Three-Particle Effects in the Pair Distribution Function for He^4 Gas*

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The diagonal elements of the three-particle density matrix for He^4 have been formulated in terms of Wiener functional integrals in order to compute both that part of the pair distribution function linear in the density and the third virial coefficient. The three-particle interaction energy was taken to be a sum of Lennard-Jones (12-6) potentials between pairs of particles. Evaluation of the Wiener integrals was carried out by a Monte Carlo sampling technique to yield the pair distribution function and third virial coefficient for temperatures from 273 to 5°K. Comparison of the linear portion of the density expansion of the pair distribution function gave qualitative agreement with experimental values for the pair distribution function in liquid He^4 measured by neutron diffraction. The values of the third virial coefficient calculated by this method are consistently smaller than the experimental values and consistently larger than the classical values of this quantity over the given temperature range.

I. INTRODUCTION

THREE-BODY computations in quantum statistics are difficult and consequently rare, but they are important for an understanding of the equation of state of quantum-mechanical systems. Here we describe some three-particle computations on He^4; in particular, the three-particle term in the density expansion for the pair distribution function and the third virial coefficient. These computations cover the temperature range 5 to 273°K. At the low end of this range we were able to compare our estimate of the pair distribution function with the measurements of Henshaw on liquid He^4; the good agreement is probably the most interesting result of these computations. We feel that this result is particularly interesting since it is usually not supposed that the two leading terms in the density expansion of the pair distribution function can satisfactorily describe the situation in a liquid. On the other hand, our results are not in good agreement with the experimental values of the third virial coefficient; the reason for this lack of agreement is probably connected with our use of the Lennard-Jones (12-6) potential.

In these computations the Wiener integral formulation has been used. We have described this method already[1] in its application to two-particle computations on He^4. Another possible approach to these computations is the binary collision expansion of Yang and Lee[2]; Larsen[3] and Pais and Uhlenbeck[4] have made calculations of the third virial coefficient in this way. Still another approach is to use the Wigner-Kirkwood expansion. The advantages which the Weiner integral approach appears to have are: Its mathematical properties are well understood; it provides a useful framework for making qualitative and semiquantitative estimates; and it is relatively simple from a computational viewpoint. Of particular importance is the fact that it is a completely trivial matter, that is, it requires no change in program logic, to increase the accuracy of a computation; the only requirement is a greater expenditure of computation time.

II. NOTATIONS AND DEFINITIONS

The spatial coordinates of the ith particle will be denoted by $\mathbf{i}$ or $\mathbf{r}_i$, and the distance between a pair of particles, i and j, by r_{ij}. Reciprocal temperature β is

$$\beta=1/kT \tag{2.1}$$

and the thermal wavelength λ is

$$\lambda=(h^2\beta/2\pi m)^{1/2}, \tag{2.2}$$

where m is the particle mass. The diagonal elements of the density matrix are

$$W_N(\mathbf{1},\mathbf{2},\cdots,\mathbf{N})=\langle\mathbf{1},\mathbf{2},\cdots,\mathbf{N}|e^{-\beta H_N}|\mathbf{1},\mathbf{2},\cdots,\mathbf{N}\rangle, \tag{2.3}$$

where H_N is the Hamiltonian for the N-particle system and the normalization is chosen so that the diagonal element is unity when the potential energy is identically zero.

The pair distribution function $g(r_{12})$ is defined as the relative probability of finding particle 1 within the volume element $d^3\mathbf{1}$ at $\mathbf{1}$ and, simultaneously, particle 2 within volume element $d^3\mathbf{2}$ at $\mathbf{2}$. Normalization has been chosen to satisfy

$$g(r_{12})\to 1, \quad \text{as} \quad r_{12}\to\infty. \tag{2.4}$$

This function can be expressed[5] as a power series in the

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[1] L. D. Fosdick and H. F. Jordan, Phys. Rev. 143, 58 (1966).
[2] C. N. Yang and T. D. Lee, Phys. Rev. 113, 1165 (1959).
[3] S. Y. Larsen, Phys. Rev. 130, 1426 (1963).
[4] A. Pais and G. E. Uhlenbeck, Phys. Rev. 116, 250 (1959).
[5] J. de Boer, Rept. Progr. Phys. 12, 305 (1949).

density n, namely

$$g(r_{12})=W_2(1,2)[1+\sum_{i=1}^{\infty} n^i g_i(r_{12})], \tag{2.5}$$

where the coefficient of the term linear in the density is

$$g_1(r_{12})=W_2(1,2)^{-1}\int [W_3(1,2,3)-W_2(1,2)W_2(1,3) -W_2(1,2)W_2(2,3)+W_2(1,2)]d^3 3. \tag{2.6}$$

It is the computation of this quantity which is the central part of the computations described here.

The virial expansion for the pressure[6] P is

$$\frac{P\beta V_0}{N_0}=1+\frac{B(T)}{V_0}+\frac{C(T)}{V_0^2}+\cdots, \tag{2.7}$$

where N_0 is Avogadro's number and V_0 the molar volume. The third virial coefficient $C(T)$ is given by

$$C(T)=\tfrac{1}{3}N_0^2\left\{\left[\int (W_2(1,2)-1)d2\right]^2 -\int g_1(r_{12})W_2(1,2)d2\right\}. \tag{2.8}$$

The interaction between particles i and j is assumed to be described by the Lennard-Jones (12-6) potential with the de Boer–Michels parameters[7] for He^4:

$$V(r_{ij})=4\kappa\left[\left(\frac{\sigma}{r_{ij}}\right)^{12}-\left(\frac{\sigma}{r_{ij}}\right)^{6}\right], \tag{2.9}$$

$$\kappa=14.04\times10^{-16}\text{ erg},\quad \sigma=2.56\times10^{-8}\text{ cm}.$$

The interaction between three particles is assumed to be described by a sum of these pair potentials:

$$U_3(1,2,3)=V(r_{12})+V(r_{13})+V(r_{23}). \tag{2.10}$$

Although the details of the computation depend on these assumptions, the main ideas do not. It would, for instance, be possible to carry through these computations with an interaction which is not pairwise additive.

III. WIENER INTEGRAL FORMULATION OF THE DENSITY MATRIX

A. Expression of Density Matrix Elements in Terms of Wiener Integrals

Since we have discussed the main formulas elsewhere,[1,8] our account here will be brief. Let $F[\mathbf{r}(\tau)]$ be a functional of the continuous function $\mathbf{r}(\tau)$, with $\mathbf{r}(0)=0$, then the conditional Wiener integral of this functional is denoted by

$$E\{F[\mathbf{r}(\tau)]\,|\,\mathbf{r}(\beta)=\mathbf{R}\},$$

the condition on the Wiener integral being that $\mathbf{r}(\beta)=\mathbf{R}$. For the present we regard $\mathbf{r}(\tau)$ and $\mathbf{R}$ as vectors with an arbitrary number of components.

Let the Hamiltonian for an N-particle system be

$$H_N=-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2+U_N(\mathbf{R}), \tag{3.1}$$

then the general density matrix element can be expressed as a conditional Wiener integral of the functional

$$F[\mathbf{r}(\tau)]=\exp\left\{-\beta\int_0^1 U_N\left(\frac{\lambda}{(2\pi)^{1/2}}\mathbf{r}(\tau)+\mathbf{R} +\tau(\mathbf{R}'-\mathbf{R})\right)d\tau\right\}, \tag{3.2}$$

namely

$$\langle\mathbf{R}\,|\,e^{-\beta H_N}\,|\,\mathbf{R}'\rangle=\exp\{-(\pi/\lambda^2)(\mathbf{R}'-\mathbf{R})^2\} \times E\{F[\mathbf{r}(\tau)]\,|\,\mathbf{r}(1)=0\}. \tag{3.3}$$

This relationship holds only for Boltzmann matrix elements. To take the symmetry requirements into proper account, these Boltzmann matrix elements must be combined in an appropriate way.

A useful intuitive picture of the Wiener integral is obtained by thinking of an imaginary motion of a system of N particles over a unit "time" interval, $0\leq\tau\leq1$. At time $\tau=0$ the coordinates of the particles are given by $\mathbf{R}$ and at time $\tau=1$ by $\mathbf{R}'$. The quantity $(\mathbf{R}'-\mathbf{R})^2$ is the sum of the squares of the distances between the initial and final positions of each particle, and the Wiener integral in Eq. (3.3) is the average, over all possible paths of the motion, of the Boltzmann factor, $e^{-\beta\langle U_N\rangle}$, with the potential energy replaced by $\langle U_N\rangle$, its average over the path. The paths are weighted by Wiener measure which is related to the average over the path of the total kinetic energy of the system.

It should be noted that $(2\pi)^{-1/2}\lambda\mathbf{r}(\tau)$ is a measure of the deviation of the motion from the shortest straight line path from $\mathbf{R}$ to $\mathbf{R}'$, and as the classical limit is obtained by letting $\lambda\to0$, the deviation vanishes in this limit. The off-diagonal matrix elements vanish in the classical limit since

$$\lim_{\lambda\to0}\exp\{-(\pi/\lambda^2)(\mathbf{R}'-\mathbf{R})^2\}=0,\quad(\mathbf{R}'\neq\mathbf{R}). \tag{3.4}$$

The diagonal element approaches the Boltzmann factor

$$\lim_{\lambda\to0}\langle\mathbf{R}\,|\,e^{-\beta H_N}\,|\,\mathbf{R}\rangle=e^{-\beta U_N(\mathbf{R})}, \tag{3.5}$$

since

$$E\{C\,|\,\mathbf{r}(1)=0\}=C \tag{3.6}$$

when C is a constant with respect to the Wiener integration.

[6] K. Huang, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1963), Chap. 14, Secs. 14.1 and 14.2.
[7] J. de Boer and A. Michels, Physica **6**, 409 (1939).
[8] L. D. Fosdick, J. Math. Phys. **3**, 1251 (1962).

B. Upper Bounds on Off-Diagonal Matrix Elements

Both diagonal and off-diagonal Boltzmann matrix elements are involved in the calculation of $g_1(r_{12})$ for a Bose or Fermi system. For example, in the evaluation of the three-particle Bose or Fermi matrix element

$$\langle 1,2,3|e^{-\beta H_3}|1,2,3\rangle_{\pm},$$

the sign denoting Bose (+) or Fermi (−), two types of off-diagonal Boltzmann matrix elements arise; specifically,

$$\begin{aligned}&\langle 1,2,3|e^{-\beta H_3}|1,2,3\rangle_{\pm}\\&=\langle 1,2,3|e^{-\beta H_3}|1,2,3\rangle\pm\langle 2,1,3|e^{-\beta H_3}|1,2,3\rangle\\&\quad\pm\langle 3,2,1|e^{-\beta H_3}|1,2,3\rangle\pm\langle 1,3,2|e^{-\beta H_3}|1,2,3\rangle\\&\quad+\langle 2,3,1|e^{-\beta H_3}|1,2,3\rangle+\langle 3,1,2|e^{-\beta H_3}|1,2,3\rangle,\end{aligned}\tag{3.7}$$

where the matrix elements on the right are Boltzmann matrix elements. Expressing the two types of Boltzmann off-diagonal elements in terms of Wiener integrals, we have

$$\begin{aligned}&\langle 2,1,3|e^{-\beta H_3}|1,2,3\rangle\\&\qquad=\exp\{-(2\pi/\lambda^2)(1-2)^2\}E\{F_1|\mathbf{r}(1)=0\}\end{aligned}\tag{3.8}$$

and

$$\begin{aligned}&\langle 2,3,1|e^{-\beta H_3}|1,2,3\rangle=\exp\{-(\pi/\lambda^2)\\&\quad\times[(2-1)^2+(3-2)^2+(1-3)^2]\}E\{F_2|\mathbf{r}(1)=0\},\end{aligned}\tag{3.9}$$

where

$$F_1=\exp\left\{-\beta\int_0^1 U_3\left(\frac{\lambda}{(2\pi)^{1/2}}\mathbf{r}(\tau)+(2,1,3)+\tau[(1,2,3)-(2,1,3)]\right)d\tau\right\}\tag{3.10}$$

and

$$F_2=\exp\left\{-\beta\int_0^1 U_3\left(\frac{\lambda}{(2\pi)^{1/2}}\mathbf{r}(\tau)+(2,3,1)+\tau[(1,2,3)-(2,3,1)]\right)d\tau\right\}.\tag{3.11}$$

The factors multiplying the Wiener integrals in these expressions yield a significant estimate of the size and temperature dependence of these off-diagonal elements for intermolecular potentials for which the particles are characterized by strong repulsive cores. Suppose the three-body potential satisfies

$$U_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=\infty,\quad\text{if}\quad r_{ij}<0\quad\text{for any } i,j.$$

The Wiener integrals in Eqs. (3.8) and (3.9) must vanish if the initial distance between any pair of particles is less than σ. Hence, wherever the matrix element is nonzero, the exponential factors satisfy

$$\exp\left\{-\frac{2\pi}{\lambda^2}(1-2)^2\right\}<\exp\left\{-\frac{2\pi\sigma^2}{\lambda^2}\right\}\tag{3.12}$$

for the two-particle exchange, and

$$\exp\left\{-\frac{\pi}{\lambda^2}[(2-1)^2+(3-2)^2+(1-3)^2]\right\}<\exp\left\{-\frac{3\pi\sigma^2}{\lambda^2}\right\}\tag{3.13}$$

for the three-particle exchange.

