JOURNAL OF COMPUTATIONAL PHYSICS 7, 157–166 (1971)

Experiments on a Superposition Approximation for Wiener Path Integrals

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Received May 25, 1970

The pair correlation function for He^4 gas is calculated in the following way: Two- and three-particle Slater sums are expressed in terms of Wiener path integrals. The three-particle path integral is approximated by a product of two-particle path integrals. From tabular values of these path integrals obtained previously, the pair correlation function is obtained by quadrature. Comparison is made with existing calculations employing the three-particle term.

1. INTRODUCTION

In classical statistical mechanics, the Mayer f function is used to develop terms in the density expansion of quantities such as the pressure and the pair distribution function. There is a quantum mechanical analog to this which reduces to the Mayer f function in the classical limit; this analogous function is called the F function. It is easy to write down the expression for any quantum mechanical cluster integral in terms of F functions; one simply replaces the product of f functions in the classical cluster integral by the Wiener integral of a product of corresponding F functions. These formal manipulations have been described by DeWitt and Fishbane [1] and they determined some of the early terms of the Wigner–Kirkwood expansion of the second and third virial coefficients with this approach. Now in the quantum mechanical cluster integral one cannot replace the Wiener integral of the product of F functions by the product of the Wiener integrals of the F functions; this corresponds to the fact that one cannot, in general, replace the average of a product by a product of averages. DeWitt and Fishbane showed that, in the case of the third virial coefficient, the error committed in such a replacement is $O(\hbar^4)$; however, they made no estimate of the actual magnitude of this error. Here some results of numerical computations are presented

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which show that this error is small down to temperatures of about 10°K. This result is particularly interesting because it suggests that one can actually compute quantum mechanical cluster integrals as easily as classical cluster integrals with reasonable accuracy above 10°K, by using the same Monte Carlo sampling scheme as used in the classical case.

2. NOTATION AND DEFINITIONS

Let H be the Hamiltonian for the system and $W_2(\mathbf{1}, \mathbf{2})$ the two-particle Slater sum; namely,

$$W_2(\mathbf{1}, \mathbf{2}) = \lambda^6 \sum_i \Psi_i^*(\mathbf{1}, \mathbf{2})\, e^{-\beta H} \Psi_i(\mathbf{1}, \mathbf{2}), \tag{1}$$

where λ is the thermal wavelength,

$$\lambda = (2\pi\hbar^2\beta/m)^{1/2}, \tag{2}$$

and the summation extends over all states without regard to symmetry. For dilute gases the pair distribution function $n_2(\mathbf{1}, \mathbf{2})$ can be expanded in a power series in the number density n and the result is

$$n_2(\mathbf{1}, \mathbf{2}) = n^2(1 + ng)\, W_2(\mathbf{1}, \mathbf{2}) + O(n^4), \tag{3}$$

where g is given by

$$g = \frac{1}{W_2(\mathbf{1}, \mathbf{2})} \int [W_3(\mathbf{1}, \mathbf{2}, \mathbf{3}) - W_2(\mathbf{1}, \mathbf{2})\, W_2(\mathbf{1}, \mathbf{3}) - W_2(\mathbf{1}, \mathbf{2})\, W_2(\mathbf{2}, \mathbf{3}) - W_2(\mathbf{1}, \mathbf{2})]\, d\mathbf{3}. \tag{4}$$

The quantity $W_3(\mathbf{1}, \mathbf{2}, \mathbf{3})$ is the three-particle Slater sum, and the particular approximation that we are concerned with here is

$$W_3(\mathbf{1}, \mathbf{2}, \mathbf{3}) \cong W_2(\mathbf{1}, \mathbf{2})\, W_2(\mathbf{1}, \mathbf{3})\, W_2(\mathbf{2}, \mathbf{3}). \tag{5}$$

Substitution of this approximation for W_3 in Eq. (4) yields the following approximation for g:

$$g \cong \hat{g} = \int [W_2(\mathbf{1}, \mathbf{3}) - 1][W_2(\mathbf{2}, \mathbf{3}) - 1]\, d\mathbf{3}, \tag{6}$$

a form reminiscent of the classical expression for the same quantity. DeWitt and

Fishbane showed that the error in this approximation is $O(\hbar^2)$, and when it is used to compute the third virial coefficient

$$C \propto \frac{1}{V} \int g \, d\mathbf{1} \, d\mathbf{2} - \left[\frac{1}{V} \int (W(\mathbf{1}, \mathbf{2}) - 1) \, d\mathbf{1} \, d\mathbf{2}\right]^2 \tag{7}$$

the error is $O(\hbar^4)$.

