 0$ , namely,<sup>10–12</sup>

$$\lim_{\rho \to 0} g(R) = \exp[-\beta U(R)], \qquad (3.4)$$

where U(R) is the pair potential.

The simplest interacting particles are HSs for which

$$U_{\rm HS}(R) = \begin{cases} \infty & \text{for } R \le \sigma \\ 0 & \text{for } R > \sigma. \end{cases}$$
(3.5)

Hence

$$G(\text{hard spheres, } \rho \to 0) = -\frac{4\pi\sigma^3}{3}.$$
 (3.6)

This is simply the excluded volume for the hard sphere particles.

For any other real gas at very low density, we can write

$$G(\text{real i.g.}) = \frac{-4\pi\sigma^3}{3} + \int_{V-V^{\text{ex}}} \{\exp[-\beta U(R) - 1]\} dR,$$
(3.7)

$$g(R) = \begin{cases} 0 & \text{for } R < \sigma \\ 1 + \rho \frac{4\pi\sigma^3}{3} \left[ 1 - \frac{3}{4} \frac{R}{\sigma} + \frac{1}{16} \left( \frac{R}{\sigma} \right)^3 \right] & \text{for } \sigma \le R \le 2\sigma \\ 1 & \text{for } R > 2\sigma. \end{cases}$$

where  $\sigma$  is the *effective* hard-core diameter. For Lennard-Jones (LJ) particles, the effective hard core diameter is usually chosen as the parameter  $\sigma$  in the Lennard-Jones potential. For the purpose of interpreting the two terms in Eq. (3.7), we ignore the difference between  $\sigma$  [the value of R at which U(R)=0], and the location of the minimum in the LJ potential [this minimum is at  $\sigma \sqrt[6]{2}$ , when  $\sigma$  is chosen as the LJ parameter (see Sec. III D). For such a system, G consists of two terms: One negative due to the excluded volume and one positive due to the positive correlation [i.e.,  $g(R) \ge 1$  in the region  $R \ge \sigma$ . The two corresponding regions of the integrand in Eq. (3.3) are shown in Fig. 2. Here we have a clear-cut separation between the positive and negative contributions to G. It should be noted that only in this case one can claim that the second term on the rhs of Eq. (3.7) is due to the attractive part of the potential function (i.e., the region  $R > \sigma$  where  $\sigma$  is chosen as the location of the minimum in the potential).

For any other density, the sign of the second contribution to the KBI, whether positive or negative, is a result of both the attractive as well as the repulsive part of the pair potential.

## C. Hard spheres at finite densities

Hard spheres are defined by their pair potential [Eq. (3.5)].

As we have seen in the previous subsection, in the limit of  $\rho \rightarrow 0$ , the only contribution to G comes from the hardcore repulsion. As we increase the density we find correlation at distances  $R > \sigma$ . This correlation will affect the value of G.

As we have seen in the limit of  $\rho \rightarrow 0$ , the value of G is simply  $-4\pi\sigma^3/3$ . We also know the first order correction to the pair correlation function, which is<sup>1,10</sup>

(3.8)



FIG. 4. The density dependence of G for hard spheres [Eq. (3.9)].

Figure 3 shows g(R) and  $G(R_M)$  for this case (the illustration is for  $\rho=0.1$  particles per  $\sigma^3$ , where  $\sigma$  is chosen as the unit of length).

For higher densities, there are several approximation for the pair correlation function, hence for  $G(R_M)$ . For instance, from the exact solution of the Percus–Yevick (PY) equation for hard spheres we have the following expression:<sup>12</sup>

$$1 + \rho G = k_B T \rho \kappa_T = \frac{(1 - \eta)^4}{(1 + 2\eta)^2},$$
(3.9)

where  $\eta = \pi \sigma^3/6$ 

From Eq. (3.9) we can obtain G as a function of  $\rho$  for hard spheres. This is shown in Fig. 4.

At any density the split of G into two parts as in Eq. (3.7) applies. The first term on the rhs of Eq. (3.7) is due to the repulsive part of the potential. So does the second term. It is sometimes said that the second term arises from the "interaction" between the particles. This is true if by "interaction" one includes both the repulsive and the attractive parts. This example shows how one cannot learn much on the molecular interactions by studying the KBIs.

