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# Kirkwood–Buff Integrals for Finite Volumes

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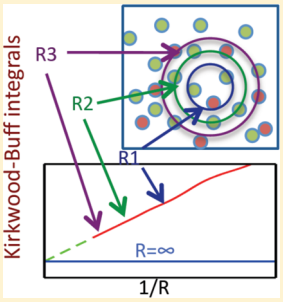
**ABSTRACT:** Exact expressions for finite-volume Kirkwood–Buff (KB) integrals are derived for hyperspheres in one, two, and three dimensions. These integrals scale linearly with inverse system size. From this, accurate estimates of KB integrals for infinite systems are obtained, and it is shown that they converge much better than the traditional expressions. We show that this approach is very suitable for the computation of KB integrals from molecular dynamics simulations, as we obtain KB integrals for open systems by simulating closed systems.




**SECTION:** Liquids; Chemical and Dynamical Processes in Solution

The prediction of macroscopic properties from information at the scale of constituent particles is a major challenge in physical chemistry. For multicomponent fluids, a powerful scheme in this respect was derived by Kirkwood and Buff (KB),[1,2] who showed that many thermodynamic quantities (e.g., activity coefficients, partial molar volumes) can be expressed in terms of integrals of pair correlation functions (PCFs) over space (KB integrals). PCFs can be computed from molecular dynamics (MD) simulations, but using these directly for calculating KB integrals is tricky: (1) KB integrals require PCFs for an infinite range of particle distances, while MD is performed on finite systems; (2) convergence of KB integrals is very slow; and (3) KB integrals need PCFs for open systems,[2,3] while MD in general provides PCFs for closed systems. This subtle difference between open and closed systems cannot be ignored. Although Monte Carlo (MC) methods can be used to simulate open systems (e.g., grand-canonical ensemble), they have difficulties for typical fluids with high density because of inefficient particle insertion procedure. To improve the convergence of KB integrals using PCFs from MD, many methods have been proposed, e.g., the use of smoothing filters for PCFs,[4] discrete Fourier transformation methods,[4] and various extrapolation schemes using approximate PCFs for large distances.[5] Although some of these methods are very efficient to obtain KB integrals, they are in general numerically rather involved, most of them rely on empirical input of some sort, and in all cases the simplicity of the original KB integrals is lost.

In this work, we derive analytic expressions for finite-size KB integrals as single integrals of PCFs in one, two, and three dimensions. The linear extrapolation of these expressions to infinite volume is shown to converge much better than the usual KB formula. The new approach is tested with analytical PCFs and confirmed by MD simulations. We also show that it is essential to take into account the finite-size dependence of PCFs obtained from MD. Essentially, our approach allows for the calculation of KB integrals for an open system while simulating a closed one, solving many of the problems encountered when computing KB integrals from MD results.

In an infinitely extended, multicomponent fluid with species $\alpha,\beta,...$, we consider an arbitrary finite (sub) volume $V$. The particle number fluctuations in $V$ can be expressed as integrals over the one- and two-particle densities $\rho_\alpha^{(1)}(\mathbf{r}_1)$ and $\rho_{\alpha\beta}^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$:[1]

$$\int_V \mathbf{dr}_1 \int_V \mathbf{dr}_2[\rho_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho_\alpha^{(1)}(\mathbf{r}_1)\rho_\beta^{(1)}(\mathbf{r}_2)] = \langle N_\alpha N_\beta\rangle - \langle N_\alpha\rangle\langle N_\beta\rangle - \delta_{\alpha\beta}\langle N_\alpha\rangle \quad (1)$$

Here, $N_\alpha$ is the number of $\alpha$-particles inside $V$, $\langle ...\rangle$ denotes grand-canonical averages, and $\delta_{\alpha\beta}$ is the Kronecker delta. In a fluid, by virtue of translational and rotational invariance, we have $\rho_\alpha^{(1)}(\mathbf{r}) = c_\alpha$ and $\rho_{\alpha\beta}^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = c_\alpha c_\beta g_{\alpha\beta}(r_{12})$, where $c_\alpha$ are macroscopic number densities, $g_{\alpha\beta}$ are PCFs, and $r_{12} \equiv |\mathbf{r}_1 - \mathbf{r}_2|$.[1] Dividing eq 1 by $c_\alpha c_\beta V$ and noting that $c_\alpha = \langle N_\alpha\rangle/V$, we define the KB integral, $G_{\alpha\beta}^V$, for a finite and open system:

$$G_{\alpha\beta}^V \equiv \frac{1}{V}\int_V\int_V (g_{\alpha\beta}(r_{12}) - 1)\,\mathbf{dr}_1\mathbf{dr}_2 = V\frac{\langle N_\alpha N_\beta\rangle - \langle N_\alpha\rangle\langle N_\beta\rangle}{\langle N_\alpha\rangle\langle N_\beta\rangle} - \frac{\delta_{\alpha\beta}}{c_\alpha} \quad (2)$$