From the viewpoint of the Wiener integral formulation [2] the approximation in Eq. (5) can be described in the following way. Let $V(\mathbf{i}, \mathbf{j})$ be the potential energy function for the interaction between the i-th and j-th particles. Let $\eta_i(\tau)$ be a three-dimensional Wiener path associated with the i-th particle. Then the two-particle Slater sum is given in terms of a conditional Wiener integral by

$$W_2(\mathbf{1}, \mathbf{2}) = E\{\exp(-\beta V_{12}^*) \mid \eta_1(1) = \eta_2(1) = 0\}, \tag{8}$$

where

$$V_{12}^* = \int_0^1 V\left(\mathbf{1} + \frac{\lambda}{\sqrt{2\pi}} \eta_1(\tau), \mathbf{2} + \frac{\lambda}{\sqrt{2\pi}} \eta_2(\tau)\right) d\tau. \tag{9}$$

It is to be noted that in the classical limit ($\lambda \to 0$)

$$\begin{aligned} V_{12}^* &\to V(\mathbf{1}, \mathbf{2}), \\ W_2(\mathbf{1}, \mathbf{2}) &\to \exp(-\beta V(\mathbf{1}, \mathbf{2})). \end{aligned} \tag{10}$$

Similarly, the three-particle Slater sum expressed in terms of Wiener integrals is

$$W_3(\mathbf{1}, \mathbf{2}, \mathbf{3}) = E\{\exp(-\beta V_{123}^*) \mid \eta_1(1) = \eta_2(1) = \eta_3(1) = 0\}, \tag{11}$$

where

$$V_{123}^* = \int_0^1 V\left(\mathbf{1} + \frac{\lambda}{\sqrt{2\pi}} \eta_1(\tau), \mathbf{2} + \frac{\lambda}{\sqrt{2\pi}} \eta_2(\tau), \mathbf{3} + \frac{\lambda}{\sqrt{2\pi}} \eta_3(\tau)\right) d\tau. \tag{12}$$

Let us now assume that the potential energy $V(\mathbf{1}, \mathbf{2}, \mathbf{3})$ describing the interaction among three particles can be expressed as a sum of pair potentials, viz.,

$$V(\mathbf{1}, \mathbf{2}, \mathbf{3}) = V(\mathbf{1}, \mathbf{2}) + V(\mathbf{2}, \mathbf{3}) + V(\mathbf{1}, \mathbf{3}). \tag{13}$$

It follows immediately that

$$W_3(\mathbf{1}, \mathbf{2}, \mathbf{3}) = E\{\exp(-\beta(V_{12}^* + V_{23}^* + V_{13}^*)) \mid \eta(1) = 0\}, \tag{14}$$

where, for short, the set of end-point conditions is written as a single equation,

$\eta(1) = 0$. In view of the fact that $V_{ij}^* \to V_{ij}$ in the classical limit, the approximation

$$W_3(\mathbf{1}, \mathbf{2}, \mathbf{3}) \cong E\{\exp(-\beta V_{12}^*) \mid \eta(1) = 0\}\, E\{\exp(-\beta V_{23}^*) \mid \eta(1) = 0\} \times E\{\exp(-\beta V_{13}^*) \mid \eta(1) = 0\} \tag{15}$$

seems like a reasonable one for small thermal wavelengths. This is exactly the approximation displayed in Eq. (5). From the viewpoint of the Wiener paths, this approximation neglects correlations between the exponentials which exist because each pair of exponentials has a common path. We will call this the superposition approximation.