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#### D. Lennard–Jones particles

LJ particles are defined through the pair potential,

$$U_{\rm LJ}(R) = 4\varepsilon \left[ \left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6 \right]. \tag{3.10}$$

Figure 5 shows the pair correlation function g(R) and the integral

$$G(R_M) = \int_0^{R_M} [g(R) - 1] 4 \pi R^2 dR, \qquad (3.11)$$

for a system of LJ particles with parameters

$$\sigma = 1, \quad \epsilon/k_B T = 0.5, 0.6, 0.7.$$
 (3.12)

In all the calculations in this section, the parameter  $\sigma$  was chosen as the unit of length, and we vary the energy parameter  $\varepsilon/k_BT$ . The results shown in Fig. 5 were computed for the limit of  $\rho \rightarrow 0$ , using the limiting form of the pair correlation function,

$$g(R) = \exp[-\beta U_{\rm LI}(R)].$$
 (3.13)

Note that all the  $G(R_M)$  curves start at zero, then decrease to a minimum at about  $R_M \approx 1$ . Beyond  $R_M \approx 1$ ,  $G(R_M)$  starts to increase and eventually levels off. Note that the limiting value of  $G(R_M)$  is reached for  $R_M$  of the order of the range of the pair potential. The limiting value of  $G(R_M)$  at  $R_M \rightarrow \infty$ , which is the KBI, is positive, and is larger the larger the energy parameter  $\varepsilon/k_BT$ . Again, we emphasize that only in this case there is a clear cut separation between the positive and the negative contributions to G (neglecting the small region  $\sigma \leq R \leq \sigma \sqrt{2}$  for which the potential is repulsive).

We next turn to higher densities for which the limiting form of g(R) in Eq. (3.13) does not apply. In all the following demonstrations in this section, we use the numerical solution of the Percus-Yevick integral equation.

The PY equation for pure spherical molecules has the following form:  $^{1,13-16}$ 



FIG. 5. g(R) and  $G(R_M)$  for Lennard– Jones particles with parameters in Eq. (3.12) in the limit of low density  $\rho \rightarrow 0$ .

$$y(\bar{R}_{1},\bar{R}_{2}) = 1 + \rho \int_{V} y(\bar{R}_{1},\bar{R}_{3}) f(\bar{R}_{1},\bar{R}_{3})$$

$$\times [y(\bar{R}_{2},\bar{R}_{3})f(\bar{R}_{2},\bar{R}_{3}) + y(\bar{R}_{2},\bar{R}_{3}) - 1]d\bar{R}_{3},$$
(3.14)

where f is the Mayer function defined as

$$f(R) = \exp[-\beta U(R)] - 1, \qquad (3.15)$$

and y(R) is defined as

$$y(R) = g(R)\exp[\beta U(R)]. \tag{3.16}$$

Another simpler and useful form of this equation is obtained by transforming to bipolar coordinates,

$$u = |\overline{R}_1 - \overline{R}_3|, \quad v = |\overline{R}_2 - \overline{R}_3|, \quad R = |\overline{R}_1 - \overline{R}_2|.$$
 (3.17)

The element of volume is expressed as

$$d\bar{R}_3 = 2\pi u\nu du d\nu/R, \qquad (3.18)$$

and Eq. (3.14) is transformed into

$$y(R) = 1 + 2\pi\rho R^{-1} \int_{0}^{\infty} y(u)f(u)udu \int_{|R-u|}^{R+u} [y(\nu)f(\nu) + y(\nu) - 1]\nu d\nu.$$
(3.19)

For the numerical solution, it is convenient to transform the PY equation by defining the following function:

$$z(R) = y(R)R. \tag{3.20}$$

Hence, we get an integral equation for z(R), which reads

$$z(R) = R + 2\pi\rho \int_{0}^{\infty} z(u)f(u)du$$
  
 
$$\times \int_{|R-u|}^{R+u} [z(\nu)f(\nu) + z(\nu) - \nu]d\nu.$$
(3.21)

The numerical solution starts by choosing the following initial input function:

 $z(R) = R, \tag{3.22}$ 

and proceeds to solve the integral equation [Eq. (3.21)] by iteration. (For more details on the PY equation and its numerical solutions, see Ref. 1).