For He^4, approximating the repulsive core diameter by the parameter

$$\sigma=2.56\times10^{-8}\text{ cm}$$

of the Lennard-Jones (12-6) potential, one finds that the larger of the two multiplying factors—that for the two-particle exchange—is approximately $e^{-0.6T}$. Thus at 5°K one expects the off-diagonal elements to be smaller than the diagonal elements by a factor of at least 0.05. The argument for the two-particle exchange term in $\langle 1,2|e^{-\beta H_2}|1,2\rangle_{\pm}$ is the same as the argument for the similar three-particle term in Eq. (3.7) and yields the same result. Due to restrictions of computing time, the numerical scheme developed below for the calculation of the diagonal matrix element is limited in accuracy at low temperatures. In all cases, the above bound on the exchange terms shows them to be negligible compared to the numerical uncertainty of the direct term. Therefore, in subsequent sections the exchange terms will be discarded, and the diagonal Boltzmann matrix element will be used as if it were the same as the diagonal element for a Bose or Fermi system.

The above argument was first used[9] in connection with the two-particle exchange term in the second virial coefficient. The suppression of this two-particle exchange term with increasing temperature is actually somewhat stronger than is indicated above. This is verified both by numerical calculations[1,10] and by upper and lower bounds obtained analytically by Lieb,[11] who shows that at high temperatures the term is asymptotically proportional to

$$\exp[-\tfrac{1}{3}\pi^3(\sigma/\lambda)^2+O((\sigma/\lambda)^{2/3})].\tag{3.14}$$

Qualitatively, the increase in the constant multiplying $-\lambda^{-2}$ in the exponent comes about because the Wiener integral in Eq. (3.3), as well as the multiplying factor, decreases exponentially with increasing temperature. This is due to the fact that the set of paths for which the "motion" of the system from time $\tau=0$ to time $\tau=1$ brings the two exchanged particles no closer than σ from each other for any τ is assigned exponentially smaller Wiener measure as $T\to\infty$.

[9] S. Y. Larsen, J. E. Kilpatrick, E. H. Lieb, and H. F. Jordan, Phys. Rev. 140, 129 (1965).
[10] S. Y. Larsen, K. Witte, and J. E. Kilpatrick, J. Chem. Phys. 44, 213 (1966).
[11] E. H. Lieb, J. Math. Phys. 8, 43 (1967).

C. Approximation of the Diagonal Matrix Element by a Multiple Riemann Integral

The calculation of the diagonal matrix elements for Boltzmann statistics is now reduced to the evaluation of a Wiener integral. For the diagonal element of the three-particle density matrix, Eq. (2.3) becomes

$$W_3(\mathbf{1,2,3})=E\left\{\exp\left[-\beta\int_0^1 U_3\left(\frac{\lambda}{(2\pi)^{1/2}}\mathbf{r}(\tau)+(\mathbf{1,2,3})\right)d\tau\right]\middle|\mathbf{r}(1)=0\right\}. \quad (3.15)$$

Except in very special cases, notably a harmonic oscillator potential, it is necessary to use an approximation scheme to evaluate this Wiener integral. Such algorithms have been proposed and applied by several authors.[1,8,12–15]

The simplest algorithm uses the approximation

$$E\{F[\mathbf{r}(\tau)]|\mathbf{r}(\beta)=\mathbf{R}\}\cong\int_{-\infty}^{+\infty}\cdots\int_{-\infty}^{+\infty}F[\mathbf{r}(\tau;p)]d\mu_p, \quad (3.16)$$

which comes directly from the definition of the Wiener integral, namely

$$E\{F[\mathbf{r}(\tau)]|\mathbf{r}(\beta)=\mathbf{R}\}=\lim_{p\to\infty}\int_{-\infty}^{+\infty}\cdots\int_{-\infty}^{+\infty}F[\mathbf{r}(\tau;p)]d\mu_p, \quad (3.17)$$

where each component of $\mathbf{r}(\tau;p)$ is a piecewise straight line with changes in slope at $\tau_1, \tau_2, \cdots, \tau_{p-1}$, and

$$\mathbf{r}(\tau_i;p)=\mathbf{r}(\tau_i)\equiv\mathbf{r}_i, \quad (\text{all } i) \quad (3.18)$$

$$\tau_0=0, \quad \tau_p=\beta, \quad (3.19)$$

and the measure $d\mu_p$ is the Gaussian

$$d\mu_p=(2\pi\beta)^{3N/2}\exp\left(\frac{\mathbf{R}^2}{2\beta}\right)\left[\prod_{i=0}^{p-1}(2\pi(\tau_{i+1}-\tau_i))^{-3N/2}\times\exp\left(-\frac{(\mathbf{r}_{i+1}-\mathbf{r}_i)^2}{2(\tau_{i+1}-\tau_i)}\right)\right]\prod_{i=}^{p-1}d\mathbf{r}_i, \quad (3.20)$$

where $d\mathbf{r}_i$ represents a volume element in the $3N$-dimensional coordinate space of an N-particle system.

Since p is large, the Monte Carlo method is used to evaluate the integral, multiplicity $p-1$, on the right of Eq. (3.16). This simple algorithm is adequate for one or two particles under the influence of a computationally simple potential and has been applied successfully to such problems.[1,8,14] However, as the evaluation of the integrand of the multiple integral becomes more complex, the computing time requirements become very large. For this reason, methods have been proposed[12,13,15] for reducing the multiplicity of the integral to be evaluated. The present calculation makes use of a slight modification of the procedure developed by Fosdick.[13]

The principal idea of the technique used here for reducing the multiplicity is to make use of the fact that it is possible to express the Wiener integral in Eq. (3.15) as a Riemann integral of a product of p Wiener integrals involving a smaller value of β (higher temperature), for which good approximations can be obtained. This possibility rests on two important properties of the Wiener integral. The first property is a separability property: Let the functional $F[\mathbf{r}(\tau)]$ be expressible as a product

$$F[\mathbf{r}(\tau)]=\prod_{i=1}^{p}f_i[\mathbf{r}(\tau)], \quad (3.21)$$

where

$$\tau_{i-1}<\tau<\tau_i \quad (\tau_0=0,\ \tau_p=1) \quad (3.22)$$

in each factor of this product, then

$$E\{F[\mathbf{r}(\tau)]|\mathbf{r}(1)=0\}=\int_{-\infty}^{+\infty}\cdots\int_{-\infty}^{+\infty}\prod_{i=1}E\{f_i[\mathbf{r}(\tau)]|\mathbf{r}(\tau_i)=\mathbf{r}_i-\mathbf{r}_{i-1}\}d\mu_p, \quad (3.23)$$

where $d\mu_p$ is defined in Eq. (3.20), and for each Wiener integral on the right of Eq. (3.23) the time interval is (τ_{i-1},τ_i) with

$$\mathbf{r}(\tau_{i-1})=0. \quad (3.24)$$

It is important to recognize that Eq. (3.23) is an equality; it is not an approximation. The functional we are concerned with can be factored, with

$$f_i[\mathbf{r}(\tau)]=\exp\left[-\beta\int_{\tau_{i-1}}^{\tau_i}U_3\left(\frac{\lambda}{(2\pi)^{1/2}}(\mathbf{r}(\tau)+\mathbf{r}_{i-1})+(\mathbf{1,2,3})\right)d\tau\right]; \quad (3.25)$$

hence it is possible for us to use Eq. (3.23). A formal derivation of this separability property follows easily from Eq. (3.17). The second property of the Wiener integral, useful to us now, is the following: Let the Wiener integral be defined for a particular time interval $(0,\beta)$, and consider a change in time scale, namely

$$\tau'=p\tau. \quad (3.26)$$

The new time interval is $(0,\beta')$, and the Weiner inte-

[12] R. H. Cameron, Duke Math. J. **18**, 111 (1951).
[13] L. D. Fosdick, Math. Comp. **19**, 225 (1965).
[14] I. M. Gel'fand and N. N. Chentsov, Zh. Eksperim. i Teor. Fiz. **31**, 1106 (1956) [English transl.: Soviet Phys.—JETP **4**, 945 (1957)].
[15] A. G. Konheim and W. L. Miranker, Math. Comp. **21**, 49 (1967).

gration $(0,\beta)$ is related to the Wiener integral on $(0,\beta')$ by

$$E\{F[\mathbf{r}(\tau)]|\mathbf{r}(\beta)=\mathbf{R}\} = E\{F[(1/\sqrt{p})\mathbf{r}(\tau')]|\mathbf{r}(\beta')=(\sqrt{p})\mathbf{R}\}. \quad (3.27)$$

Again, this property follows easily from Eq. (3.17). There is, actually, an obvious third property which is used here; namely, that $d\mu_p$ is invariant to a change of origin of the space coordinate or of the time coordinate. Now let us suppose that $\tau_i-\tau_{i-1}$ is a constant,

$$\tau_i-\tau_{i-1}=1/p. \quad (3.28)$$

Then, making use of the above properties, we find for our functional

$$E\{F[\mathbf{r}(\tau)]|\mathbf{r}(1)=0\} = \int_{-\infty}^{+\infty}\cdots\int_{-\infty}^{+\infty} d\mu_p \prod_{i=1}^{p} E\{h_i[\mathbf{r}(\tau)]|\mathbf{r}(1)=0\}, \quad (3.29)$$

where now each Wiener integral on the right is defined on the time interval (0,1) and

$$h_i[\mathbf{r}(\tau)]=\exp\left[-\frac{\beta}{p}\int_0^1 U_3\left(\frac{\lambda}{(2\pi)^{1/2}}\left(\frac{\mathbf{r}(\tau)}{\sqrt{p}}+\mathbf{r}_{i-1} +\tau(\mathbf{r}_i-\mathbf{r}_{i-1})\right)\right)\right]. \quad (3.30)$$

Notice that in the last equation we have the factors β/p and $\lambda/\sqrt{p}$; hence each Wiener integral in the product on the right of Eq. (3.29) can be regarded as a Wiener integral like that in Eq. (3.15) except that now the temperature is higher by a factor p:

$$T'=pT. \quad (3.31)$$

We make use of this result by finding a high-temperature approximation for the Wiener integral and using Eq. (3.29) to extend its range of validity.

The high-temperature approximation to be used is the well-known Wigner-Kirkwood expansion[16,17] in powers of β and λ^2. The most useful form of this expansion for the following work will be the expansion for the quantity

$$G=\ln E\left\{\exp\left[-\beta\int_0^1 U_3\left(\frac{\lambda}{(2\pi)^{1/2}}\mathbf{r}(\tau)+\mathbf{r} +\tau(\mathbf{s}-\mathbf{r})\right)d\tau\right]\middle|\mathbf{r}(1)=0\right\}. \quad (3.32)$$

The expansion is carried out by introducing a parameter η multiplying the path, $\mathbf{r}(\tau)$, expanding G as a Taylor's series in η about $\eta=0$, and finally setting $\eta=1$ in the resulting series. Upon exchanging the order of Wiener integration and integration with respect to τ, the Wiener integrals have integrands which are products of the path variable $\mathbf{r}(\tau)$ and can be performed analytically.[18] The result to order T^{-2} is

$$G\simeq-\beta\int_0^1 U_3(\mathbf{r}+\tau(\mathbf{r}-\mathbf{s}))d\tau -\frac{\beta\lambda^2}{4\pi}\int_0^1 \nabla^2 U_3(\mathbf{r}+\tau(\mathbf{s}-\mathbf{r}))\tau(1-\tau)d\tau. \quad (3.33)$$

If Eq. (3.33) is used for the Wiener integrals on the right side of Eq. (3.29), one obtains the approximation

$$E\{F[\mathbf{r}(\tau)]|\mathbf{r}(1)=0\} \simeq\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} d\mu_p F[\mathbf{r}(\tau;p)]C_p, \quad (3.34)$$

where

$$C_p=\prod_{i=1}^{p}\exp\left[-\frac{\beta\lambda^2}{4\pi p^2}\int_0^1\nabla^2 U_3\left(\frac{\lambda}{(2\pi)^{1/2}}[\mathbf{r}_{i-1}+\tau(\mathbf{r}_i-\mathbf{r}_{i-1})] +(1,2,3)\right)\tau(1-\tau)d\tau\right]. \quad (3.35)$$

If, for each $i=1, 2, \cdots, p$, the exponential in Eq. (3.35) is replaced by the first two terms in its power series expansion, it is seen that to order p^{-2},

$$C_p=\prod_{i=1}^{p}\left[1-\frac{\beta\lambda^2}{4\pi p^2}\int_0^1\nabla^2 U_3\left(\frac{\lambda}{(2\pi)^{1/2}}[\mathbf{r}_{i-1}+\tau(\mathbf{r}_i-\mathbf{r}_{i-1})] +(1,2,3)\right)\tau(1-\tau)d\tau\right]. \quad (3.36)$$

Equation (3.34) with Eq. (3.36) for C_p is precisely the formula obtained by Fosdick,[13] who shows that if U_3 is sufficiently regular, the formula is correct to order p^{-2}. In the present application, where

$$U_3(1,2,3)=\sum_{i=j=1}^{3} V(r_{ij})$$

with $V(r)$ a (12-6) Lennard-Jones potential, the regularity conditions are not satisfied due to the singularity of $V(r)$ at $r=0$. It has been found from calculations of the two-particle density matrix elements that the use of Eq. (3.35) for C_p gives better results for small p than are obtained using Eq. (3.36) because at the singularities of U_3, Eq. (3.35) is bounded in absolute value while Eq. (3.36) is not. For this reason the exponential form for C_p will be used in the following calculations.

