Finite-size estimates of Kirkwood–Buff and similar integrals

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A recent method [P. Krüger and T. J. H. Vlugt, Phys. Rev. E 97, 051301(R) (2018)] to approximate an improper integral \( \int_0^\infty dr F(r) \) by a finite-range integral \( \int_0^L dr F(r) W(r/L) \), with an appropriate weight function \( W(x) \), is extended to an arbitrary (embedding) dimensionality \( d \). A study of three-dimensional Kirkwood–Buff integrals, where \( F(r) = 4\pi r^2 h(r) \), \( h(r) \) being the pair correlation function, shows that, in general, a choice \( d \neq 3 \) (e.g., \( d = 7 \)) for the embedding dimensionality significantly reduces the error of the approximation \( \int_0^\infty dr F(r) \approx \int_0^L dr F(r) W(r/L) \).

I. INTRODUCTION

In the statistical-mechanical theory of liquids, Kirkwood–Buff (KB) integrals play a distinguished role [1–3]. They have the form

\[
I[F(r)] = \int_0^\infty dr F(r),
\]

where \( F(r) = 4\pi r^2 h(r) \), \( h(r) \) being the pair correlation function [4–6]. On the other hand, if \( h(r) \) is obtained from computer simulations or from numerical solutions of integral-equation theories, its knowledge is limited to a finite range \( r < L \), so that the conventional method consists in estimating the KB integral by a truncated integral, i.e.,

\[
I[F(r)] \approx \int_0^L dr F(r).\tag{2}
\]

However, the correlation function \( h(r) \) is usually oscillatory, which generally makes the convergence of the estimate (2) rather slow. It is then highly desirable to design alternative approximate methods to estimate \( I[F(r)] \) that, while relying upon the knowledge of \( F(r) \) for \( r < L \) only, are much more efficient than Eq. (2). One possibility is to approximate Eq. (1) by a finite-size integral of the form [7, 8]

\[
I_L[F(r)] = \int_0^L dr F(r) W(r/L),\tag{3}
\]

with an appropriate weight function \( W(x) \neq 1 \).

Of course, the computational problem described above is not limited to KB integrals but extends, with different physical interpretations of the isotropic function \( F(r) \), to practically all branches of physics where improper integrals of the form (1) are relevant.

In Ref. [8], Krüger and Vlugt proposed a simple, practical, and accurate general prescription to approximate an improper integral of the form (1) by the finite-size integral (3), where the weight function \( W(x) \) is given by

\[
W_3^{(2)}(x) = 1 - \frac{23x^3}{8} + \frac{3x^4}{4} + \frac{9x^5}{8}.\tag{4}
\]

More specifically,

\[
I[F(r)] = I_L[F(r)] + O(L^{-3}).\tag{5}
\]

Let me rephrase and summarize the two main steps leading to the derivation of Eqs. (4) and (5). First, it is assumed that \( I[F(r)] \) comes from the three-dimensional volume integral

\[
I[F(r)] = \int \frac{d^3r}{4\pi r^2} F(r),\tag{6}
\]

after passing to spherical coordinates and integrating over the angular variables. Next, use is made of the authors’ proof that

\[
\int \frac{d^3r}{4\pi r^2} F(r) y_3(r/L) = I[F(r)] - \frac{3}{2L} I[F(r)r/L] + O(L^{-3}),\tag{7}
\]

where \( 4\pi y_3(x) \) is the intersection volume of two spheres of unit diameter separated a distance \( x \), i.e.,

\[
y_3(x) = \left(1 - \frac{3x}{2} + \frac{x^3}{2}\right) \Theta(1 - x).\tag{8}
\]

Actually, the proof in Ref. [8] extends Eq. (7) to nonspherical shapes, in which case the function \( y_3(x) \) depends on the particular shape, \( L = 6V/A \) (\( V \) and \( A \) being the volume and surface area, respectively), and, in general, \( O(L^{-3}) \to O(L^{-2}) \). On the other hand, a spherical shape, and hence Eq. (8), is needed for the derivation of Eq. (4) as

\[
W_3^{(2)}(x) = y_3(x) \left(1 + \frac{3x}{2} + \frac{9x^2}{4}\right).\tag{9}
\]

In their paper [8], Krüger and Vlugt motivate the result posed by Eqs. (4) and (5) as a useful way to estimate three-dimensional (3D) KB integrals, in which case \( F(r) = 4\pi r^2 h(r) \). On the other hand, as said before,
TABLE I. Coefficient \( a_d \) and function \( y_d(x) \) for the first few odd values of \( d \). The Heaviside function \( \Theta(1 - x) \) is omitted for clarity.