Figure 6 shows the functions g(R) and  $G(R_M)$  for the LJ parameters  $\sigma=1$  and  $\varepsilon/k_BT=0.7$ , but at three different densities. At very low densities  $\rho=0.01$ , the curve in Fig. 6(a) is similar to the one shown in Fig. 5. The G values are negative for  $R_M \leq \sigma$ , but increase to positive values that depend on the energy parameter  $\varepsilon/k_BT$ . As the density increases new maxima and minima appear in the pair correlation function as well as in the function  $G(R_M)$ . Figure 6(b) shows the curves g(R) and  $G(R_M)$  for an intermediate density  $\rho=0.4$ , and Fig. 6(c) for a high density  $\rho=0.4$  and negative at  $\rho=0.8$ . Again, we can conclude that nothing can be learned on the strength of the interactions from the values of G.

Figure 7(a) shows the function  $G(R_M)$  for fixed molecular parameters  $\sigma=1$  and  $\varepsilon/k_BT=0.5$ , but at varying densities.



FIG. 6. g(R) and  $G(R_M)$  for Lennard-Jones particles at three densities.

As can be seen, the limiting values of  $G(R_M)$  at  $R_M \rightarrow \infty$  initially decrease as we increase the density, but at higher densities it reaches a value nearly equal to -1.

On the other hand, Fig. 7(b) shows the same plots for the molecular parameters  $\sigma=1$  and  $\varepsilon/k_BT=0.7$ . Here in contrast to the case of Fig. 7(a), the limiting value of  $G(R_M)$  initially increases with the increase in the density, then decrease to negative value and reaches a value, again of about G=-1, at higher densities.

Clearly, the increase or decrease of G as a function of  $\rho$  cannot be attributed to the changes in the strength of the molecular interaction.

A similar conclusion may be drawn by comparing the two sets of results in Figs. 7(a) and 7(b) at each density. For instance, at  $\rho$ =0.1, we see that G is positive and increases



FIG. 7. Dependence of  $G(R_M)$  on the density for (a)  $\sigma=1$  and  $\varepsilon/k_BT=0.5$  and (b)  $\sigma=1$  and  $\varepsilon/k_BT=0.7$ .

with  $\varepsilon/k_BT$ . The same is true for  $\rho=0.2$  and  $\rho=0.4$ , however, for  $\rho=0.7$  and  $\rho=0.8$ . The values of the KBI almost do not change.

Again we conclude that there exists no simple relationship between the strength of the molecular interactions and the values of the KBIs. This is true even if we deduct from Gthat part of the integral between zero and  $\sigma$ , as in Eq. (2.16).

Figure 8 summarizes the density dependence of G, for three values of  $\varepsilon/k_BT$ . It is clearly seen that at low densities, G is positive and increases with  $\varepsilon/k_BT$ , while at higher densities all the values of G converge to about -1, and they are almost insensitive to the changes in the energy parameter.



FIG. 8. The density dependence of G for Lennard–Jones particles, with different energy parameters.

Figure 9 shows the "two components" of the KBI. In (a), the two components are obtained from the compressibility equation, written in the form

$$G = k_B T \kappa_T - 1/\rho. \tag{3.23}$$

As expected, at very low density ( $\rho \le 0.3$ ) both of the terms on the rhs of Eq. (3.23) are large, but of opposite signs. The difference between  $k_B T \kappa_T$  and  $1/\rho$  is, however, finite. At higher densities the term  $k_B T \kappa_T$  is usually very small and G is determined by the value of  $-1/\rho = -V_M$ . This is true for most of the real liquids discussed in the following sections.

Figure 9(b) shows the split of G into two regions of the interaction as in Eq. (2.16). It is clear that by adding  $V^{\text{ex}}$  to G one merely shifts the curve of G, but one cannot gain any new information from L which is not contained in G.