[16] J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), Chap. 6.

[17] T. Kihara, Y. Midzuno, and T. Shizume, J. Phys. Soc. Japan **10**, (1955).

[18] I. M. Gel'fand and A. M. Yaglom, J. Math. Phys. **1**, 48 (1960).

The Wigner-Kirkwood expansion can be carried out in the above manner to obtain approximations which are correct to order p^{-m} for any m under the appropriate regularity conditions on U. However, the increasing complexity of the C_p obtained in this way causes an increase in computing time which must be balanced against the decrease obtained by using a smaller value of p in Eq. (3.34). The special case $p=1$, which is equivalent to expanding the logarithm of the diagonal matrix element directly, is simplified by the fact that the τ integrals may be done immediately. The result of the expansion to order T^{-3} in this case is

$$\ln E\left\{\exp\left[-\beta\int_0^1 U_3\left(\frac{\lambda}{(2\pi)^{1/2}}[\mathbf{r}(\tau)+(\mathbf{1},\mathbf{2},\mathbf{3})]\right)\times d\tau\right]\middle|\mathbf{r}(1)=0\right\}\simeq-\beta U_3(\mathbf{1},\mathbf{2},\mathbf{3})-\frac{\beta\lambda^2}{24\pi}\nabla^2 U_3(\mathbf{1},\mathbf{2},\mathbf{3})+\frac{\beta^2\lambda^2}{48\pi}[\nabla U_3(\mathbf{1},\mathbf{2},\mathbf{3})]^2+\frac{\beta\lambda^4}{960\pi^2}\nabla^4 U_3(\mathbf{1},\mathbf{2},\mathbf{3}). \quad (3.37)$$

IV. EVALUATION OF $g_1(r_{12})$

A. Multiple Integral Approximation for $g_1(r_{12})$

The complexity of the three-particle functions entering into the calculation of $g_1(r_{12})$ can be reduced somewhat by consideration of the symmetries of the problem. Since there is no fixed external field, the density matrix must depend only on the relative positions of the particles, and hence the first simplification should be to separate out the c.m. motion. Define the usual c.m. and relative coordinates for a system of three particles (Fig. 1) by

$$\begin{aligned}\mathbf{r}_{\text{c.m.}}&=\tfrac{1}{3}(\mathbf{1}+\mathbf{2}+\mathbf{3}),\\ \mathbf{r}_{12}&=\mathbf{2}-\mathbf{1},\\ \mathbf{Q}&=\mathbf{3}-\tfrac{1}{2}(\mathbf{2}+\mathbf{1}).\end{aligned} \quad (4.1)$$

The Jacobian of this transformation is unity, and furthermore

$$\frac{\hbar^2}{2m}\sum_{i=1}^{3}\nabla_i^2=\frac{\hbar^2}{2m}(\tfrac{1}{3}\nabla_{\text{c.m.}}^2+2\nabla_{12}^2+\tfrac{3}{2}\nabla_Q^2) \quad (4.2)$$

so that the coordinates $\mathbf{r}_{\text{c.m.}}$, $\mathbf{r}_{12}$, and $\mathbf{Q}$ behave as independent particles of masses $3m$, $\frac{1}{2}m$, and $\frac{2}{3}m$, respectively.

Taking U_3 to be the sum of pair interactions, as in Eq. (2.10), and noting that $\mathbf{r}_{13}=\mathbf{3}-\mathbf{1}=\mathbf{Q}+\frac{1}{2}\mathbf{r}_{12}$ and $\mathbf{r}_{23}=\mathbf{3}-\mathbf{2}=\mathbf{Q}-\frac{1}{2}\mathbf{r}_{12}$, it is seen that $W_3(\mathbf{1},\mathbf{2},\mathbf{3})$ can be separated into the product of a c.m. factor which is independent of U_3 and a factor containing only the relative coordinates, $\mathbf{r}_{12}$ and $\mathbf{Q}$:

$$\begin{aligned}W_3(\mathbf{1},\mathbf{2},\mathbf{3})&=\langle\mathbf{1},\mathbf{2},\mathbf{3}|e^{-\beta H_3}|\mathbf{1},\mathbf{2},\mathbf{3}\rangle\\ &=\langle\mathbf{r}_{\text{c.m.}}|e^{-\beta K_{\text{c.m.}}}|\mathbf{r}_{\text{c.m.}}\rangle\langle\mathbf{r}_{12},\mathbf{Q}|e^{-\beta H_{\text{rel}}}|\mathbf{r}_{12},\mathbf{Q}\rangle,\end{aligned} \quad (4.3)$$

where

$$K_{\text{c.m.}}=-\hbar^2\nabla_{\text{c.m.}}^2/2(3m) \quad (4.4)$$

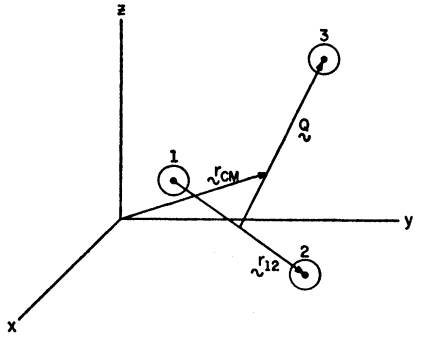

FIG. 1. Center-of-mass and relative coordinates for three particles.

is the kinetic energy of the c.m. motion and

$$H_{\text{rel}}=-\frac{\hbar^2\nabla_{12}^2}{2(m/2)}-\frac{\hbar^2\nabla_Q^2}{2(2m/3)}+U_3(\mathbf{r}_{12},\mathbf{Q}) \quad (4.5)$$

is the Hamiltonian operator for the relative coordinates. Since we associate a different mass with each particle coordinate, it is necessary to distinguish between the thermal wavelengths associated with these coordinates; we have

$$\lambda_{\text{c.m.}}=\lambda/\sqrt{3},\quad \lambda_{12}=\lambda\sqrt{2},\quad \lambda_Q=\lambda\sqrt{\tfrac{3}{2}}. \quad (4.6)$$

The normalization of the density matrix elements yields

$$\langle\mathbf{r}_{\text{c.m.}}|e^{-\beta K_{\text{c.m.}}}|\mathbf{r}_{\text{c.m.}}\rangle=1 \quad (4.7)$$

so that, using Eq. (3.15), the diagonal density matrix element can be expressed in terms of a Wiener integral over paths in the six-dimensional relative coordinate space of $\mathbf{r}_{12}$ and $\mathbf{Q}$:

$$W_3(\mathbf{1},\mathbf{2},\mathbf{3})=E\left\{\exp\left[-\beta\int_0^1 U_3(\mathbf{r}(\tau),\mathbf{q}(\tau);\mathbf{r}_{12},\mathbf{Q})d\tau\right]\middle|\times\mathbf{r}(1)=\mathbf{q}(1)=0\right\}, \quad (4.8)$$

where

$$\begin{aligned}U_3(\mathbf{r}(\tau),\mathbf{q}(\tau);\mathbf{r}_{12},\mathbf{Q})&=V((\lambda/\sqrt{\pi})\mathbf{r}(\tau)+\mathbf{r}_{12})\\ &+V[(\lambda/2\sqrt{\pi})(\sqrt{3}\mathbf{q}(\tau)+\mathbf{r}(\tau))+\mathbf{Q}+\tfrac{1}{2}\mathbf{r}_{12}]\\ &+V[(\lambda/2\sqrt{\pi})(\sqrt{3}\mathbf{q}(\tau)-\mathbf{r}(\tau))+\mathbf{Q}-\tfrac{1}{2}\mathbf{r}_{12}]\end{aligned} \quad (4.9)$$

and $V(r)$ is given by Eq. (2.9).

The c.m. motion can also be eliminated from the two-particle density matrix elements occurring in the expression for $g_1(r_{12})$, Eq. (2.6). A typical two-particle diagonal matrix element is

$$W_2(\mathbf{1},\mathbf{3})=E\left\{\exp\left[-\beta\int_0^1 V\left(\frac{\lambda}{\sqrt{\pi}}\mathbf{q}(\tau)+\mathbf{Q}+\tfrac{1}{2}\mathbf{r}_{12}\right)d\tau\right]\middle|\times\mathbf{q}(1)=0\right\}. \quad (4.10)$$

One can thus write

$$g_1(r_{12})=W_2(\mathbf{1},\mathbf{2})^{-1}$$
$$\times\int d^3\mathbf{Q}[E\{F_{123}(\mathbf{r}(\tau),\mathbf{q}(\tau))\,|\,\mathbf{r}(1)=\mathbf{q}(1)=0\}$$
$$-E\{F_{12}(\mathbf{r}(\tau))F_{13}(\mathbf{q}(\tau))\,|\,\mathbf{r}(1)=\mathbf{q}(1)=0\} \quad (4.11)$$
$$-E\{F_{12}(\mathbf{r}(\tau))F_{23}(\mathbf{q}(\tau))\,|\,\mathbf{r}(1)=\mathbf{q}(1)=0\}$$
$$+E\{F_{12}(\mathbf{r}(\tau))\,|\,\mathbf{r}(1)=0\}],$$

where

$$F_{123}(\mathbf{r}(\tau),\mathbf{q}(\tau))$$
$$=\exp\left[-\beta\int_0^1 U_3(\mathbf{r}(\tau),\mathbf{q}(\tau);\,\mathbf{r}_{12},\mathbf{Q})d\tau\right], \quad (4.12)$$

$$F_{12}(\mathbf{r}(\tau))=\exp\left[-\beta\int_0^1 V\left(\frac{\lambda}{\sqrt{\pi}}\mathbf{r}(\tau)+\mathbf{r}_{12}\right)d\tau\right], \quad (4.13)$$

$$F_{13}(\mathbf{q}(\tau))$$
$$=\exp\left[-\beta\int_0^1 V\left(\frac{\lambda}{\sqrt{\pi}}\mathbf{q}(\tau)+\mathbf{Q}+\tfrac{1}{2}\mathbf{r}_{12}\right)d\tau\right], \quad (4.14)$$

and

$$F_{23}(\mathbf{q}(\tau))$$
$$=\exp\left[-\beta\int_0^1 V\left(\frac{\lambda}{\sqrt{\pi}}\mathbf{q}(\tau)+\mathbf{Q}-\tfrac{1}{2}\mathbf{r}_{12}\right)d\tau\right]. \quad (4.15)$$

Since the expectation value is a linear operator, the quantity $g_1(r_{12})$ can then be written in terms of a single Wiener integral:

$$g_1(r_{12})=W_2(\mathbf{1},\mathbf{2})^{-1}\int d^3\mathbf{Q}E\{F_{123}(\mathbf{r}(\tau),\mathbf{q}(\tau))$$
$$-F_{12}(\mathbf{r}(\tau))F_{13}(\mathbf{q}(\tau))-F_{12}(\mathbf{r}(\tau))F_{23}(\mathbf{q}(\tau))$$
$$+F_{12}(\mathbf{r}(\tau))\,|\,\mathbf{r}(1)=\mathbf{q}(1)=0\}. \quad (4.16)$$

Now let

$$G(\mathbf{r}_{12},\mathbf{Q})=W_2(\mathbf{1},\mathbf{2})^{-1}[W_3(\mathbf{1},\mathbf{2},\mathbf{3})-W_2(\mathbf{1},\mathbf{2})W_2(\mathbf{1},\mathbf{3})$$
$$-W_2(\mathbf{1},\mathbf{2})W_2(\mathbf{2},\mathbf{3})+W_2(\mathbf{1},\mathbf{2})] \quad (4.17)$$

be the Q integrand of $g_1(r_{12})$. Noting that the interaction potentials depend only upon the magnitude of the separations, $\mathbf{r}_{12}$, $\mathbf{r}_{13}$, and $\mathbf{r}_{23}$ between the particles, it can be seen that if $\mathbf{r}_{12}$ is taken to lie along the axis of polar coordinates, $(\rho_Q,\theta_Q,\varphi_Q)$, for $\mathbf{Q}$, then $G(\mathbf{r}_{12},\mathbf{Q})$ is independent of the direction of the polar axis and of φ_Q. Thus one can write

$$g_1(r_{12})=2\pi\int_0^\pi \sin\theta_Q d\theta_Q\int_0^\infty \rho_Q{}^2 d\rho_Q G(r_{12},\rho_Q,\theta_Q). \quad (4.18)$$

The integral over the position of the third particle which appears in $g_1(r_{12})$ can thus be reduced to a twofold integral.