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In the limit $V \to \infty$, the double integral on the right-hand side (r.h.s.) can be reduced to a simple integral by the variable transformation $\mathbf{r}_2 \to \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$.

$$G_{\alpha\beta}^{\infty} = \int_0^{\infty} (g_{\alpha\beta}(r) - 1)\, \mathbf{dr} \tag{3}$$

This infinite volume case was already considered by Kirkwood and Buff,[1] and $G_{\alpha\beta}^{\infty}$ in eq 3 are referred to in the literature as KB integrals. In the remainder, we consider a fixed pair of species and drop the indices $\alpha,\beta$. We further define $h(r) \equiv g(r) - 1$. It is crucial to note that for finite $V$, the double integral in eq 2 cannot be reduced to a single one by the transformation $\mathbf{r}_2 \to \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, because the integration domain of $\mathbf{r}$ depends on $\mathbf{r}_1$. Therefore, the truncation of eq 3 to radius $2R$,

$$\tilde{G}^R \equiv \int_0^{2R} h(r) 4\pi r^2\, \mathrm{d}r \tag{4}$$

does *not* provide finite-size density fluctuations.[6] Still, the use $\tilde{G}^R$ for large $R$ as a replacement for $G^{\infty}$ is widespread,[2] despite its poor convergence.

The KB integral of eq 2 can be rewritten by introducing the function

$$w(r) \equiv \frac{1}{V} \int_V \int_V \delta(r - r_{12}) \mathbf{dr}_1\, \mathbf{dr}_2 \tag{5}$$

where $\delta(r - r_{12})$ is the Dirac delta function. $w(r)$ can be calculated analytically for hyperspheres of radius $R$ (see Table 1 where we use the notation $w(r,x)$ with $x = r/(2R)$). Using eq 2, we then find for the KB integrals

$$G^V = G^R = \int_0^{2R} h(r) w(r, x)\, \mathrm{d}r \tag{6}$$

**Table 1. Geometrical Functions for $d$ = 1,2,3 Dimensions, in Agreement with Giorgini et al.[7,a]**

| $d$ | KB | $w$ | $w - x(\partial w/\partial x)$ |
|---|---|---|---|
| 1 | 1 | $1 - x$ | 1 |
| 2 | $2\pi r$ | $4r(\arccos(x) - x(1 - x^2)^{1/2})$ | $4r(\arccos(x) + x(1 - x^2)^{1/2})$ |
| 3 | $4\pi r^2$ | $4\pi r^2(1 - 3x/2 + x^3/2)$ | $4\pi r^2(1 - x^3)$ |

[a] $x = r/(2R)$. $w$ and $-x(\partial w/\partial x)$ are strictly zero for $x \geq 1$. The functions that correspond to $w$ in the usual KB theory (eq 4) are listed under "KB".

We show now that $G^R$ varies asymptotically with the inverse size of any system having a finite correlation length $\xi$. Consider the quantity $F \equiv \int_V \mathbf{dr}_1 \int_{\Omega - V} \mathbf{dr}_2 h(r_{12})$, where $V$ is a closed volume with surface $S$, $\Omega$ is the whole space, and $\Omega - V$ is the space outside $V$. For sufficiently large $V$, only particles in a layer of thickness $\xi$ on either side of the surface contribute to $F$. Therefore, when $V$ increases, $F$ scales as the surface $S$. We can write $F = \int_V \mathbf{dr}_1 \int_{\Omega} \mathbf{dr}_2 h(r_{12}) - \int_V \mathbf{dr}_1 \int_V \mathbf{dr}_2 h(r_{12})$. In the integral over $\Omega$, using $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ for any $\mathbf{r}_1$, we obtain $F = \int_V \mathbf{dr}_1 \int_{\Omega} \mathbf{dr} h(r) - \int_V \mathbf{dr}_1 \int_V \mathbf{dr}_2 h(r_{12}) = VG^{\infty} - VG^V$. As $F \sim S$ for large $V$, we have $G^V - G^{\infty} \sim S/V \sim 1/R$ for volumes of any shape and dimension that are large compared to $(2\xi)^d$. The only assumption is the existence of a finite correlation length, which solely breaks down in the critical point. The proportionality factor of the inverse size dependence can be estimated by a first-order Taylor expansion of $G^R$: $G^{\infty} \approx G^R - (1/R)(\mathrm{d}G^R/\mathrm{d}(1/R)) \equiv \hat{G}^R$, resulting in

$$\hat{G}^R = \int_0^{2R} h(r) \left( w - x \frac{\partial w}{\partial x} \right) \mathrm{d}r \tag{7}$$

$w - x(\partial w)/(\partial x)$ is also listed in Table 1.