# E. Inert gases

The calculated results of this and the following sections were based on data from Hirschfelder *et al.*<sup>17</sup> and Lemmon *et al.*<sup>18</sup>

Figure 10 shows the functions g(R) and  $G(R_M)$  for the Lennard–Jones parameters corresponding to neon, argon, krypton, and xenon, where all plots are based on Eqs. (3.10), (3.11), and (3.13) with parameters given in Table I and T = 273 K. In contrast to Fig. 5 where the diameter is held constant, here, both the diameter and the energy parameters change. As can be seen from the Fig. 10, for neon at very low densities, the excluded volume term  $V^{\text{ex}}$  in Eq. (2.16) is the dominant contribution to G, making the value of G negative. In all other cases, the values of G are positive indicating that the attractive part of the potential dominates Eq. (2.16) and the resulting values of G are all positive.

Figure 11(a) shows the values of G calculated from data on the densities and the compressibilities of the gases at



FIG. 9. Two different splits of G into two terms: (a) Eq. (3.22) and (b) Eq. (2.16).

1 atm. As can be seen in this case, all the values of G, including those of neon, are positive. The temperature dependence of G for neon is different from all the other gases.

Figure 11(b) shows the values of G at pressures and temperatures corresponding to the liquid state and only three points are shown for each gas. Here, the order of the Gvalues is reversed. First, note that all the G values are negative, and that the larger the molecules, the larger the negative value of G. Clearly, these results are consistent with the well known fact that in the liquid state the KBIs are dominated by the excluded volume which is proportional to the size of the atoms.

#### F. Hydrocarbons

We next move on to linear hydrocarbons. Figures 12(a) and 12(b) show the values of G for propane and butane as a function of temperature for two pressures. At 1 atm, we see

that the butane curve is above propane's curve, and all values are positive. Clearly, in this case the molecules are in the gaseous phase and the attractive part of the interaction dominates the value of G. This explains both the positive values of G and the relative magnitude of G. On the other hand, at high pressure, the role of the two contributions to G is reversed; here we observe *negative* values of G for the two gases and the reversal of the relative order of magnitude, i.e., the larger the molecule, the larger the excluded volume, and hence from Eq. (2.16) it also follows that the larger the negative values of G.

A similar trend is observed for the higher hydrocarbons at 1 atm. Figure 13(a) shows that the values of G (at 1 atm) are negative and decrease with the increase of temperature. The larger the size of the molecule, the larger the size of the negative G values. These results are consistent with the dominating contribution of  $V^{\text{ex}}$  in Eq. (2.16).



FIG. 10. Values of g(R) and  $G(R_M)$  for inert gases at low densities  $(\rho \to 0)$  with parameters given in Table I and T=273 K (R in Å).

TABLE I. Values of  $\sigma$  and of  $\varepsilon/k_B$  for the Lennard–Jones function fitted to obtain the second virial coefficient of some simple gases [from Hirschfelder *et al.* (1954) (Ref. 17)].

Gas	$\sigma$ (Å)	$\varepsilon/k_B$ (K)
Ne	2.78	34.9
Ar	3.40	119.8
Kr	3.60	171.0
Xe	4.10	221.0

In Fig. 13(b), we show the effect of increasing the pressure on the G values of hexane. Here, the increase in pressure causes a decrease of the negative values of G.

Finally, in Fig. 13(c), the values of the KBI for hexane and cyclohexane are compared. It is worthwhile noting that the values of the KBI for cyclohexane are much smaller (in absolute magnitude compared with hexane) and are even smaller than the values of G for pentane. The interpretation of this finding is that cycling of the hydrocarbon considerably reduces the effective excluded volume of the molecule, hence reducing the values of G. Note that reducing the chain length by one carbon atom reduces |G| by about  $15-17 \text{ cm}^3 \text{ mol}^{-1}$  [Fig. 13(a)]. The effect of cycling the hexane on G (basically on  $V^{\text{ex}}$ ) is more than reducing the length of the hydrocarbon by one carbon atom.