It will be noted from this discussion that the F function, mentioned in the introduction, is

$$F_{ij} = \exp(-\beta V_{ij}^*) - 1.$$

The quantum mechanical analog of the classical cluster integral,

$$b = \frac{1}{V} \iiint f_{12} f_{13} f_{23}\, d\mathbf{1}\, d\mathbf{2}\, d\mathbf{3},$$

is

$$b_q = \frac{1}{V} \iiint E\{F_{12} F_{13} F_{23} \mid \eta(1) = 0\}\, d\mathbf{1}\, d\mathbf{2}\, d\mathbf{3}.$$

3. COMPUTATIONS

These computations are for a Lennard–Jones potential,

$$V(\mathbf{i}, \mathbf{j}) = 4\alpha \left[\left(\frac{r}{\sigma}\right)^{-12} - \left(\frac{r}{\sigma}\right)^{-6} \right], \tag{16}$$

$$r = |\mathbf{i} - \mathbf{j}|,$$

with the deBoer and Michels values

$$\alpha = 14.04 \times 10^{-16}\ \text{erg}, \qquad \sigma = 2.56 \times 10^{-8}\ \text{cm} \tag{17}$$

appropriate for He^4. For this potential the computation of g, Eq. (4), has already been done [3]. That computation did not employ the approximation in Eq. (5) and we will call those results "exact." Here we have computed $\hat{g}$ using the expression on the right side of Eq. (6), resulting from the approximation in Eq. (5), and compared them with the exact results. For the purpose of this computation we used values of W_2 tabulated in an earlier computation [4], and the integral in Eq. (6) was evaluated numerically from those tabulated values. Some details of the numerical evaluation of this integral follow.

Cylindrical coordinates are used to describe the location of the third molecule and the z axis is chosen so that molecules 1 and 2 lie on the z axis and are symmetrically displaced a distance a with respect to the origin.[1] This is illustrated in Fig. 1. Hence we have the relations

$$\begin{aligned} |\mathbf{1}-\mathbf{3}| &= \sqrt{r^2+(b+a)^2} \equiv R_+ , \\ |\mathbf{2}-\mathbf{3}| &= \sqrt{r^2+(b-a)^2} \equiv R_- , \qquad (18) \\ |\mathbf{1}-\mathbf{2}| &= 2a \equiv R_{12} . \end{aligned}$$

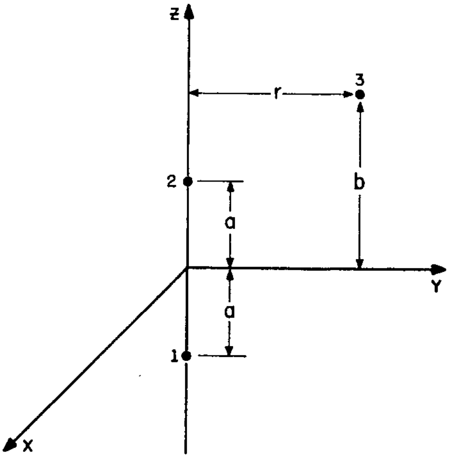

FIG. 1. Coordinate system describing position of third particle.

Since the integrand is independent of the azimuth and invariant to the reflection $z \to -z$, we can obtain immediately

$$\hat{g} = 2\pi \int_0^\infty \int_0^\infty (W_2(R_+) - 1)(W_2(R_-) - 1)\, d\xi\, dz, \qquad (19)$$

where

$$\xi = r^2. \qquad (20)$$

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[1] It occurred to us only later that bipolar coordinates would have been a better choice and we have used them in subsequent work. The advantage of bipolar coordinates was also pointed out by a referee.