The exact expression (eq 6) and the extrapolated one (eq 7), derived for hyperspheres and not for other geometries, are our main results, which for $R \to \infty$ both reduce to the KB integral (eq 3). Although eq 4 and eqs 6 and 7 look very similar, their physical meaning is completely different. The integral in eq 4 is centered on one particle. Therefore, eq 4 does not respect the symmetry of the fluid except in the limit $V \to \infty$. This implies, e.g., that the average density in the finite volume $V$ considered in eq 4 differs from the macroscopic value. In sharp contrast, eqs 6 and 7 respect the symmetry of the system because no particular point is singled out in eq 2. The volume centering in eqs 6 and 7 is explicitly taken into account in the function $w(r)$, so the average density inside any finite volume $V$ equals the macroscopic value. This point is essential when dealing with ionic systems, as it is well-known that a key criterion for meaningful physics is to respect the average charge neutrality in the sampled volume.

The convergence of eqs 4,6, and 7 can be tested using oscillatory decaying functions.[8,9] We consider the following PCF mimicking a liquid with atoms of diameter $\sigma$:

$$h(r) = \begin{cases} \dfrac{3/2}{r/\sigma} \exp\left( \dfrac{1 - r/\sigma}{\chi} \right) \cos\left[ 2\pi \left( \dfrac{r}{\sigma} - \dfrac{21}{20} \right) \right], & \dfrac{r}{\sigma} \geq \dfrac{19}{20} \\ -1, & r < \dfrac{19}{20}\sigma \end{cases} \tag{8}$$

The length scale at which fluctuations of $h(r)$ decay is controlled by $\chi$. Despite its simplicity, this model provides detailed insight into the differences in convergence of $\tilde{G}^R$, $G^R$, and $\hat{G}^R$ (see Figure 1). In all cases, $\tilde{G}^R$, $G^R$, and $\hat{G}^R$ eventually

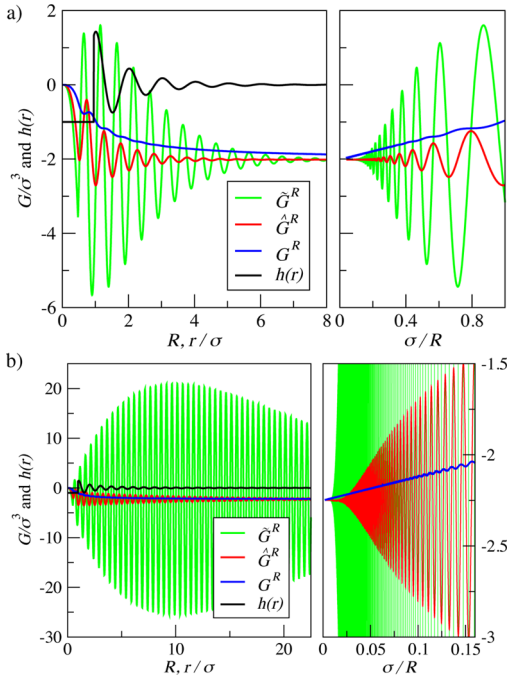


**Figure 1.** Various approaches to compute KB integrals from PCFs. $h(r)$ (eq 8) for $\chi = 2$ (a) and $\chi = 20$ (b), and $\tilde{G}^R$, $G^R$, and $\hat{G}^R$ obtained using eqs 4,6, and 7, respectively, as a function of reduced values of $r$, $R$ (left) and their inverse (right).