## G. Methanol and ethanol

Figure 14 shows the KBI for methanol and ethanol as a function of temperature at 1 atm. Since the overall attractive part of the intermolecular interactions is the same, the relative difference in the KBI is expected to depend on the size of the molecules.

The KBI for both molecules are negative and the temperature dependence is negative too. The general trends are similar to the hydrocarbons except for the relatively higher values of G for the alcohols compared with the expected values of the hydrocarbons of the same size, in the liquid state (note that hydrocarbon molecules of the "same-size" would not be in the liquid state at this range of temperatures and pressures). This is probably due to the stronger attractive interactions between the alcohol molecules compared with the corresponding hydrocarbon molecules of similar sizes.

# H. Liquid water

Liquid water is an outstanding liquid.<sup>19–23</sup> It is both an interesting and an important substance; interesting because of its unusual properties, and important because of its being an indispensable medium for sustaining life.

The outstanding properties of water can be roughly divided into two groups: One that includes properties that are unique or almost unique (e.g., the negative temperature dependence of the volume, the large entropy of solvation of inert gases in it, etc.) and some that are not unique but have outstanding values (e.g., the high value of the heat capacity).

One practical criterion that can be used to make a decision as to which group a given property belongs is to draw the values of the property for a series of linear alcohols having the formula  $CH_3(CH_2)_{n-1}OH$  and extrapolate the value of that property for the case n=0.

Figure 15 shows the KBI for a series of linear alcohols as a function of the number of carbon atoms. It is seen that the values are all negative and decreases with n. Clearly, the larger the chain, the larger the contribution from the hardcore repulsion, hence the more negative the value of the KBI. If we extrapolate from these values to n=0, we get the value of G for the hypothetical alcohol with no carbon atoms. Interestingly, the value of the KBI for water almost coincides with the extrapolated value from the series of alcohols. This finding is quite puzzling for the following reasons. As can be seen from Eq. (3.22), the KBI is determined by both the molar volume and the compressibility of water. These two properties show anomalous behavior as a function of temperature (Fig. 16). Yet, the combination of the two produces a quantity that seems to behave "normally."

Figure 17 shows the values of G for water as a function of temperature at 1 atm. From what we have learned in the previous sections, we would have expected that for a small molecule such as water, with an effective diameter similar to



FIG. 11. Values of G for inert gases at various temperatures and P=1 atm.



FIG. 12. Values of G for propane and butane at different pressures.

that of neon, and with such strong interactions (hydrogenbonding), the positive contribution to the KBI would dominate the value of G. Yet the values of the KBI of water are all negative over the entire range of temperatures. Had we calculated the KBI for low density steam, the value of G would have been large and positive. The reason is that in the gaseous phase at low density, the pair interaction determines the pair correlation function [Eq. (3.4)], hence strong interactions (hydrogen-bonding) should contribute large positive values to the KBI. In the liquid state, the pair correlation function is determined not only by the pair interactions but also on higher order, nonadditive potentials. The net effect of these interactions is to produce a relatively narrow first peak of the pair correlation function of water. This is equivalent to small coordination numbers. Hence, in this case the effect of the strong attractive forces is reduced, and the value of Gbecomes negative.

Figure 17 shows the values of the KBI for  $H_2O$  and  $D_2O$  at 1 atm computed from experimental data on molar volume and isothermal compressibilities. It is interesting to note that the temperature dependence of G is almost linear in the entire range of temperature.

The values of G for  $D_2O$  are systematically lower than the corresponding values of  $H_2O$ . This curve goes through a maximum value at about 6 °C (not corresponding to either the minimum of the volume or the compressibility of  $D_2O$ ).

Since  $H_2O$  and  $D_2O$  have almost the same effective diameters one cannot explain the larger negative values of G of  $D_2O$  due to a larger excluded volume. Hence Eq. (2.16) is of no help in this regard. On the other hand, looking at the compressibility equation, we notice that the term  $k_BT\kappa_T$  is much smaller than the molar volume  $V_M$ . We can interpret the difference in the KBI of  $H_2O$  and  $D_2O$  in terms of the molar volumes. The molar volumes, in turn, may be interpreted in terms of the "relative degree of structure" of the two liquids. The strength of the hydrogen-bond energy of  $D_2O$  is known to be larger than that of  $H_2O$ . This leads to more molecules being engaged in hydrogen-bonding, hence, to a larger concentration of the open structure component, and hence to larger and larger negative KBI.