Equations (4.9) and (4.12)–(4.15) show that F_{123} can be written as a product:

$$F_{123}(\mathbf{r}(\tau),\mathbf{q}(\tau))=F_{12}(\mathbf{r}(\tau))F_{13}(\tfrac{1}{2}\sqrt{3}\mathbf{q}(\tau)+\tfrac{1}{2}\mathbf{r}(\tau))$$
$$\times F_{23}(\tfrac{1}{2}\sqrt{3}\mathbf{q}(\tau)-\tfrac{1}{2}\mathbf{r}(\tau)). \quad (4.19)$$

It should be noted that if $\mathbf{r}(\tau)$ and $\mathbf{q}(\tau)$ are conditional Wiener paths with $\mathbf{r}(0)=\mathbf{q}(0)=\mathbf{r}(1)=\mathbf{q}(1)=0$ and variance $[\tau(1-\tau)]^{1/2}$, then the linear combinations

$$\mathbf{s}_\pm(\tau)=\tfrac{1}{2}\sqrt{3}\mathbf{q}(\tau)\pm\tfrac{1}{2}\mathbf{r}(\tau) \quad (4.20)$$

are conditional Wiener paths with the same distributions as $\mathbf{r}(\tau)$ and $\mathbf{q}(\tau)$.

We now define the quantity

$$g_c(r_{12})=\int d^3\mathbf{Q}\; G_c(r_{12},\mathbf{Q}), \quad (4.21)$$

where

$$G_c(r_{12},\mathbf{Q})=W_2(\mathbf{1},\mathbf{2})^{-1}E\{F_{123}(\mathbf{r}(\tau),\mathbf{q}(\tau))$$
$$-F_{12}(\mathbf{r}(\tau))F_{13}(\mathbf{s}_+(\tau))-F_{12}(\mathbf{r}(\tau))F_{23}(\mathbf{s}_-(\tau))$$
$$+F_{12}(\mathbf{r}(\tau))\,|\,\mathbf{r}(1)=\mathbf{q}(1)=0\}. \quad (4.22)$$

Because of an oversight, the quantity $g_c(r_{12})$ rather than $g_1(r_{12})$ was originally calculated. The difference between these two quantities arises because, although the distributions of the arguments of F_{13} and F_{23} in Eq. (4.22) are the same as the distributions of the arguments of these functions in Eq. (4.16), the use of a linear combination of $\mathbf{q}(\tau)$ and $\mathbf{r}(\tau)$ as the argument of F_{13} in Eq. (4.22) introduces a spurious correlation between

$$F_{13}(\mathbf{s}_+(\tau))$$

and the functional $F_{12}(\mathbf{r}(\tau))$ multiplying it and similarly for the product $F_{12}F_{23}$. The two factors in these products should be uncorrelated since they arise from the product of two independent Wiener integrals. The function $g_1(r_{12})$ can be written as the sum of $g_c(r_{12})$ and a term which corrects for the unwanted correlation

$$g_1(r_{12})=g_c(r_{12})+g_e(r_{12}), \quad (4.23)$$

where

$$g_e(r_{12})=\int d^3\mathbf{Q}\; G_e(r_{12},\mathbf{Q})$$

and

$$G_e(r_{12},\mathbf{Q})=W_2(\mathbf{1},\mathbf{2})^{-1}E\{F_{12}(\mathbf{r}(\tau))[F_{13}(\mathbf{s}_+(\tau))-F_{13}(\mathbf{q}(\tau))$$
$$+F_{23}(\mathbf{s}_-(\tau))-F_{23}(\mathbf{q}(\tau))]\,|\,\mathbf{r}(1)=\mathbf{q}(1)=0\}. \quad (4.24)$$

The numerical calculation will thus involve separate evaluations of the terms $g_c(r_{12})$ and $g_e(r_{12})$.

Using Eq. (4.19), the quantity $G_c(r_{12},\mathbf{Q})$ can be written in the form

$$G_c(r_{12},\mathbf{Q})=W_2(\mathbf{1},\mathbf{2})^{-1}E\{F_{12}(\mathbf{r}(\tau))[F_{13}(\mathbf{s}_+(\tau))-1]$$
$$\times[F_{23}(\mathbf{s}_-(\tau))-1]\,|\,\mathbf{r}(1)=\mathbf{q}(1)=0\}. \quad (4.25)$$

The results of Sec. III C may now be used in order to

express $G_c(r_{12},\mathbf{Q})$ and $G_e(r_{12},\mathbf{Q})$ in terms of multiple Riemann integrals over a $6p$-dimensional space. Let $\mathbf{r}(\tau;p)$ be the broken straight-line path defined in Sec. III A with breakpoints at $\mathbf{r}_i$, $i=0, 1, \cdots, p$ and similarly for $\mathbf{q}(\tau;p)$ and let $\mathbf{s}_\pm(\tau;p)$ be the obvious extension of Eq. (4.20). Define the functions

$$D_{12}(\mathbf{r}(\tau;p))=F_{12}(\mathbf{r}(\tau;p))\exp\left[-\sum_{i=1}^{p}\frac{\beta\lambda^2}{2\pi p^2}\int_0^1 V''\left(\frac{\lambda}{\sqrt{\pi}}[\mathbf{r}_{i-1}+\tau(\mathbf{r}_i-\mathbf{r}_{i-1})]+\mathbf{r}_{12}\right)\tau(1-\tau)d\tau\right], \tag{4.26}$$

$$D_{13}(\mathbf{q}(\tau;p))=F_{13}(\mathbf{q}(\tau;p))\exp\left[-\sum_{i=1}^{p}\frac{\beta\lambda^2}{2\pi p^2}\int_0^1 V''\left(\frac{\lambda}{\sqrt{\pi}}[\mathbf{q}_{i-1}+\tau(\mathbf{q}_i-\mathbf{q}_{i-1})]+\mathbf{Q}+\tfrac{1}{2}\mathbf{r}_{12}\right)\tau(1-\tau)d\tau\right], \tag{4.27}$$

$$D_{23}(\mathbf{q}(\tau;p))=F_{23}(\mathbf{q}(\tau;p))\exp\left[-\sum_{i=1}^{p}\frac{\beta\lambda^2}{2\pi p^2}\int_0^1 V''\left(\frac{\lambda}{\sqrt{\pi}}[\mathbf{q}_{i-1}+\tau(\mathbf{q}_i-\mathbf{q}_{i-1})]+\mathbf{Q}-\tfrac{1}{2}\mathbf{r}_{12}\right)\tau(1-\tau)d\tau\right], \tag{4.28}$$

where

$$V''(\mathbf{r})=\nabla^2 V(\mathbf{r}). \tag{4.29}$$

The approximations for G_c and G_e are then

$$G_c(r_{12},\mathbf{Q})\simeq W_2(\mathbf{1},\mathbf{2})^{-1}\times\int_{-\infty}^{+\infty}\cdots\int_{-\infty}^{\infty}D_{12}(\mathbf{r}(\tau;p))[D_{13}(\mathbf{s}_+(\tau;p))-1]\times[D_{23}(\mathbf{s}_-(\tau;p))-1]d\mu_{rp}d\mu_{qp} \tag{4.30}$$

and

$$G_e(r_{12},\mathbf{Q})\simeq W_2(\mathbf{1},\mathbf{2})^{-1}\times\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}D_{12}(\mathbf{r}(\tau;p))\times[D_{13}(\mathbf{s}_+(\tau;p))-D_{13}(\mathbf{q}(\tau;p))+D_{23}(\mathbf{s}_-(\tau;p))-D_{23}(\mathbf{q}(\tau;p))]d\mu_{rp}d\mu_{qp}, \tag{4.31}$$

where

$$d\mu_{bp}=(2\pi)^{3/2}(2\pi/p)^{-3p/2}\times\exp\left[-\sum_{i=1}^{p}\frac{(\mathbf{b}_i-\mathbf{b}_{i-1})^2}{2(1/p)}\right]\prod_{i=1}^{p-1}d^3b_i, \tag{4.32}$$

with $b=r$ or q.

From the discussion in Sec. III C of the order of accuracy of Eq. (3.34) as an approximation for the Wiener integral, it is seen that the above approximations for G_c and G_e cannot be expected to be correct to more than order p^{-2}. The order of accuracy may be less due to the singularity of $V(r)$. In view of this fact, the integrals over τ in Eq. (4.29) may be replaced by their Simpson's rule approximations without decreasing the order of accuracy of these formulas. Let $\mathbf{r}^{(p)}$ and $\mathbf{q}^{(p)}$ be the $3p$-dimensional vectors $(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_p)$ and $(\mathbf{q}_1,\mathbf{q}_2,\cdots,\mathbf{q}_p)$, respectively, and let $\mathbf{s}_\pm{}^{(p)}$ be an obvious extension of Eq. (4.20). Recalling that $\mathbf{r}_0=\mathbf{q}_0=\mathbf{r}_p=\mathbf{q}_p=0$, then

$$G_c(r_{12},\mathbf{Q})=W_2(\mathbf{1},\mathbf{2})^{-1}\times\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}D_{12}(\mathbf{r}^{(p)})[D_{13}(\mathbf{s}_+{}^{(p)})-1]\times[D_{23}(\mathbf{s}_-{}^{(p)})-1]d\mu_{rp}d\mu_{qp} \tag{4.33}$$

and

$$G_e(r_{12},\mathbf{Q})=W_2(\mathbf{1},\mathbf{2})^{-1}\times\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}D_{12}(\mathbf{r}^{(p)})[D_{13}(\mathbf{s}_+{}^{(p)})-D_{13}(\mathbf{q}^{(p)})+D_{23}(\mathbf{s}_-{}^{(p)})-D_{23}(\mathbf{q}^{(p)})]d\mu_{rp}d\mu_{qp}, \tag{4.34}$$

where

$$D_{12}(\mathbf{r}^{(p)})=\exp\left\{\frac{-\beta}{6p}\sum_{i=1}^{p}\left[V\left(\frac{\lambda}{\sqrt{\pi}}\mathbf{r}_{i-1}+\mathbf{r}_{12}\right)+4V\left(\frac{\lambda}{\sqrt{\pi}}\tfrac{1}{2}(\mathbf{r}_i+\mathbf{r}_{i-1})+\mathbf{r}_{12}\right)+V\left(\frac{\lambda}{\sqrt{\pi}}\mathbf{r}_i+\mathbf{r}_{12}\right)+\frac{\lambda^2}{2\pi p}V''\left(\frac{\lambda}{\sqrt{\pi}}\tfrac{1}{2}(\mathbf{r}_i+\mathbf{r}_{i-1})+\mathbf{r}_{12}\right)\right]\right\}, \tag{4.35}$$

$$D_{\{23\}}^{\{13\}}(\mathbf{q}^{(p)})=\exp\left\{\frac{-\beta}{6p}\sum_{i=1}^{p}\left[V\left(\frac{\lambda}{\sqrt{\pi}}\mathbf{q}_{i-1}+\mathbf{Q}\pm\tfrac{1}{2}\mathbf{r}_{12}\right)+4V\left(\frac{\lambda}{\sqrt{\pi}}\tfrac{1}{2}(\mathbf{q}_i+\mathbf{q}_{i-1})+\mathbf{Q}\pm\tfrac{1}{2}\mathbf{r}_{12}\right)+V\left(\frac{\lambda}{\sqrt{\pi}}\mathbf{q}_i+\mathbf{Q}\pm\tfrac{1}{2}\mathbf{r}_{12}\right)+\frac{\lambda^2}{2\pi p}V''\left(\frac{\lambda}{\sqrt{\pi}}\tfrac{1}{2}(\mathbf{q}_i+\mathbf{q}_{i-1})+\mathbf{Q}\pm\tfrac{1}{2}\mathbf{r}_{12}\right)\right]\right\}, \tag{4.36}$$

where the plus sign in the last equation corresponds to D_{13} and the minus sign to D_{23}.