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converge to the same value for $G^\infty$. The standard, truncated KB-integral, $\tilde{G}^R$, is a strongly oscillating function with an amplitude that increases for $R < \chi\sigma/2$. For $R > \chi\sigma/2$, a very slow convergence sets in. The oscillations in $h(r)$ (black) are hugely amplified in $\tilde{G}^R$ (green). Our new expression $\hat{G}^R$ (red) is also oscillating, but with an amplitude that never increases and is always much smaller than that of $\tilde{G}^R$. Consequently, $\hat{G}^R$ converges much faster than $\tilde{G}^R$. For $\chi = 2$ and $R = 2.5\sigma$, $\hat{G}^R$ converges to $G^\infty$ within $\pm 0.2\sigma^3$, while at the same $R$, the difference between $\tilde{G}^R$ and $G^\infty$ is $\pm 2\sigma^3$ (1 order of magnitude larger). The superior convergence of $\hat{G}^R$ compared to $\tilde{G}^R$ is even more obvious for $\chi = 20$: for $R = 20\sigma$, $\hat{G}^R$ converges to $G^\infty$ within $\pm 0.2\sigma^3$, while $\tilde{G}^R$ oscillates with an amplitude almost 2 orders of magnitude larger ($15\sigma^3$). The exact finite volume expression $G^R$ is a very smooth and essentially monotonic function (blue). $G^R$ shows weak oscillations, but their amplitude is 2 orders of magnitude smaller than that of $\hat{G}^R$. The oscillations in $G^R$ are even smaller than those of $h(r)$. While $\tilde{G}^R$ hugely amplifies $h(r)$ oscillations, the exact expression $G^R$ strongly suppresses them and is thus free of the major convergence problem of the usual KB expression (eq 4). As shown in the right panels of Figure 1, $G^R - G^\infty$ scales as $1/R$ for large $R$, so a precise estimation of $G^\infty$ can be obtained by a linear extrapolation of $G^R$ to $1/R \to 0$.[10] In the case where the PCF is known only in a small range, the most precise estimate of $G^\infty$ is $G^R$. Alternatively, an accurate estimate of $G^\infty$ is provided by $\hat{G}^R$, which has a much smaller error (1 or 2 orders of magnitude) than the truncated integral $\tilde{G}^R$.

When KB integrals are calculated using PCFs from MD of a closed system of $N$ particles ($h_N(r)$), it is known that $h_N(r)$ has a finite-size scaling[2] and does not converge to 0 for $r \to \infty$. The difference between $h_N(r)$ and $h_\infty(r)$ can be expanded in a Taylor series in $1/N$[11]

$$h_N(r) \approx h_\infty(r) + \frac{c(r)}{N} \tag{9}$$

where $c(r)$ is a function that depends on $r$ but not on $N$. From MD simulations of one thermodynamic state for different system sizes, $c(r)$ and $h_\infty(r)$ follow trivially from eq 9. To test the linear scaling prediction of eq 9, MD simulations of a binary WCA fluid were performed for different simulation box sizes ($L$), while keeping the number density $\rho = N/(L/\sigma)^3$, temperature $T$, and mixture composition constant (see Figure 2). Clearly, for larger simulation boxes, $h(r)$ approaches 0, and shows a linear scaling with $1/N$.

In Figure 3 (left), the integrals $\tilde{G}^R$ and $\hat{G}^R$ are plotted for PCFs of two system sizes, $L/\sigma = 10$ and $L/\sigma = 40$. For $L/\sigma = 10$, the integrals show a characteristic $R^3$ divergence for large $r$, which is due to the fact that $h_N(r)$ does not go to 0 for $r \to \infty$. This finite size effect was corrected by estimating $h_\infty(r)$ (eq 9), resulting in $\tilde{G}^R_\infty$ and $\hat{G}^R_\infty$. They practically coincide with the KB integrals of the largest system $L/\sigma = 40$. In Figure 3 (right), the corresponding exact finite volume KB integrals $G^R$ are plotted as a function of $\sigma/R$. The $R^3$ divergence in the data for $L/\sigma = 10$ is completely removed when the corrected PCF is used and the regime linear in $1/R$ appears clearly. A linear extrapolation of $G^R_\infty$ thus leads to its value in the thermodynamic limit, $G^\infty$. Calculation of the correction function $c(r)$ requires simulations of two system sizes. These can be done quickly for two small systems, without losing accuracy, and result therefore in a large reduction in computing time as compared to a single simulation on a large system. The combined use of $h_\infty(r)$ and eq 6 (or its approximation eq 7) enables the efficient calculation of KB

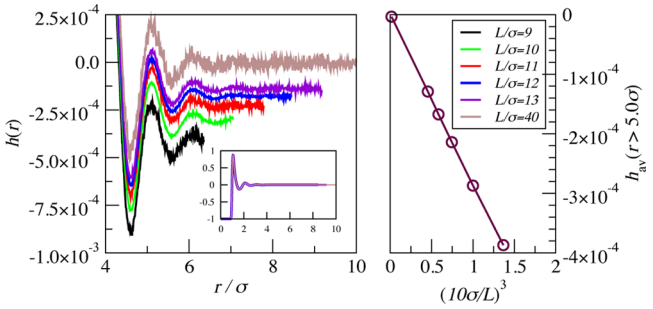


**Figure 2.** MD results for a binary 75/25 WCA fluid ($d = 3$) at $T = 1.8$ and constant density $\rho = 0.7$ (reduced units; see ref 12 for more details). Left: $h(r)$ of 1−1 correlations as a function of $r$ for different system sizes ($L$). The inset exhibits the function $h(r)$ from 0 to $10\sigma$ ($\sigma$ being the particle diameter). Right: averages of $h(r)$ (left figure) for $r > 5\sigma$ as a function of the inverse simulation box volume. Similar results were found for the other interaction pairs. The PCFs were computed for distances up to $L\sqrt{2}/2$.