The pressure dependence of the KBI for  $H_2O$  and  $D_2O$  at 25 °C is shown in Fig. 18. The two curves are almost linear and almost parallel to each other. Again, we see that  $D_2O$  has the larger (negative) values of the KBI in the entire range of pressures.



FIG. 13. Values of G for some linear hydrocarbons as a function of temperature and pressure.



FIG. 14. Values of G for methanol and ethanol as a function of temperature at 1 atm.

# IV. DISCUSSION AND CONCLUSION

Originally, the KBIs were defined in terms of the pair correlation functions. This is true for both a one-component system and mixtures of any number of components. The compressibility equation was mainly used to calculate the isothermal compressibility from the pair correlation function.<sup>10–12</sup> The results obtained from this calculation could be compared with the experimental results. The extent of agreement between the calculated and the measured quantities could serve as a sensitive test of the accuracy of the computed pair correlation functions. This procedure could, in principle, be used also to examine the quality of the pair correlation functions in mixtures. However, in practice this procedure was rarely used, simply because it was difficult to obtain the pair correlation functions for mixtures neither from experiments nor from a theory.

The procedure advocated in this article is essentially to inverse the role of input and output in the calculations. Here, as well as in mixtures,<sup>1-3</sup> we use macroscopically measurable quantities as input to extract microscopic information as output. Since the KBI are integrals over the pair correlation functions, much of the microscopic information contained in the pair correlation functions is lost by the integration. Nevertheless, the KBI still convey local information. This local character of the KBI is due to the fact that the pair correlations have short range, and the main contribution to the integrals comes from a range of few molecular diameters only.

In the case of mixtures, the KBI provides information on the local density, local composition, and local preferential solvation around each molecule. In one-component systems, the KBI provides only information on local density, the change in the average number of particles in the correlation sphere caused by placing a molecule as its center.

In the past there were attempts to extract information on the intermolecular interactions from the KBIs. Although it is



FIG. 15. Values of G for pure linear alcohols at 1 atm and 25 °C. The extrapolated value at n=0 is indicated by the arrow.

true that the values of KBIs are ultimately *determined* by the intermolecular interactions, the extraction of the latter from the KBIs is not possible.

As we have learned in this article, one cannot learn anything on the intermolecular interactions from the KBI. This is true for one-component system as well as for mixtures. In spite of this obvious fact some authors suggested to either modify the KBI or to reinterpret the KBI so as to extract information on the molecular interactions. As we have seen in Sec. III A, some information on the intermolecular interactions can be obtained from the low density limit ( $\rho \rightarrow 0$ ) of the KBI, but none in the liquid densities. If one is interested in local interactions, the best way to study this is from solvation quantities and not from the KBI.<sup>1</sup>

Following a suggestion of a reviewer of this article, I would like to add two comments.

First, in practice, when the KBIs are calculated from experimental or simulated data, one always calculates the integral with a *finite* upper limit, say,

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$$G(R_M) = \int_0^{R_M} [g(R) - 1] 4\pi R^2 dR, \qquad (4.1)$$

where g(R) is the experimental or simulated pair correlation function, and  $R_M$  is the largest distance at which g(R) is known.

Assuming that  $R_M$  is larger than the correlation distance  $R_{\text{corr}}$ , one can extend the upper limit of the integral in Eq. (4.1) to infinity, by *defining*  $g(R) \equiv 1$  for  $R \ge R_M$ . Since the pair correlation function in the region  $0 \le R \le R_{\text{corr}}$  is nearly the same, if one measures g(R) in an open or in a closed system, it follows that by simply extending the upper limit of the integral in Eq. (4.1) to infinity, one gets the KBI. This is also true for simulated results carried out in the T, V, N, the T, P, N, or the  $T, V, \mu$  ensembles. The identification of the experimental (or simulated) quantity  $G(R_M)$  with the KBI is a result of the assumption that  $g(R) \equiv 1$  for  $R \ge R_M$ .