B. Monte Carlo Evaluation of the Multiple Integrals

It has been indicated above that the $6(p-1)$-fold integrals appearing in Eqs. (4.33) and (4.34) can be evaluated by a Monte Carlo procedure. The quantities $d\mu_{rp}$ and $d\mu_{qp}$ have the properties of probability densities on $3(p-1)$-dimensional spaces since the integral of either of these quantities over any $3(p-1)$-dimensional Borel set is non-negative and the integral over the whole space is unity. The simplest Monte Carlo scheme for evaluating the multiple integrals is to choose a sequence of independent $6p$-dimensional vectors $(\mathbf{r}_l^{(p)},\mathbf{q}_l^{(p)})$, $\mathbf{r}_{p,l}=\mathbf{q}_{p,l}=0$, $l=1, 2, \cdots, M$, with probability $d\mu_{rp}d\mu_{qp}$, evaluate the integrands of G_c and G_e for each vector, and average over the set of M vectors. If one lets $I_c(\mathbf{r}^{(p)},\mathbf{q}^{(p)})$ and $I_e(\mathbf{r}^{(p)},\mathbf{q}^{(p)})$ represent the integrands of G_c and G_e, respectively, then by the law of large numbers

$$\lim_{M\to\infty}\frac{1}{M}\sum_{l=1}^{M} I_c(\mathbf{r}_l^{(p)},\mathbf{q}_l^{(p)})$$

$$=\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} I_c(\mathbf{r}^{(p)},\mathbf{q}^{(p)})d\mu_{rp}d\mu_{qp}=G_c, \quad (4.37)$$

with probability 1, and similarly for G_e.

Vectors $\mathbf{r}^{(p)}$ with distribution $d\mu_{rp}$ can be generated from $3(p-1)$-independent, normally distributed random variables by means of an interpolation formula.[19] The end-point conditions require that $\mathbf{r}_0=\mathbf{r}_p=0$, and the other $3(p-1)$ coordinates can be generated by the equation

$$\mathbf{r}_i=\frac{\mathbf{r}_{i-1}(1-i/p)}{1-(i-1)/p}+\xi_i\left[\frac{(1/p)(1-i/p)}{1-(i-1)/p}\right]^{1/2}, \quad (4.38)$$

for $i=1, 2, \cdots, p-1$, where ξ_i is a three-dimensional random variable, the coordinate variables of which are normally distributed with mean 0 and variance 1. The vectors $\mathbf{q}_l^{(p)}$ can be generated by the same procedure. This straightforward Monte Carlo scheme has been used[1] to compute the two-particle density matrix element, $W_2(1,2)$.

The three-particle functions G_c and G_e are well adapted to a more sophisticated Monte Carlo procedure which should have a smaller variance than the straightforward scheme, thereby reducing the number of samples necessary for a given accuracy. This procedure is the importance sampling technique first introduced by Metropolis *et al.*[20] for evaluating averages over the Boltzmann distribution. The following discussion is, to some extent, an extension to a continuous sample space of the description of this technique given by Hammersly and Handscomb.[21]

Let G_c and G_e both be typified by

$$G_d(r_{12},\mathbf{Q})=\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} I(\mathbf{r}^{(p)},\mathbf{q}^{(p)})d\mu_{rp}d\mu_{qp}, \quad (4.39)$$

where

$$I(\mathbf{r}^{(p)},\mathbf{q}^{(p)})=\frac{D_{12}(\mathbf{r}^{(p)})}{W_2(1,2)}L(\mathbf{r}^{(p)},\mathbf{q}^{(p)}), \quad (4.40)$$

and let

$$P(\mathbf{r}^{(p)})=\frac{D_{12}(\mathbf{r}^{(p)})}{W_2(1,2)}. \quad (4.41)$$

This factor, which appears in the integrands of both G_c and G_e, in the basis for the importance sampling procedure. It is seen from the definition, Eq. (4.35), of $D_{12}(\mathbf{r}^{(p)})$ that this quantity is non-negative. Furthermore, to the order of the approximation used in Eqs. (4.30) and (4.31), one can write

$$W_2(1,2)=\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} D_{12}(\mathbf{r}^{(p)})d\mu_{rp}, \quad (4.42)$$

and hence

$$\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} P(\mathbf{r}^{(p)})d\mu_{rp}=1. \quad (4.43)$$

Thus $P(\mathbf{r}^{(p)})d\mu_{rp}$ has the properties of a probability density in the $3(p-1)$-dimensional space of $\mathbf{r}^{(p)}$. If vectors $\mathbf{r}^{(p)}$ and $\mathbf{q}^{(p)}$ are generated with probability $P(\mathbf{r}^{(p)})d\mu_{rp}d\mu_{qp}$ and $L(\mathbf{r}^{(p)},\mathbf{q}^{(p)})$ is averaged over the vectors so generated, the average will approach G_d with probability one as the number of samples becomes infinite. Qualitatively, the advantage of this scheme over straightforward sampling is that some of the variation in the integrand $I(\mathbf{r}^{(p)},\mathbf{q}^{(p)})$ has been absorbed into the probability density. The variance reduction is indicated intuitively by the fact that vectors $\mathbf{r}^{(p)}$ for which $D_{12}(\mathbf{r}^{(p)})$ and hence $I(\mathbf{r}^{(p)},\mathbf{q}^{(p)})$ are small will be generated with low probability by the importance sampling procedure.

It remains to show how vectors $\mathbf{r}^{(p)}$ can be generated with probability $P(\mathbf{r}^{(p)})d\mu_{rp}$. This is accomplished by producing a Markov chain, $\{\mathbf{r}_t^{(p)}, t=1, 2, 3, \cdots\}$, with a stationary transition probability function $\rho(\mathbf{r}_{t+1}^{(p)}\,|\,\mathbf{r}_t^{(p)})$, satisfying

$$\int_J\cdots\int P(\mathbf{r}'^{(p)})d\mu_{r'p}=\int_J\cdots\int\int_{-\infty}^{\infty}\cdots$$

$$\times\int_{-\infty}^{\infty}\rho(\mathbf{r}'^{(p)}\,|\,\mathbf{r}^{(p)})P(\mathbf{r}^{(p)})d\mu_{rp}d^{3(p-1)}\mathbf{r}', \quad (4.44)$$

where

$$d^{3(p-1)}\mathbf{r}'=d^3\mathbf{r}_1'd^3\mathbf{r}_2'\cdots d^3\mathbf{r}_{p-1}', \quad (4.45)$$

[19] P. Levy, *Memorial des Sciences Mathematiques* (Gauthier Villars, Paris, 1954), Fascicule 126.

[20] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).

[21] J. M. Hammersly and D. C. Handscomb, *Monte Carlo Methods* (John Wiley & Sons, Inc., New York, 1954).

and where J is any set in the $3(p-1)$-dimensional space of $\mathbf{r}'^{(p)}$ which is measurable with respect to $P(\mathbf{r}'^{(p)})d\mu_{r'p}$. The law of large numbers for Markov chains[22] states that if the Markov chain, $\{\mathbf{r}_t^{(p)}\}$, is such that Eq. (4.44) is satisfied and if there is only one ergodic set, then

$$\lim_{M\to\infty}\frac{1}{M}\sum_{t=1}^{M}L(\mathbf{r}_t^{(p)},\mathbf{q}^{(p)})$$

$$=\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}L(\mathbf{r}^{(p)},\mathbf{q}^{(p)})P(\mathbf{r}^{(p)})d\mu_{rp} \quad (4.46)$$

for almost all realizations of the Markov chain. Thus if $L(\mathbf{r}^{(p)},\mathbf{q}^{(p)})$ is averaged over $\mathbf{r}^{(p)}$ produced by the Markov chain and $\mathbf{q}^{(p)}$ generated by the straightforward Monte Carlo scheme, the result will be an approximation for G_d.

We must now demonstrate a procedure which will generate a Markov chain which satisfies the above conditions. It will be convenient for the rest of this section to deal with only the x components, x_i, of each three-dimensional vector $\mathbf{r}_i$. All quantities defined above in terms of the $3p$-dimensional vector, $\mathbf{r}^{(p)}=(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_p)$, $\mathbf{r}_0=\mathbf{r}_p=0$, are assumed to have analogous definitions in terms of the p-dimensional vector $\mathbf{x}=(x_1,x_2,\cdots,x_p)$, $x_0=x_p=0$. The generalization to three space components will be obvious, and the notation will be much simplified if we assume all vectors to be p-dimensional and drop the use of p as a superscript or subscript to indicate dimensionality for the rest of this section.

Let $w(\mathbf{x})$ be defined by

$$d\mu_x=w(\mathbf{x})d^{p-1}\mathbf{x}, \quad d^{p-1}\mathbf{x}=dx_1dx_2\cdots dx_{p-1}, \quad (4.47)$$

so that

$$w(\mathbf{x})=(2\pi)^{1/2}\left(\frac{p}{2\pi}\right)^{p/2}\exp[-\tfrac{1}{2}p\sum_{i=1}^{p}(x_i-x_{i-1})^2]. \quad (4.48)$$

A transition probability function $\rho(\mathbf{x}'|\mathbf{x})$ is then needed to satisfy Eq. (4.44), which now becomes

$$\int_J\cdots\int P(\mathbf{x}')w(\mathbf{x}')d^{p-1}\mathbf{x}'=\int_J\cdots\int\int_{-\infty}^{\infty}\cdots \times\int_{-\infty}^{\infty}\rho(\mathbf{x}'|\mathbf{x})P(\mathbf{x})w(\mathbf{x})d^{p-1}\mathbf{x}d^{p-1}\mathbf{x}'. \quad (4.49)$$

First define the function

$$\rho^*(\mathbf{x}'|\mathbf{x})$$

$$=\left(\frac{p}{\pi}\right)^{p-1/2}\exp[-p\sum_{i=1}^{p-1}(x_i'-\tfrac{1}{2}(x_{i-1}'+x_{i+1}))^2]. \quad (4.50)$$

This function satisfies the criteria for a transition probability function, since

$$\rho^*(\mathbf{x}'|\mathbf{x})\geq 0 \quad (4.51)$$

and

$$\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\rho^*(\mathbf{x}'|\mathbf{x})d^{p-1}\mathbf{x}'=1. \quad (4.52)$$

The function $\rho(\mathbf{x}'|\mathbf{x})$ is now defined by

$$\rho(\mathbf{x}'|\mathbf{x})=\rho^*(\mathbf{x}'|\mathbf{x})(P(\mathbf{x}')/P(\mathbf{x})), \quad \text{if} \quad P(\mathbf{x}')<P(\mathbf{x})$$

$$=\rho^*(\mathbf{x}'|\mathbf{x})+\delta(\mathbf{x}',\mathbf{x})\int_{\{\mathbf{x}''|P(\mathbf{x}'')<P(\mathbf{x})\}}\cdots\int\rho^*(\mathbf{x}''|\mathbf{x})\left[1-\frac{P(\mathbf{x}'')}{P(\mathbf{x})}\right]d^{p-1}\mathbf{x}'', \quad \text{if} \quad P(\mathbf{x}')\geq P(\mathbf{x}) \quad (4.53)$$

where $\{\mathbf{x}''|P(\mathbf{x}'')<P(\mathbf{x})\}$ is the set of all $\mathbf{x}''$ such that $P(\mathbf{x}'')<P(\mathbf{x})$ and δ is the Dirac δ function. The function $\rho(\mathbf{x}'|\mathbf{x})$ is a valid transition function, since it is non-negative and satisfies

$$\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\rho(\mathbf{x}'|\mathbf{x})d^{p-1}\mathbf{x}'$$

$$=\int_{\{\mathbf{x}'|P(\mathbf{x}')\geq P(\mathbf{x})\}}\cdots\int\left[\rho^*(\mathbf{x}'|\mathbf{x})+\delta(\mathbf{x}',\mathbf{x})\int_{\{\mathbf{x}''|P(\mathbf{x}'')<P(\mathbf{x})\}}\cdots\int\rho^*(\mathbf{x}''|\mathbf{x})\left(1-\frac{P(\mathbf{x}'')}{P(\mathbf{x})}\right)d^{p-1}\mathbf{x}''\right]d^{p-1}\mathbf{x}' \quad (4.54)$$

$$+\int_{\{\mathbf{x}'|P(\mathbf{x}')<P(\mathbf{x})\}}\cdots\int\rho^*(\mathbf{x}'|\mathbf{x})\frac{P(\mathbf{x}')}{P(\mathbf{x})}d^{p-1}\mathbf{x}'$$

$$=\int_{\{\mathbf{x}'|P(\mathbf{x}')\geq P(\mathbf{x})\}}\cdots\int\rho^*(\mathbf{x}'|\mathbf{x})d^{p-1}\mathbf{x}'+\int_{\{\mathbf{x}''|P(\mathbf{x}'')<P(\mathbf{x})\}}\cdots\int\rho^*(\mathbf{x}'|\mathbf{x})d^{p-1}\mathbf{x}''$$

$$=1.$$

[22] J. L. Doob, *Stochastic Processes* (John Wiley & Sons, Inc., New York, 1953), Chap. 5.