| \( d \) | \( a_d \) | \( y_d(x)/(1 - x)^{(d+1)/2} \)
|---|---|---|
| 1 | 1 | 1 |
| 3 | 3 | \( 1 + \frac{x}{2} \) |
| 5 | \( \frac{21}{8} \) | \( 1 + \frac{9x}{8} + \frac{3x^2}{2} \) |
| 7 | \( \frac{35}{16} \) | \( 1 + \frac{29x}{16} + \frac{8x^2}{4} + \frac{5x^3}{16} \) |
| 9 | \( \frac{315}{128} \) | \( 1 + \frac{325x}{128} + \frac{345x^2}{128} + \frac{175x^3}{128} + \frac{35x^4}{128} \) |

The main goal of this paper is to perform such an extension and, additionally, show that a choice \( d = 3 \) allows one to obtain alternative weight functions \( W(x) \) that are generally more efficient than Eq. (4), even in the case of 3D KB integrals.

II. EMBEDDING IN A \( d \)-DIMENSIONAL SPACE

Let us assume that the isotropic function \( F(r) \) is embedded in a vector space of \( d \) dimensions. In such a case, the result is not restricted \( a \ priori \) to 3D KB integrals, i.e., \( F(r) \) can be in principle any function such that the (formally one-dimensional) integral \( \mathcal{I}[F(r)] \) converges. It is then tempting to wonder how the procedure summarized above would be generalized by freely assuming that the function \( F(r) \) is embedded in a \( d \)-dimensional space and rewriting \( \mathcal{I}[F(r)] \) as a \( d \)-dimensional volume integral. The main goal of this paper is to perform such an extension and, additionally, show that a choice \( d \neq 3 \) allows one to obtain alternative weight functions \( W(x) \) that are generally more efficient than Eq. (4), even in the case of 3D KB integrals.

\[
\mathcal{I}[F(r)] = \int \frac{d^d r}{\Omega_d r^{d-1}} F(r),
\]

where \( \Omega_d = 2\pi^{d/2}/\Gamma(d/2) \) is the total solid angle in \( d \) dimensions. Following essentially the same steps as done in Ref. [8] to derive Eq. (7), it is possible to generalize it as

\[
\int \frac{d^d r}{\Omega_d r^{d-1}} F(r) y_d(r/L) = \mathcal{I}[F(r)] - \frac{a_d}{L} \mathcal{I}[F(r)r] + \mathcal{O}(L^{-3}),
\]

where

\[
a_d \equiv \frac{d\pi^{-1/2}\Gamma(d/2)}{\Gamma(1/2 + d/2)}
\]

and \( \Omega_d y_d(x) \) is the intersection volume of two \( d \)-dimensional spheres of unit diameter separated a distance \( x \). This quantity appears, for instance, in the context of the virial expansion of the pair correlation function [6]. Its general expression is

\[
y_d(x) = I_{1 - x^2} (1/2 + d/2, 1/2),
\]
The explicit values of $a$ where $d (y \chi I)$ respectively. ($\text{complete beta function}$). Panels (a) and (b) correspond to $L = 5$ and $L = 20$, respectively.

where $I_{2}(a, b) = B_{2}(a, b)/B(a, b)$ is the regularized incomplete beta function [9, 10]. If $d = odd, y_{d}(x) - 1$ is an odd polynomial of degree $d$ [11–13], namely

$$y_{d}(x) = \left[1 - a_{d} \sum_{j=0}^{(d-1)/2} c_{j, d} x^{2j+1}\right] \Theta(1 - x), \quad (14)$$

where

$$c_{j, d} = \frac{(-1)^{j} \Gamma(1/2 + d/2)}{(2^{j+1}) j^{j} \Gamma(2 + d/2 - j)}. \quad (15)$$

If $d = even$, Eq. (14), with the upper summation limit $(d - 1)/2$ replaced by $\infty$, gives the power series expansion of $y_{d}(x)$. In particular, in the case of disks, one has

$$y_{2}(x) = \frac{2}{\pi} \left(\cos^{-1} x - x \sqrt{1 - x^{2}} \right) \Theta(1 - x). \quad (16)$$

The explicit values of $a_{d}$ and expressions of $y_{d}(x)$ for odd embedding dimensionalities $1 \leq d \leq 9$ are given in Table I.