The second comment regards the lower limit of the integral. Clearly, the lower limit of the KBI results from the transformation of variables and the integration over the *entire* volume of the system. This lower limit has nothing to do with the size of the particles, neither in one-component nor in mixtures. This comment sounds trivial. Unfortunately, an



FIG. 16. Two anomalous behaviors of water: (a) The molar volume and (b) the isothermal compressibility.

erroneous interpretation of the lower limit of the KBI appeared in the literature. A more detailed critique of some misinterpretations of the KBI, in general, and the lower limit of the integral, in particular, may be found elsewhere.<sup>24,25</sup>

This work was partially done while I was at NIST. I also wish to thank my host Raymond Mountain for his hospitality while I was visiting NIST, Gaithersburg, Maryland, U.S.A.

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# APPENDIX A: THE KBI IN AN IDEAL-GAS SYSTEM

We start with a hypothetical ideal-gas, a system of strictly noninteracting particles. For a system of such particles, it is known that the pair correlation functions in the open and the closed systems are  $^{1,10-12}$ 

$$g_O(R) = 1, \tag{A1}$$

$$g_C(R) = 1 - \frac{1}{N}.$$
 (A2)

The corresponding KBIs are defined as



FIG. 17. (a) Values of G for  $H_2O$  and  $D_2O$  as a function of temperatures at 1 atm and (b) details at low temperatures.



FIG. 18. The pressure dependence of G for  $H_2O$  and  $D_2O$  at 25 °C.

$$G_{O} = \int_{V} [g_{O}(R) - 1] d\bar{R} = 0, \qquad (A3)$$

$$G_{C} = \int_{V} [g_{C}(R) - 1] d\bar{R} = -\frac{1}{N} \int d\bar{R} = -\frac{1}{\rho},$$
(A4)

where the integration is carried over the entire volume of the system.

Clearly, the two quantities  $G_O$  and  $G_C$  are very different. While  $G_O$  is identically zero, the quantity  $G_C$  is finite, and diverges to  $-\infty$  when  $\rho \rightarrow 0$ .

Next, we examine ideal gas systems of "real particles," i.e., interacting particles, but at very low densities  $\rho \rightarrow 0$ . For the open and closed systems we have<sup>1,10-12</sup>

$$g_O(R) = \exp[-\beta U(R)], \tag{A5}$$

$$g_C(R) = \exp\left[-\beta U(R)\right] \left(1 - \frac{1}{N}\right). \tag{A6}$$

We define the functions  $G(R_M)$  for spherical systems of radius  $R_M$  as

$$G_O(R_M) = \int_0^{R_M} \exp[-\beta U(R) - 1] 4\pi R^2 dR,$$
 (A7)

$$G_{C}(R_{M}) = G_{O}(R_{M}) - \int_{0}^{R_{M}} \frac{\exp[-\beta U(R)]}{N} 4\pi R^{2} dR.$$
 (A8)

Clearly, while  $G_O(R_M)$  converges to the KBI at the limit of large  $R_M$ , the corresponding function in the closed system diverges for  $R_M \rightarrow \infty$ .

For instance, for hard spheres of diameter  $\sigma$  we have

$$G_O(R_M) = \int_0^\sigma -4\pi R^2 dR = \frac{-4\pi\sigma^3}{3},$$
 (A9)

$$G_{C}(R_{M}) = \frac{-4\pi\sigma^{3}}{3} - \int_{0}^{R_{M}} \frac{-4\pi R^{2}}{N} dR$$
$$= \frac{-4\pi\sigma^{3}}{3} - \frac{4\pi R_{M}^{3}}{3N} \xrightarrow{R_{M} \to \infty} -\infty.$$
(A10)

Thus, to obtain the correct KBI, we can either use the pair correlation function  $g_O(R)$  in an open system and take the macroscopic limit of the integral  $G_O(R_M)$  or we can *first* take the macroscopic limit of  $g_C(R)$  (i.e., we let  $N \rightarrow \infty$ , and  $V \rightarrow \infty$ , but N/V constants), *then* perform the integration, i.e.,

$$\lim_{R_{\mathcal{M}}\to\infty}\int_{0}^{R_{\mathcal{M}}}\lim_{N\to\infty}[g_{C}(R)-1]4\pi R^{2}dR\to G_{O}.$$
 (A11)

However, if one first takes the integral  $G_C(R_M)$  as in Eq. (A8), and then take the limit  $R_M \rightarrow \infty$ , the result diverges.