In order to show that $\rho(\mathbf{x}'|\mathbf{x})$ satisfies Eq. (4.49), it will be useful to define the "transpose" $\mathbf{x}^T$ of a vector $\mathbf{x}=(x_1,x_2,\cdots,x_p)$, $x_0=x_p=0$, by $x_i{}^T=x_{p-i}$, $i=0, 1, \cdots, p$. From Eqs. (4.32), (4.41), and (4.48), it can be seen that

$$w(\mathbf{x})=w(\mathbf{x}^T) \tag{4.55}$$

and

$$P(\mathbf{x})=P(\mathbf{x}^T). \tag{4.56}$$

Since $P(\mathbf{x})w(\mathbf{x})d^{p-1}\mathbf{x}=P(\mathbf{x}^T)w(\mathbf{x}^T)d^{p-1}\mathbf{x}^T$, it follows that Eq. (4.49) is equivalent to

$$\int_J\cdots\int P(\mathbf{x}')w(\mathbf{x}')d^{p-1}\mathbf{x}'=\int_J\cdots\int\tfrac{1}{2}[P(\mathbf{x}')w(\mathbf{x}')+P(\mathbf{x}'^T)w(\mathbf{x}'^T)]d^{p-1}\mathbf{x}'$$

$$=\int_J\cdots\int\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\tfrac{1}{2}[\rho(\mathbf{x}'|\mathbf{x})+\rho(\mathbf{x}'^T|\mathbf{x}^T)]P(\mathbf{x})w(\mathbf{x})d^{p-1}\mathbf{x}d^{p-1}\mathbf{x}'. \tag{4.57}$$

As a lemma for the proof of Eq. (4.57), it is shown in Appendix A that

$$\rho^*(\mathbf{x}'|\mathbf{x})w(\mathbf{x})=\rho^*(\mathbf{x}^T|\mathbf{x}'^T)w(\mathbf{x}'^T). \tag{4.58}$$

To prove that $\rho(\mathbf{x}'|\mathbf{x})$ satisfies Eq. (4.57), it is sufficient to show that

$$\begin{aligned}v(\mathbf{x}')&=\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}[\rho(\mathbf{x}'|\mathbf{x})+\rho(\mathbf{x}'^T|\mathbf{x}^T)]P(\mathbf{x})w(\mathbf{x})d^{p-1}\mathbf{x}\\&=2P(\mathbf{x}')w(\mathbf{x}'),\end{aligned} \tag{4.59}$$

where $v(\mathbf{x}')$ is defined by the above equation. Using the definition [Eq. (4.53)] of $\rho(\mathbf{x}'|\mathbf{x})$ and keeping in mind that $P(\mathbf{x})$ and $w(\mathbf{x})$ are invariant under transposition of the coordinates of $\mathbf{x}$, it follows that

$$v(\mathbf{x}')=\int_{\{\mathbf{x}|P(\mathbf{x})>P(\mathbf{x}')\}}\cdots\int[\rho^*(\mathbf{x}'|\mathbf{x})+\rho^*(\mathbf{x}'^T|\mathbf{x}^T)]P(\mathbf{x}')w(\mathbf{x})d^{p-1}\mathbf{x}+\int_{\{\mathbf{x}|P(\mathbf{x})<P(\mathbf{x}')\}}\cdots\int\Big\{[\rho^*(\mathbf{x}'|\mathbf{x})+\rho^*(\mathbf{x}'^T|\mathbf{x}^T)]$$

$$+\delta(\mathbf{x}',\mathbf{x})\int_{\{\mathbf{x}''|P(\mathbf{x}'')\le P(\mathbf{x})\}}\cdots\int[\rho^*(\mathbf{x}''|\mathbf{x})+\rho^*(\mathbf{x}''^T|\mathbf{x}^T)][1-(P(\mathbf{x}'')/P(\mathbf{x}))]d^{p-1}\mathbf{x}''\Big\}P(\mathbf{x})w(\mathbf{x})d^{p-1}\mathbf{x}, \tag{4.60}$$

where the integral multiplying the δ function can be extended over the set $\{\mathbf{x}''|P(\mathbf{x}'')\le P(\mathbf{x})\}$ since the integrand vanishes for $P(\mathbf{x}'')=P(\mathbf{x})$. Performing the integral over the δ function $v(\mathbf{x}')$ becomes

$$v(\mathbf{x}')=P(\mathbf{x}')\int_{\{\mathbf{x}|P(\mathbf{x})>P(\mathbf{x}')\}}\cdots\int[\rho^*(\mathbf{x}'|\mathbf{x})+\rho^*(\mathbf{x}'^T|\mathbf{x}^T)]w(\mathbf{x})d^{p-1}\mathbf{x}$$

$$+\int_{\{\mathbf{x}|P(\mathbf{x})\le P(\mathbf{x}')\}}\cdots\int[\rho^*(\mathbf{x}'|\mathbf{x})+\rho^*(\mathbf{x}'^T|\mathbf{x}^T)]P(\mathbf{x})w(\mathbf{x})d^{p-1}\mathbf{x}$$

$$+\int_{\{\mathbf{x}''|P(\mathbf{x}'')\le P(\mathbf{x}')\}}\cdots\int[\rho^*(\mathbf{x}''|\mathbf{x}')+\rho^*(\mathbf{x}''^T|\mathbf{x}'^T)]P(\mathbf{x}')w(\mathbf{x}')d^{p-1}\mathbf{x}''$$

$$-\int_{\{\mathbf{x}''|P(\mathbf{x}'')\le P(\mathbf{x}')\}}\cdots\int[\rho^*(\mathbf{x}''|\mathbf{x}')+\rho^*(\mathbf{x}''^T|\mathbf{x}'^T)]P(\mathbf{x}'')w(\mathbf{x}')d^{p-1}\mathbf{x}''. \tag{4.61}$$

Applying Eq. (4.58) to the first and second terms in the last equation, one finds that the second and fourth terms cancel and there remains

$$v(\mathbf{x}')=P(\mathbf{x}')w(\mathbf{x}')\int_{\{\mathbf{x}|P(\mathbf{x})>P(\mathbf{x}')\}}\cdots\int[\rho^*(\mathbf{x}^T|\mathbf{x}'^T)+\rho^*(\mathbf{x}|\mathbf{x}')]d^{p-1}\mathbf{x}$$

$$+P(\mathbf{x}')w(\mathbf{x}')\int_{\{\mathbf{x}''|P(\mathbf{x}'')\le P(\mathbf{x}')\}}\cdots\int[\rho^*(\mathbf{x}''|\mathbf{x}')+\rho^*(\mathbf{x}''^T|\mathbf{x}'^T)]d^{p-1}\mathbf{x}''. \tag{4.62}$$

Since the sets over which the two integrations are carried out are complements, the integrals may be combined into an integral over the whole space. Bearing in mind that the variable of integration, $\mathbf{x}$, may just as well be replaced by $\mathbf{x}^T$, one obtains the result

$$v(\mathbf{x}')=P(\mathbf{x}')w(\mathbf{x}')\Big[\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\rho^*(\mathbf{x}|\mathbf{x}')d^{p-1}\mathbf{x} + \int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\rho^*(\mathbf{x}^T|\mathbf{x}'^T)d^{p-1}\mathbf{x}^T\Big] \quad (4.63)$$
$$=2P(\mathbf{x}')w(\mathbf{x}'),$$

where the final step makes use of the normalization condition on $\rho^*(\mathbf{x}|\mathbf{x}')$ [Eq. (4.52)].

It can be seen from the definitions of $\rho(\mathbf{x}'|\mathbf{x})$ and $\rho^*(\mathbf{x}'|\mathbf{x})$ that there can be only one ergodic class since the probability of the one step transition from any vector, $\mathbf{x}$, to a vector in the volume $d^{p-1}\mathbf{x}'$ about $\mathbf{x}'$ is strictly greater than zero for all vectors, $\mathbf{x}'$, satisfying $P(\mathbf{x}')>0$. Equation (4.46) is thus satisfied for the $\rho(\mathbf{x}'|\mathbf{x})$ defined above, and a procedure which generates a Markov chain with this transition function is a valid importance sampling scheme for the present problem. The transition from a vector $\mathbf{x}$ of the chain to the next vector $\mathbf{x}'$ can be made using $p-1$ normally distributed random variables and one uniformly distributed random variable. Let

$$x_0''=x_p''=0,$$
$$x_i''=\sqrt{(1/2p)}\xi_i+\tfrac{1}{2}(x_{i-1}''+x_{i+1}), \quad i=1, 2, \cdots, p-1 \quad (4.64)$$

where ξ_i, $i=1, 2, \cdots, p-1$, are normally distributed random variables with mean 0 and variance 1. If $P(\mathbf{x}'')<P(\mathbf{x})$, generate a random variable ζ which is uniformly distributed on the interval (0,1) and set

$$\mathbf{x}'=\mathbf{x}'', \quad \text{if} \quad \zeta<P(\mathbf{x}'')/P(\mathbf{x}) \quad (4.65)$$
$$=\mathbf{x}, \quad \text{otherwise.}$$

If $P(\mathbf{x}'')\geq P(\mathbf{x})$, set

$$\mathbf{x}'=\mathbf{x}''. \quad (4.66)$$

It can be seen that the probability of $\mathbf{x}''$ given $\mathbf{x}$ is $\rho^*(\mathbf{x}''|\mathbf{x})$ while the probability of $\mathbf{x}'$ given $\mathbf{x}$ is $\rho(\mathbf{x}'|\mathbf{x})$.

C. Integration over the Position of the Third Particle

Besides the $6(p-1)$-fold integration arising from the approximation to the Wiener integral, it is also necessary to perform the twofold integration over the position of the third particle. This is the integration over (ρ_Q,θ_Q) in Eq. (4.18). Since a large number of Monte Carlo samples are necessary for reasonable accuracy in the Wiener integral approximation, it is impractical to compute $G_c(r_{12},\mathbf{Q})$ and $G_e(r_{12},\mathbf{Q})$ at each point of a two-dimensional grid in Q and apply a standard numerical integration technique. If we perform this last twofold integration by a Monte Carlo technique, however, the sampling may be combined with that for the $6(p-1)$-fold integrals. The procedure then is to generate M samples $[(\mathbf{r}_t^{(p)},\mathbf{q}_t^{(p)},\mathbf{Q}_t), t=1, 2, \cdots, M]$ and to form

$$g_d(r_{12};M)=\frac{1}{M}\sum_{t=1}^{M}L(\mathbf{r}_t^{(p)},\mathbf{q}_t^{(p)},\mathbf{Q}_t)\Gamma^{-1}(\mathbf{Q}_t), \quad (4.67)$$

where d stands for e or c, L is defined by Eq. (4.40), $\mathbf{r}_t^{(p)}$ is generated from the Markov chain, $\mathbf{q}_t^{(p)}$ is produced by the straightforward sampling scheme for Wiener paths, and $\mathbf{Q}_t=(\rho_Q,\theta_Q,0)$ is picked according to a two-dimensional distribution

$$\Gamma(\mathbf{Q})d^2\mathbf{Q}=\Gamma_\rho(\rho_Q)\Gamma_\theta(\theta_Q)d\rho_Q d\theta_Q \quad (4.68)$$

or

$$\Gamma(\mathbf{Q})d^2\mathbf{Q}=\Gamma_x(Q_x)\Gamma_y(Q_y)dQ_x dQ_y, \quad (4.69)$$

in Cartesian coordinates. If Eq. (4.69) is used, a factor of $\frac{1}{2}$ must be included in L if the range of Q_y is $-\infty<Q_y<\infty$. One will then have from the law of large numbers that

$$\lim_{M\to\infty} g_d(r_{12};M)=g_d(r_{12}) \quad (4.70)$$

with probability 1, where $g_d(r_{12})$ represents either $g_c(r_{12})$ or $g_e(r_{12})$ depending on the form of the integrand $L(\mathbf{r}^{(p)},\mathbf{q}^{(p)},\mathbf{Q})$.