A grid in the ξ, z plane was laid down with spacing

$$\begin{aligned} c &= \Delta\xi = \text{constant}, \\ d &= \Delta z = \text{constant}, \end{aligned} \tag{21}$$

and the following elementary approximation for the integral was used:

$$\int_0^\infty \int_0^\infty F(\xi, z)\, d\xi,\, dz \cong cd \sum_{i=1}^{M} \sum_{j=1}^{M} F(\bar{\xi}_i, \bar{z}_j), \tag{22}$$

where

$$\begin{aligned} \bar{\xi}_i &= (i - \tfrac{1}{2})\, c, \\ \bar{z}_j &= (j - \tfrac{1}{2})\, d, \end{aligned} \tag{23}$$

and the determination of M is described below. So, in particular, we have

$$\hat{g} \cong 2\pi cd \sum_{i=1}^{M} \sum_{j=1}^{M} [W_2(R_{ij}^{+}) - 1][W_2(R_{ij}^{-}) - 1], \tag{24}$$

where

$$R_{ij}^{\pm} = \{(i - \tfrac{1}{2})\, c + ((j - \tfrac{1}{2})\, d \pm a)^2\}^{1/2}. \tag{25}$$

The determination of M was made in the following way. When R is sufficiently large, $W_2(R)$ can be approximated by the leading term in the Wigner–Kirkwood expansion, viz.,

$$\begin{aligned} W_2(R) &\cong e^{+4\beta\alpha(\rho/R)^6}, \\ \rho &= \sigma \sqrt{\pi/\lambda}. \end{aligned} \tag{26}$$

The criterion for using this approximation was chosen, somewhat arbitrarily, to be that the ratio of the next two terms to the $(\rho/R)^6$ term be 10^{-2} or less. Writing the Wigner–Kirkwood expansion to this many terms we have

$$W_2(R) = \exp\left[4\beta\alpha\left(\frac{\rho}{R}\right)^6 - 4\beta\alpha\left(\frac{\rho}{R}\right)^{12} + \frac{10\beta\alpha}{\rho^2}\left(\frac{\rho}{R}\right)^8 + O\left(\left(\frac{\rho}{R}\right)^{10}\right)\right]. \tag{27}$$

Consequently the maximum value of R is chosen to satisfy the inequalities

$$\begin{aligned} \frac{2.5}{\rho^2}\left(\frac{\rho}{R_{\max}}\right)^2 &\leqslant 10^{-2}, \\ \frac{(\rho/R_{\max})^{12}}{(\rho/R_{\max})^6} &\leqslant 10^{-2}. \end{aligned} \tag{28}$$

From the first of these we get

$$R_{\max} \geqslant 16 \tag{29}$$

and from the second

$$R_{\max} \geqslant 2.2\rho, \tag{30}$$

and since, from Eq. (25),

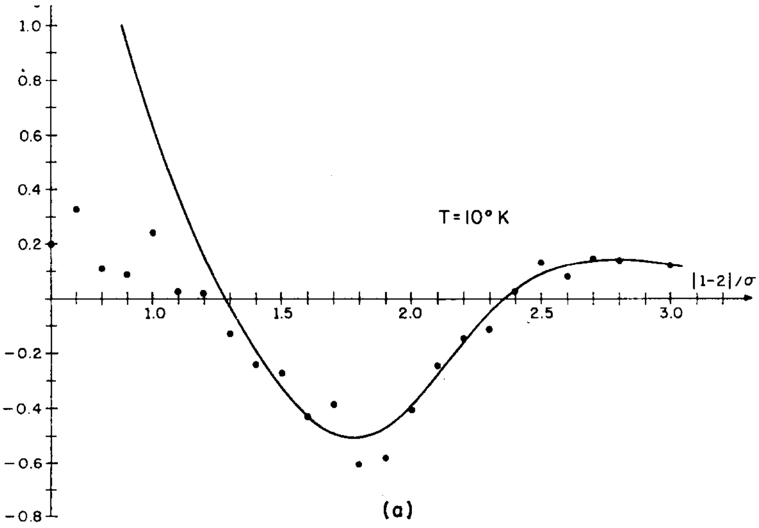
$$R_{\max} \simeq Md, \tag{31}$$

we obtain as the equation for the determination of M

$$M = \text{integer part}\left[\max\left\{\frac{16}{d}, \frac{2.2\rho}{d}\right\}\right]. \tag{32}$$