The replacement $F(r) \rightarrow F(r)r^{n}$ in Eq. (11) yields (provided the integrals exist)

$$\mathcal{I}[F(r)r^{n}] = \int \frac{d^{d}r}{\Omega_{d} r^{d-1}} F(r)r^{n} y_{d}(r/L) + \frac{a_{d}}{L} \mathcal{I}[F(r)r^{n+1}] + \mathcal{O}(L^{-3}). \quad (17)$$

Recursive application of Eq. (17) in Eq. (11) up to $n = k$ gives

$$\mathcal{I}[F(r)] = \mathcal{I}^{(k)}_{L, d}[F(r)] + \mathcal{O}(L^{-3}), \quad (18)$$

where

$$\mathcal{I}^{(k)}_{L, d}[F(r)] = \int_{0}^{L} dr \ F(r) W_{d}^{(k)}(r/L), \quad (19a)$$

$$W_{d}^{(k)}(x) \equiv y_{d}(x) \sum_{n=0}^{k} (a_{d} x)^{k}. \quad (19b)$$

Equations (18), (19a), and (19b) generalize Eqs. (5), (3), and (4), respectively, which correspond to the particular choices $d = 3$ and $k = 2$. Incidentally, the choice $d = 1$ with $k = 2$ leads to $W_{1}^{(2)}(x) = 1 - x^{3}$, which is the weight function proposed in Ref. [7] by a different method.
shows the weight functions (terms neglected in Eq. (19b)) so that the influence of the choice of dimensionality diminishes. Moreover, due to the prefactor \((1 - x)^{(d+1)/2}\) the curves have a flatter shape near \(x = 1\) as \(d\) increases.

Notice that
\[
W^{(k)}_d(x) = 1 + O(x^{-3}), \quad k \geq 2,
\]
so that the influence of the choice of \(d\) and \(k \geq 2\) on \(W^{(k)}_d(r/L)\) is of \(O(L^{-3})\), i.e., of the same order as the terms neglected in Eq. (18). On the other hand, from a practical point of view, the error \(\left| \mathcal{I}^{(k)}_{L,d}[F(r)] - \mathcal{I}[F(r)] \right|\) can be minimized by an appropriate choice of the embedding dimensionality \(d\) and of the index \(k\) for a given function \(F(r)\) and a given cutoff distance \(L\).

III. DISCUSSION

One might argue that the choice of the embedding dimensionality \(d\) in the approximation (18) must be dictated by the dimensionality of the physical problem underlying the evaluation of the (one-dimensional) integral
\[
\mathcal{I}[F(r)].
\]

According to this reasoning, if the physical problem consists in the computation of the 3D KB integral, i.e., \(F(r) = 4\pi r^2h(r)\), then one should take \(d = 3\). On the other hand, from a strict mathematical point of view, the integral one wants to approximate by application of Eq. (18) is blind to the physical origin of the problem, so one can always assume that \(F(r)\) is embedded in a higher-dimensional space.

To further elaborate on the previous point, let us take \(F(r) = 4\pi r^2h(r)\) and consider the same model 3D pair correlation function as given by Eq. (25) of Ref. [8], namely
\[
h(r) = \begin{cases} 
-1, & r < \frac{19}{20} \\
3 \cos \left[ \frac{2\pi}{20} \left( r - \frac{21}{20} \right) \right] e^{-r(1-\chi)}, & r < \frac{19}{20} 
\end{cases}
\]

where \(\chi\) represents the correlation length. For simplicity, let us restrict ourselves to odd dimensionalities \(d = 3, 5, 7,\) and 9, and to indices \(k = 2\) and 3. Figures 2(a) and 2(b) show the relative error \(\left| \mathcal{I}^{(k)}_{L,d}[F(r)] - \mathcal{I}[F(r)] \right|\) versus \(L\) for \(\chi = 2\) and \(\chi = 20\), respectively. Although not shown, in the case \(\chi = 20\) one can check that the error presents rapid oscillations as a function of \(L\), except for the combinations \((d,k) = (7,2), (9,2),\) and \((9,3)\). To make cleaner the general picture, only integer values of

FIG. 5. Plot of the relative error \(|\mathcal{I}^{(k)}_{L,d}[F(r)]/\mathcal{I}[F(r)] - 1|\) versus \(\phi\), where \(F(r) = 4\pi r^2h(r)\) and \(h(r)\) is the exact solution of the PY integral equation for hard spheres. Panels (a) and (b) correspond to \(L = 5\) and \(L = 10\), respectively.