Including the integration over $\mathbf{Q}$ in the Monte Carlo scheme will increase the number of samples necessary for a given accuracy since $L(\mathbf{r}^{(p)},\mathbf{q}^{(p)},\mathbf{Q})$ will have an increased variation on being taken as a function of $\mathbf{Q}$ as well as of $\mathbf{r}^{(p)}$ and $\mathbf{q}^{(p)}$. The variation with respect to $\mathbf{Q}$ turns out to be the dominant part of the variance of the Monte Carlo scheme at moderate temperatures with the distributions of $\mathbf{r}^{(p)}$ and $\mathbf{q}^{(p)}$ being fairly sharply peaked about $\mathbf{r}^{(p)}=\mathbf{q}^{(p)}\equiv 0$. This variance in $\mathbf{Q}$ can be reduced somewhat by making use of the latitude that exists in the choice of the distribution $\Gamma(\mathbf{Q})$. Qualitatively, the variance with respect to $\mathbf{Q}$ will be reduced if the global behavior of $\Gamma(\mathbf{Q})$ is similar to that of $L(\mathbf{r}^{(p)},\mathbf{q}^{(p)},\mathbf{Q})$ as a function of $\mathbf{Q}$. Since L is also a function of $\mathbf{r}^{(p)}$ and $\mathbf{q}^{(p)}$, computing time restrictions indicate that it would probably not be worthwhile to develop an elaborate importance sampling scheme in the variable $\mathbf{Q}$. The choice of $\Gamma(\mathbf{Q})$ will therefore be restricted to distributions which can be generated easily from uniform or normally distributed pseudo random numbers.

In order to get an idea of the form of $L(\mathbf{r}^{(p)},\mathbf{q}^{(p)},\mathbf{Q})$ as a function of $\mathbf{Q}$, one must consider $g_c(r_{12})$ and $g_e(r_{12})$ separately. For the function $g_c(r_{12})$ the integrand is

$$L_c(\mathbf{r}^{(p)},\mathbf{q}^{(p)},\mathbf{Q})=[D_{13}(\mathbf{s}_+^{(p)})-1] \times[D_{23}(\mathbf{s}_-^{(p)})-1], \quad (4.71)$$

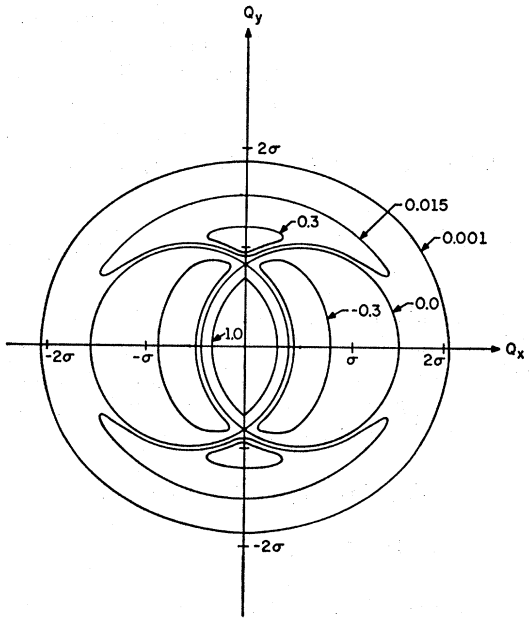

FIG. 2. $f_{13}(r_{12},\mathbf{Q})\times f_{23}(r_{12},\mathbf{Q})$ as a function of $\mathbf{Q}$ for $r_{12}=1.1\sigma$ and $T=20°$K.

while for $g_e(r_{12})$ the integrand is

$$L_e(\mathbf{r}^{(p)},\mathbf{q}^{(p)},\mathbf{Q})=[D_{13}(\mathbf{s}_+{}^{(p)})-D_{13}(\mathbf{q}^{(p)}) +D_{23}(\mathbf{s}_-{}^{(p)})-D_{23}(\mathbf{q}^{(p)})]. \quad (4.72)$$

Since the distributions of $\mathbf{r}^{(p)}$ and $\mathbf{q}^{(p)}$ are peaked near $\mathbf{r}^{(p)}=\mathbf{q}^{(p)}\equiv 0$, the function

$$L_c(0,0,\mathbf{Q})=[\exp\{-\beta V(\mathbf{Q}+\tfrac{1}{2}\mathbf{r}_{12}) -(\beta\lambda^2/2\pi p)V''(\mathbf{Q}+\tfrac{1}{2}\mathbf{r}_{12})\}-1][\exp\{-\beta V(\mathbf{Q}-\tfrac{1}{2}\mathbf{r}_{12}) -(\beta\lambda^2/2\pi p)V''(\mathbf{Q}-\tfrac{1}{2}\mathbf{r}_{12})\}-1] \quad (4.73)$$

gives some idea of the variation of L_c with respect to $\mathbf{Q}$. Equation (4.73) is just the second-order Wigner-Kirkwood approximation to the classical cluster function

$$f_{13}f_{23}=(e^{-V(\mathbf{r}_{13})}-1)(e^{-V(\mathbf{r}_{23})}-1), \quad (4.74)$$

so that the behavior of this classical function with respect to $\mathbf{Q}$ will give some idea of the global structure of L_c as a function of $\mathbf{Q}$.

Figure 2 shows a rough contour map of $f_{13}f_{23}$ for $T=20°$K and $r_{12}=1.1\sigma$, where σ is defined by Eq. (2.10). The structure of this cluster function is too complex to attempt to fit it in detail with a simple probability distribution. It can be seen, however, that the structure of the function is centered about $\mathbf{Q}=0$ and that the function becomes negligible at a distance of two or three times σ in the Q_y direction and at a slightly larger distance in the Q_x direction. A reasonable sampling distribution for such a function might be a two-dimensional normal distribution with a standard deviation on the order of σ in the Q_y direction and a standard deviation in the Q_x direction on the order of $\sigma+\text{const}\times r_{12}$. The distribution used for the integration over $\mathbf{Q}$ in the numerical computations to follow was

$$\Gamma_c(\mathbf{Q})d^2\mathbf{Q}=((2\pi)^{1/2}\gamma_x)^{-1}e^{-Q_x^2/2\gamma_x^2} \times((2\pi)^{1/2}\gamma_y)^{-1}e^{-Q_y^2/2\gamma_y^2}dQ_x dQ_y, \quad (4.75)$$

where the standard deviations γ_x and γ_y were chosen empirically to minimize the variance of $g_c(r_{12};M)$ for a small value of M.

If one tries to take $\mathbf{r}^{(p)}=\mathbf{q}^{(p)}\equiv 0$ in $L_e(\mathbf{r}^{(p)},\mathbf{q}^{(p)},\mathbf{Q})$, the function vanishes. In fact this function vanishes to order T^{-3} in the Wigner-Kirkwood expansion, and it is thus to be expected that the correction term $g_e(r_{12})$ will be negligible except at low temperatures and for small r_{12}. In order to find an efficient sampling scheme for $g_e(r_{12})$, advantage can be taken of several symmetries of the integrand. The function g_e can be written as the sum of two integrals:

$$g_e(r_{12})=g_e{}^{(1)}(r_{12})+g_e{}^{(2)}(r_{12}), \quad (4.76)$$

where

$$g_e{}^{(1)}(r_{12})=\frac{1}{W_2(1,2)}\int d^3\mathbf{Q} \times E\{F_{12}(\mathbf{r}(\tau))[F_{13}(\mathbf{s}_+(\tau))-F_{13}(\mathbf{q}(\tau))]| \times\mathbf{r}(1)=\mathbf{q}(1)=0\}, \quad (4.77)$$

$$g_e{}^{(2)}(r_{12})=\frac{1}{W_2(1,2)}\int d^3\mathbf{Q} \times E\{F_{12}(\mathbf{r}(\tau))[F_{23}(\mathbf{s}_-(\tau))-F_{23}(\mathbf{q}(\tau))]| \times\mathbf{r}(1)=\mathbf{q}(1)=0\}, \quad (4.78)$$

and where F_{12}, F_{13}, and F_{23} are defined by Eqs. (4.13), (4.14), and (4.15). Both $g_e{}^{(1)}$ and $g_e{}^{(2)}$ are functions of the magnitude r_{12} only so $\mathbf{r}_{12}$ may be replaced by $-\mathbf{r}_{12}$ wherever it appears in $g_e{}^{(2)}(r_{12})$. Furthermore, Wiener measure on $\mathbf{r}(\tau)$ is invariant to the replacement of of $\mathbf{r}(\tau)$ by $-\mathbf{r}(\tau)$. If one makes the two changes of variables $\mathbf{r}_{12}\to-\mathbf{r}_{12}$ and $\mathbf{r}(\tau)\to-\mathbf{r}(\tau)$ in $g_e{}^{(2)}$, then $F_{12}(\mathbf{r}(\tau))$ is unchanged due to the spherical symmetry of $V(r)$, while

$$F_{23}(\mathbf{s}_-(\tau))\to F_{13}(\mathbf{s}_+(\tau)) \quad (4.79)$$

and

$$F_{23}(\mathbf{q}(\tau))\to F_{13}(\mathbf{q}(\tau)). \quad (4.80)$$

Thus

$$g_e{}^{(1)}(r_{12})=g_e{}^{(2)}(r_{12}) \quad (4.81)$$

and $g_e(r_{12})$ may be written as

$$g_e(r_{12})=\frac{2}{W_2(1,2)}\int d^3\mathbf{Q} \times E\{F_{12}(\mathbf{r}(\tau))[F_{13}(\mathbf{s}_+(\tau))-F_{13}(\mathbf{q}(\tau))]| \times\mathbf{r}(1)=\mathbf{q}(1)=0\}. \quad (4.82)$$

In this last form a more natural origin for the integration over $\mathbf{Q}$ is $\mathbf{Q}=\frac{1}{2}(-\mathbf{r}_{12})$, so let the variable of

integration be changed to

$$\mathbf{Q}'=\mathbf{Q}+\tfrac{1}{2}\mathbf{r}_{12}. \tag{4.83}$$

Then

$$g_e(r_{12})=\int d^3\mathbf{Q}'G_e(r_{12},\mathbf{Q}'), \tag{4.84}$$

where

$$G_e(r_{12},\mathbf{Q}')=2E\left\{\frac{F_{12}(\mathbf{r}(\tau))}{W_2(\mathbf{1},\mathbf{2})}[F_{13}(\mathbf{Q}',\mathbf{s}_+(\tau))-F_{13}(\mathbf{Q}',\mathbf{q}(\tau))]|\mathbf{r}(1),\mathbf{q}(1)=0\right\}, \tag{4.85}$$

and where

$$F_{13}(\mathbf{Q}',\mathbf{q}(\tau))=\exp\left[-\beta\int_0^1 V\left(\frac{\lambda}{\sqrt{\pi}}\mathbf{q}(\tau)+\mathbf{Q}'\right)d\tau\right]. \tag{4.86}$$

The prime on $\mathbf{Q}'$ will be dropped for the remainder of the discussion of $g_e(r_{12})$. In spherical coordinates the cylindrical symmetry in φ_Q is not altered by the change in origin provided the polar axis remains in the Q_x direction.

The integrand of $g_e(r_{12})$ is the difference of two terms depending on $\mathbf{Q}$. This difference will be small if both terms are small or nearly equal, so we consider the behavior of

$$F_{13}(\mathbf{Q},0)=e^{-\beta V(\mathbf{Q})} \tag{4.87}$$

with respect to $\mathbf{Q}$. This function is the limit of both of the terms in the square brackets in Eq. (4.85) for $\mathbf{r}(\tau)=\mathbf{q}(\tau)\equiv 0$. For $\rho_Q<\sigma$, $F_{13}(\mathbf{Q},0)$ goes to zero rapidly. The function has a maximum at $\rho_Q\simeq 1.12\sigma$ and approaches one asymptotically as $(1+\sigma^6/\rho_Q{}^6)$ for $\rho_Q\gg\sigma$. The integrand in Eq. (4.84) should thus be zero for $\rho_Q\ll\sigma$ and approach zero again for $\rho_Q\gg\sigma$ as both terms in the difference approach unity. A simple probability distribution with this same qualitative behavior is the χ^2 distribution with n degrees of freedom for $n\geq 4$. For the $\mathbf{Q}$ integration in $g_e(r_{12})$ then, a χ^2 distribution with 12 degrees of freedom was used for ρ_Q and $\xi_Q=\cos\theta_Q$ was chosen from a uniform distribution, $-1\leq\xi_Q\leq 1$. Thus we define

$$\Gamma_e(\mathbf{Q})d^3\mathbf{Q}=\frac{\rho_Q{}^5}{6!\gamma_p{}^2}e^{-\rho_Q/\gamma_p}d\rho_Q d\xi_Q. \tag{4.88}$$

The number of degrees of freedom and the value of γ_p were chosen empirically during preliminary computations to minimize the variance of $g_e(r_{12};M)$ for small M.