If ϵ denotes the error committed in restricting the quadrature to a region of finite extent in the ξ, z plane, say the rectangle $0 \leqslant z \leqslant z_m$, $0 \leqslant \xi \leqslant \xi_m$, then under the approximation of the last paragraph

$$\begin{aligned}\epsilon < {} & 2\pi \int_0^\infty \int_{z_m}^\infty \left(e^{4\alpha\beta(\rho/R_+)^6} - 1\right)\left(e^{4\alpha\beta(\rho/R_-)^6} - 1\right) dz\, d\xi \\ & + 2\pi \int_{\xi_m}^\infty \int_0^\infty \left(e^{4\alpha\beta(\rho/R_+)^6} - 1\right)\left(e^{4\alpha\beta(\rho/R_-)^6} - 1\right) dz\, d\xi. \end{aligned} \tag{33}$$



(a)

FIGURE 2

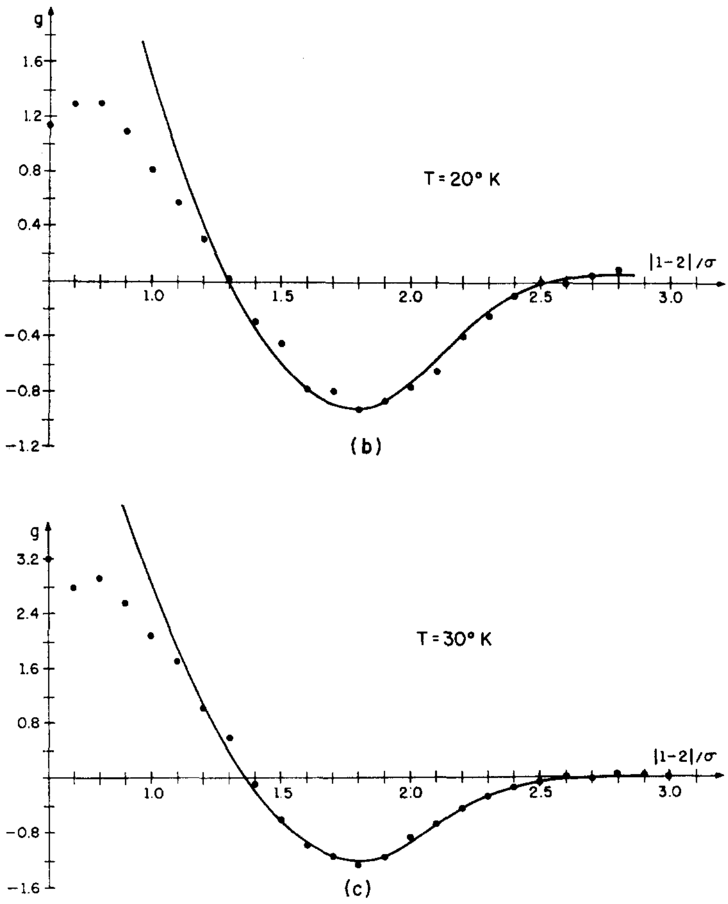


FIG. 2. Pair correlation function, g, as a function of $| \mathbf{1} - \mathbf{2} |/\sigma$ at 10°K, 20°K, 30°K. The continuous line represents computed values of the approximation $\hat{g}$, and the points indicate the "exact" values of g according to Ref. [3].

TABLE I

Third Virial Coefficient $C(T)$ in Units of cm^6/mole^2 at Different Temperatures Obtained from the Superposition Approximation Used Here and from the Work of Jordan and Fosdick [3]

T(°K)	10	20	30	40	50	75	100	273
$C(T)$ (Sup. approx.)	381	258	212	184	176	152	142	183
$C(T)$ (Jordan and Fosdick, Ref. [3])	515	286	226	195	178	162	150	107

An estimation of the integrals on the right side of this inequality shows ϵ to be negligible for most values of a. The error is only large when a is very large, corresponding to the molecules being close to the edge of the finite region.