When the pair correlation function is available only in finite range, say, between zero and  $R_M$ , one can simply obtain the KBI by extending the upper limit of the integral to infinity. This is true provided that  $R_M$  is larger than the correlation length.

- <sup>1</sup>A. Ben-Naim, *Molecular Theory of Solutions* (Oxford University Press, Oxford, 2006).
- <sup>2</sup>A. Ben-Naim, J. Chem. Phys. 128, 084510 (2008).
- <sup>3</sup>A. Ben-Naim, M. Navarro, and J. M. Leal, Phys. Chem. Chem. Phys. **10**, 2451 (2008).
- <sup>4</sup>I. Prigogine, *The Molecular Theory of Solutions* (North Holland, Amsterdam, 1957).
- <sup>5</sup>H. C. Van Ness and M. M. Abbott, *Classical Thermodynamics of Non-Electrolyte Solutions* (McGraw-Hill, New York, 1982).
- <sup>6</sup>J. S. Rowlinson and F. L. Swinton, *Liquid and Liquid Mixtures*, 3rd ed. (Butterworth, London, 1982).
- <sup>7</sup> A. Ben-Naim, Statistical Thermodynamics for Chemists and Biochemists (Plenum, New York, 1992).
- <sup>8</sup>J. G. Kirkwood and F. P. Buff, J. Chem. Phys. 19, 774 (1951).
- <sup>9</sup>L. S. Ornstein and F. Zernike, Proc. R. Acad. Sci. Amsterdam 17, 793 (1914).
- <sup>10</sup>T. L. Hill, Statistical Mechanics, Principles and Selected Applications (McGraw-Hill, New York, 1956).
- <sup>11</sup> A. Munster, Statistical Thermodynamics (Springer-Verlag, Berlin, 1969), Vol. 1.
- <sup>12</sup> J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 3rd ed. (Elsevier, Amsterdam, 2006).
- <sup>13</sup> J. K. Percus and G. J. Yevick, Phys. Rev. 110, 1 (1958).
- <sup>14</sup>E. W. Grundke and D. Henderson, Mol. Phys. 24, 269 (1972).
- <sup>15</sup> A. A. Broyles, J. Chem. Phys. 33, 456 (1960); 35, 493 (1961).
- <sup>16</sup>G. J. Throop and R. J. Bearman, J. Chem. Phys. **42**, 2838 (1965); **44**, 1423 (1966).
- <sup>17</sup>J. O. Hirschfelder, C. P. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
- <sup>18</sup>E. W. Lemmon, M. L. Huber, and M. O. McLinden, *REFPROP: Refer*ence Fluid Thermodynamic Properties (National Institute of Standards and Technology, Gaithersburg, Maryland, USA, 2007).
- <sup>19</sup>A. Ben-Naim, Water and Aqueous Solutions (Plenum, New York, 1974).
   <sup>20</sup>G. W. Robinson, S. B. Zhu, S. Singh, and M. W. Evans, Water in Biology,
- Chemistry and Physics (World Scientific, Singapore, 1999). <sup>21</sup> Water, A Comprehensive Treatise edited by F. Franks (Plenum, New York, 1972), Vol. 1.
- <sup>22</sup> Y. Koga, Solution Thermodynamics and its Application to Aqueous Solutions, A Differential Approach (Elsevier, Amsterdam, 2007).
- <sup>23</sup>A. Ben-Naim, Molecular Theory of Water and Aqueous Solutions (World Scientific, Singapore, in press).
- <sup>24</sup> A. Ben-Naim, J. Phys. Chem. B 112, 5874 (2008).
- <sup>25</sup>A. Ben-Naim, J. Phys. Chem. B 111, 2896 (2007).

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