FIG. 6. Plot of the \(\mathcal{I}^{(k)}_{L,d}[F(r)]\) versus \(L^{-3}\) \((L \geq 5)\), where \(F(r) = 2h(r)\) and \(h(r)\) is the exact pair correlation function for a 1D system of hard rods at a packing fraction \(\phi = 0.8\). The inset is a magnification of the small framed region \((L \geq 10)\) in the main figure.
$L$ are considered in Fig. 2. We observe that an appropriate choice of $(d,k)$ can significantly reduce the error. In contrast to what is inferred from Ref. [8], the cases with $k = 3$ generally perform better than with $k = 2$. On the other hand, the optimal dimensionality $d$ depends on the correlation length: it is $d = 3$ for $\chi = 2$ and $d = 7$ for $\chi = 20$.

To investigate the influence of the correlation length $\chi$ on the relative error, Figures 3(a) and 3(b) show the relative error $|I_{L,d}^{(k)}[F(r)]/I[F(r)] - 1|$ versus $\chi$ for $L = 5$ and $L = 20$, respectively. The best behaviors are presented by $d = 3$ if $L = 5$ and by $d = 7$ if $L = 20$, in both cases with $k = 3$.

As a second (and more realistic) illustrative example, let us take the exact solution of the Percus–Yevick (PY) integral equation for 3D hard spheres [6, 14–18], which is exactly known for any packing fraction $\phi$. The results are displayed in Figs. 4 and 5. Again, the choices with $k = 3$ are typically more accurate than with $k = 2$. Also, as happened in the case of Eq. (21), the optimal choice of $d$ depends on the range of $b(r)$; while $d = 3$ is appropriate for $\phi = 0.2$, $d = 7$ is preferable for $\phi = 0.5$.

In the case of more general functions $F(r)$ where the sought integral $I[F(r)]$ is not known, the optimal choice of the embedding dimensionality $d$ and the index $k$ can be estimated by plotting $I_{L,d}^{(k)}[F(r)]$ versus $L^{-3}$ for several combinations of $(d,k)$ and selecting the one with the smoothest variation allowing for an easy extrapolation to $L^{-3} \rightarrow 0$.

To illustrate this method, let us now consider the one-dimensional (1D) KB integral of hard rods (Tonks gas). In that case, $F(r) = 2b(r)$ is exactly known [6, 19–25], but we can pretend that the associated KB integral $I[F(r)]$ is unknown. Figure 6 shows the integrals $I_{L,d}^{(k)}[F(r)]$ versus $L^{-3}$ at a packing fraction $\phi = 0.8$. In all the cases, the integrals $I_{L,d}^{(k)}[F(r)]$ are seen to converge to the exact value $I[F(r)] = \phi - 2 = -1.2$. In general, the amplitudes of the oscillations are smaller with $k = 3$ than with $k = 3$ and decrease as the embedding dimensionality $d$ increases. On the other hand, the slopes of the lines around which the oscillations take place are smaller with $k = 3$ than with $k = 2$ and decrease as the $d$ decreases. Thus, the optimal choice of $(d,k)$ would depend on the accessible region of $L$: if $L \sim 5$, $(d,k) = (9,3)$ seems to be a good choice for the extrapolation to $L^{-3} \rightarrow 0$, while $(d,k) = (7,3)$ seems preferable if $L \sim 10$.

IV. CONCLUSION

In summary, the generalization to any embedding dimensionality $d$ and any index $k$ of the weight function $W_{3}^{(d)}(x)$, Eq. (4), proposed in Ref. [8] can significantly improve the cutoff estimate $I_{L,d}^{(k)}[F(r)]$ of an improper integral $I[F(r)]$, even if the latter represents a KB integral corresponding to a 3D or 1D pair correlation function.

In the case of KB integrals, the results reported here show that an optimal choice of the index is $k = 3$. As for the embedding dimensionality, its optimal value tends to increase as the correlation length increases, i.e., as the error due to the finite cutoff distance $L$ grows. As a practical compromise between simplicity and accuracy, a recommended weight function seems to be the one corresponding to $d = 7$ and $k = 3$, namely

$$W_{7}^{(3)}(x) = (1-x)^4 \left( 1 + \frac{35x}{16} \right) \left( 1 + \frac{125x^2}{256} \right) \times \left( 1 + \frac{29x}{16} + \frac{5x^2}{4} + \frac{5x^3}{16} \right).$$  \hspace{1cm} (22)$$

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