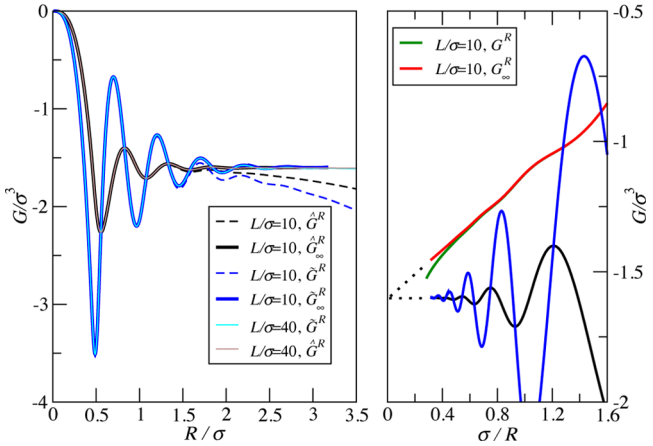


**Figure 3.** Left: MD calculations of various $G(R)$ (eqs 4, 6, and 7) for the WCA system of Figure 2 using $h(r)$ or $h_\infty(r)$. Results for a much larger system ($L/\sigma = 40$) are also shown. Right: $G^R$ calculated using $h(r)$ and $h_\infty(r)$ as a function of $\sigma/R$; $\tilde{G}^R_\infty$ and $\hat{G}^R_\infty$ are also shown. As a guide to the eye, we added linear extrapolations of $G^R_\infty$, $\tilde{G}^R_\infty$, and $\hat{G}^R_\infty$ (dotted lines) until the same value, $G^\infty = -1.60 \pm 0.01$. In all cases, $h_\infty(r)$ was calculated from eq 9 using $h(r)$ for two system sizes ($L/\sigma = 10$ and $L/\sigma = 9$).

integrals corresponding to the thermodynamic limit using MD simulations of relatively small systems, and is therefore superior to the traditional approach of eq 4, which shows a poor convergence.

Instead of calculating the upper side of eq 2 (resulting in eq 6), in principle, one could also directly compute the lower side of eq 2 from MD simulations. This requires the sampling of particle number fluctuations in subvolumes $V \sim R^d$ embedded in a simulation box of volume $L^d$. Of course, these local fluctuations also scale with $1/R$ and $G^\infty$ can be estimated by extrapolating the linear regime to $1/R \to 0$. This so-called small subsystem approach was used by us in earlier work.[12−15] Although correct in the thermodynamic limit, it has severe disadvantages compared to eqs 6 and 7: (1) the connection to PCFs is lost, and therefore the connections to quantities that intimately depend of PCFs (e.g., pressure tensor[17]) as well as theoretical approaches that rely on knowledge of PCFs are also lost; (2) finite-size corrections as eq 9 cannot be applied, so the range where linear scaling of fluctuations with $1/R$ is observed


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is limited (and is sometimes not easy to detect), and the final result still depends on the system size; (3) statistics are significantly worse as local particle number fluctuations can behave as telegraph signals. However, it is important to indicate that, contrary to the present approach, the fluctuation method is also well adapted to nonisotropic systems, which has been clearly documented for adsorbed phases in all-silica MFI-type zeolites.[12,16]

In summary, an exact expression of KB integrals for finite volumes has been derived for hyperspheres in one, two, and three dimensions. The new formalism was applied to an analytical PCF and to MD simulation results. For systems with a finite correlation length, the finite volume integrals converge to the thermodynamic limit linearly as $1/R$. The new expressions (eqs 6 and 7) converge much faster than the usual KB integral (eq 4). The reason is that the new integrals are volume centered and therefore respect the symmetry of the fluid, in sharp contrast to the traditional integrals. Moreover, a simple method was proposed to correct for the system size dependence of PCFs. Our approach enables efficient calculations of KB integrals for open systems, using MD simulation results for relatively small closed systems. Much smaller systems are needed compared to the traditional approach (eq 4). We feel that the calculation of KB integrals will be greatly facilitated by the present theory, in particular for situations where the use of open systems is prohibited, like in ionic systems.[2]

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### Notes

The authors declare no competing financial interest.

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