In Figs. 2a, b, and c, g as a function of $|\mathbf{1} - \mathbf{2}|/\sigma$ is shown for temperatures 10°K, 20°K, and 30°K, respectively. The isolated points represent the "exact" results. Rather good agreement is seen between the "exact" results and those which were obtained from the superposition approximation. The discrepancies at small $|\mathbf{1} - \mathbf{2}|/\sigma$ are not particularly important since $W_2(\mathbf{1}, \mathbf{2})$ is nearly zero when $|\mathbf{1} - \mathbf{2}|/\sigma$ is less than about 0.8 and it is the product $W_2(\mathbf{1}, \mathbf{2})g$ which enters in the pair distribution function $n_2(\mathbf{1}, \mathbf{2})$. In Figs. 3a and b the pair distribution function at $T = 10$°K and 20°K at two densities is shown. The isolated points represent the exact results. Finally, in Table I the third virial coefficient in the superposition approximation is compared with the "exact" values. The

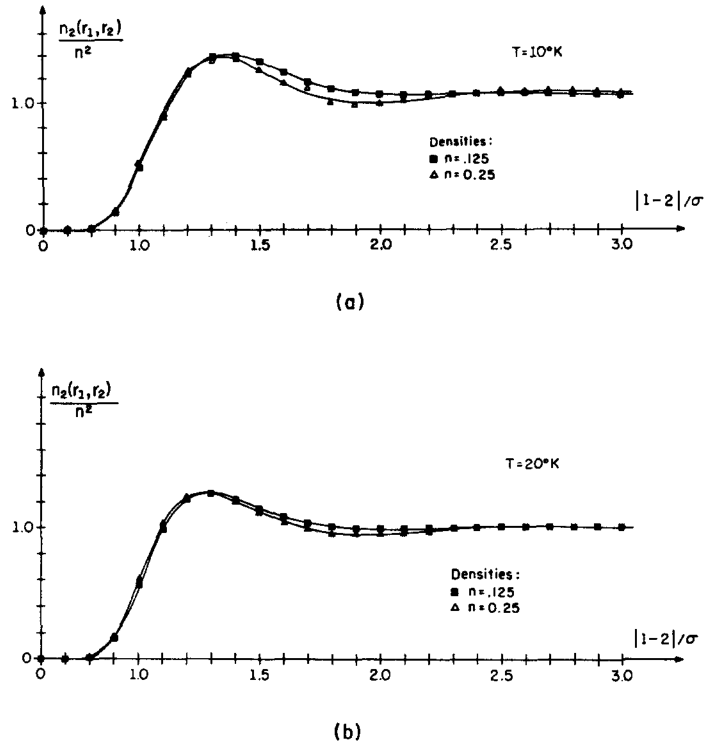


FIG. 3. Pair distribution function $n_2(1, 2)$ as a function of $|\mathbf{1} - \mathbf{2}|/\sigma$ at 10°K, 20°K, and different densities.

discrepancy in the virial coefficient values at high temperatures is probably due to the error in estimating the contribution from values of g at large values of $|\mathbf{1} - \mathbf{2}|/\sigma$ which are needed in the numerical evaluation of the integral on the right side of Eq. (7). The discrepancy at 10°K, somewhat greater than 20%, is probably a result of the cumulative effect of the error due to the integration. Since the contribution to the integral at large $|\mathbf{1} - \mathbf{2}|/\sigma$ also seems to be important at 10°K this effect may also increase the error.

REFERENCES

1. HUGH DE WITT AND PAUL FISHBANE, Failure of the Mayer irreducible cluster theorem with wave mechanics, *J. Math. Phys.* **7** (1966), 798–801.
2. LLOYD D. FOSDICK, The Monte Carlo method in quantum statistics, *SIAM Rev.* **10** (1968), 315–327.
3. HARRY F. JORDAN AND LLOYD D. FOSDICK, Three-particle effects in the pair distribution function for He gas, *Phys. Rev.* **171** (1968), 128–149.
4. LLOYD D. FOSDICK AND HARRY F. JORDAN, Path integral calculation of the two-particle Slater sum for He^4, *Phys. Rev.* **143** (1966), 58–66.