In initial calculations of $g_e(r_{12};M)$ it was found that $g_e(r_{12})$ was indeed small compared to $g_c(r_{12})$ but that the variance of $g_e(r_{12};M)$ was quite large. It was thus necessary to apply a further variance reducing technique to the Monte Carlo sampling in the calculation of g_e. The technique used was the method of antithetic variates described by Hammersly and Handscomb,[21] and although it applies to the Monte Carlo sampling as a whole, it is best described in connection with the sampling in the $\mathbf{Q}$ integration. The principle of the antithetic variates method is to generate several correlated samples simultaneously, in such a way that their sum has a considerably smaller variance than the samples taken independently. In the present case it is recognized that $g_e(r_{12})$ is small so that one tries to correlate the samples in such a way that their sum is near zero.

From Eq. (4.85) it can be seen that the cylindrical symmetry of $G_e(r_{12},\mathbf{Q})$ about the Q_x axis requires that

$$G_e(r_{12},-\mathbf{Q})=G_e(r_{12},\rho_Q,\theta_Q+\tfrac{1}{2}\pi,\varphi_Q). \tag{4.89}$$

Thus the range of θ_Q can be restricted to $0\leq\theta_Q\leq\pi$, $(0\leq\xi_Q\leq 1)$ and the integrand taken as the sum of $G_e(r_{12},\mathbf{Q})$ and $G_e(r_{12},-\mathbf{Q})$. Another pairing of samples can be made due to the fact that the probability of a Wiener path $\mathbf{q}(\tau)$ is the same as the probability of $-\mathbf{q}(\tau)$. Since successive path approximations $\mathbf{q}^{(p)}$ are chosen independently, the samples for $\mathbf{q}^{(p)}$ and $-\mathbf{q}^{(p)}$ may be combined.

From Eqs. (4.34), (4.35), (4.36), and (4.40) it is seen that the integrand of the multiple integral approximation for $G_e(r_{12},\mathbf{Q})$ as given in Eq. (4.85) is

$$L_e(\mathbf{r}^{(p)},\mathbf{q}^{(p)},\mathbf{Q})=2[D_{13}(\mathbf{Q},\mathbf{s}_+{}^{(p)})-D_{13}(\mathbf{Q},\mathbf{q}^{(p)})], \tag{4.90}$$

where

$$D_{13}(\mathbf{Q},\mathbf{q}^{(p)})=\exp\left\{\frac{-\beta}{6p}\sum_{i=1}^{p}\left[V\left(\frac{\lambda}{\sqrt{\pi}}\mathbf{q}_{i-1}+\mathbf{Q}\right)+4V\left(\frac{\lambda}{\sqrt{\pi}}\tfrac{1}{2}(\mathbf{q}_i+\mathbf{q}_{i-1})+\mathbf{Q}\right)+V\left(\frac{\lambda}{\sqrt{\pi}}\mathbf{q}_i+\mathbf{Q}\right)+\frac{\lambda^2}{2\pi p}V''\left(\frac{\lambda}{\sqrt{\pi}}\tfrac{1}{2}(\mathbf{q}_i+\mathbf{q}_{i-1})+\mathbf{Q}\right)\right]\right\}. \tag{4.91}$$

Then if $\mathbf{r}_t{}^{(p)}$ is generated from the Markov chain, $\mathbf{q}_t{}^{(p)}$ is generated by the straightforward scheme for Wiener paths, and $\mathbf{Q}_t$ is chosen from the distribution $\Gamma_e(\mathbf{Q})$ defined by Eq. (4.88), but with ξ_Q restricted to the range $0\leq\xi_Q\leq 1$, then with probability 1,

$$g_e(r_{12})=\lim_{M\to\infty}\frac{1}{M}\sum_{t=1}^{M}A(\mathbf{r}_t{}^{(p)},\mathbf{q}_t{}^{(p)},\mathbf{Q}_t)\Gamma_e{}^{-1}(\mathbf{Q}_t), \tag{4.92}$$

where the antithetic variates sample

$$A(\mathbf{r}^{(p)},\mathbf{q}^{(p)},\mathbf{Q})$$

is defined by

$$A(\mathbf{r}^{(p)},\mathbf{q}^{(p)},\mathbf{Q})=\tfrac{1}{2}[L_e(\mathbf{r}^{(p)},\mathbf{q}^{(p)},\mathbf{Q})+L_e(\mathbf{r}^{(p)},\mathbf{q}^{(p)},-\mathbf{Q})+L_e(\mathbf{r}^{(p)},-\mathbf{q}^{(p)},\mathbf{Q})+L_e(\mathbf{r}^{(p)},\mathbf{q}^{(p)},-\mathbf{Q})]. \tag{4.93}$$

This sum should be more nearly zero than its component terms, since the portion of L_e which is antisymmetric in $\mathbf{Q}$ will cancel between terms 1 and 2 and between terms 3 and 4 on the right side of Eq. (4.93), while

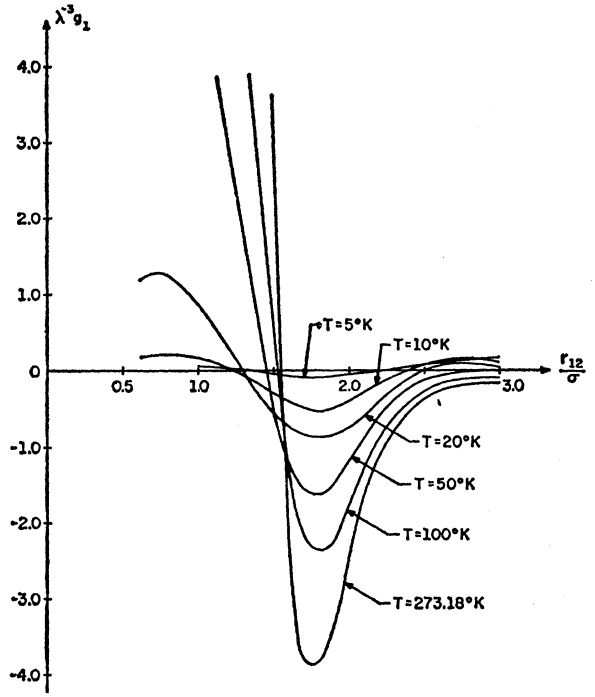

FIG. 3. $\lambda^{-3}g_1(r_{12}; 20\,000)$ as a function of r_{12}/σ and T.

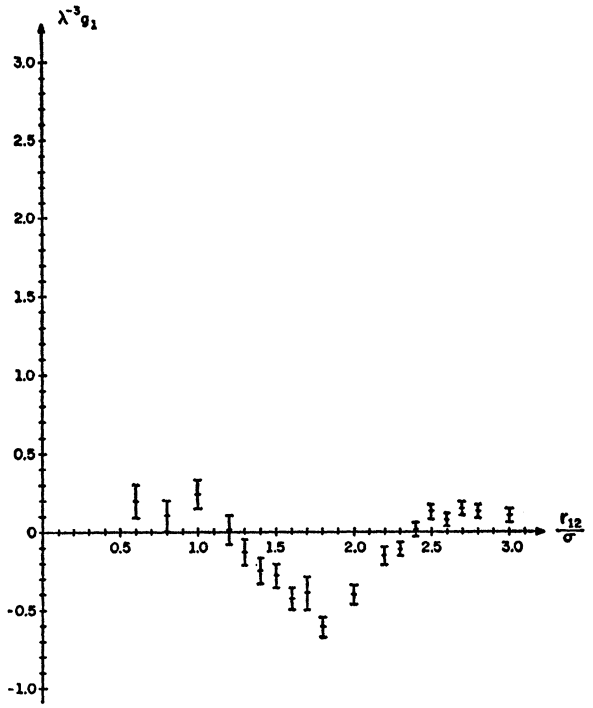

FIG. 5. $\lambda^{-3}g_1$ and sampling error for $T=10°K$.

similar cancellation will take place for the component of L_e which is antisymmetric in the variable $\mathbf{q}^{(p)}$ between terms 1 and 3 and between terms 2 and 4.

V. NUMERICAL RESULTS

A. Results and Accuracy Considerations

Using the methods developed in the preceding sections, $g_c(r_{12}; 20\,000)$ and $g_e(r_{12}; 20\,000)$ were calculated

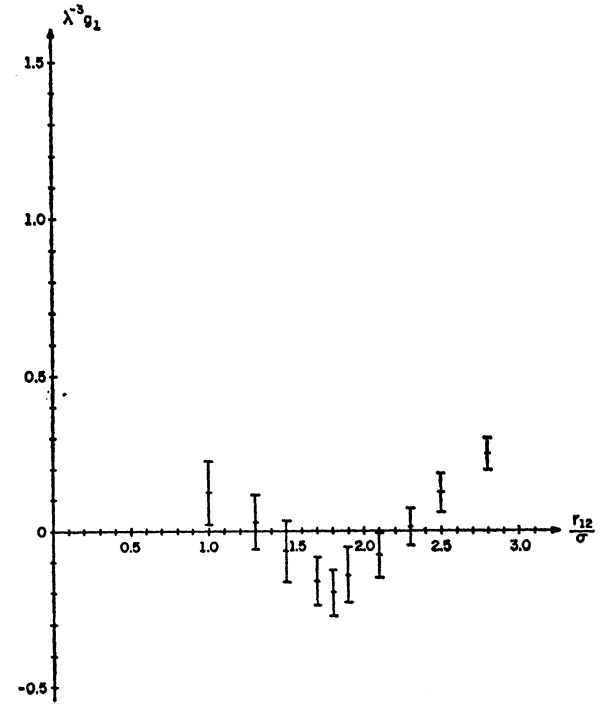

FIG. 4. $\lambda^{-3}g_1$ and sampling error for $T=5°K$.

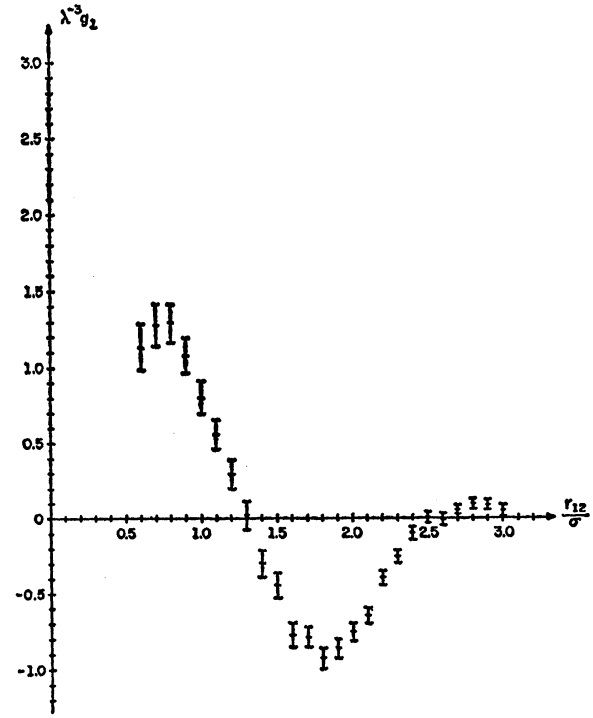

FIG. 6. $\lambda^{-3}g_1$ and sampling error for $T=20°K$.

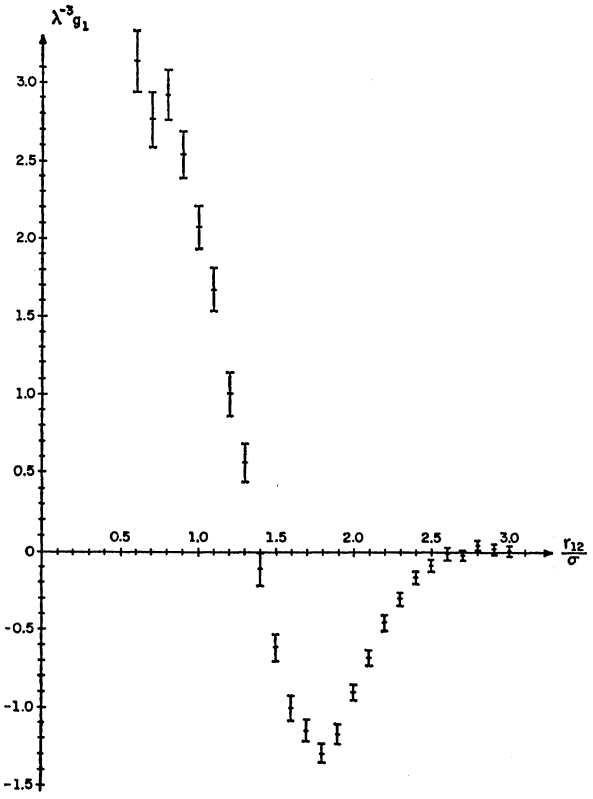

FIG. 7. $\lambda^{-3}g_1$ and sampling error for $T=30°K$.

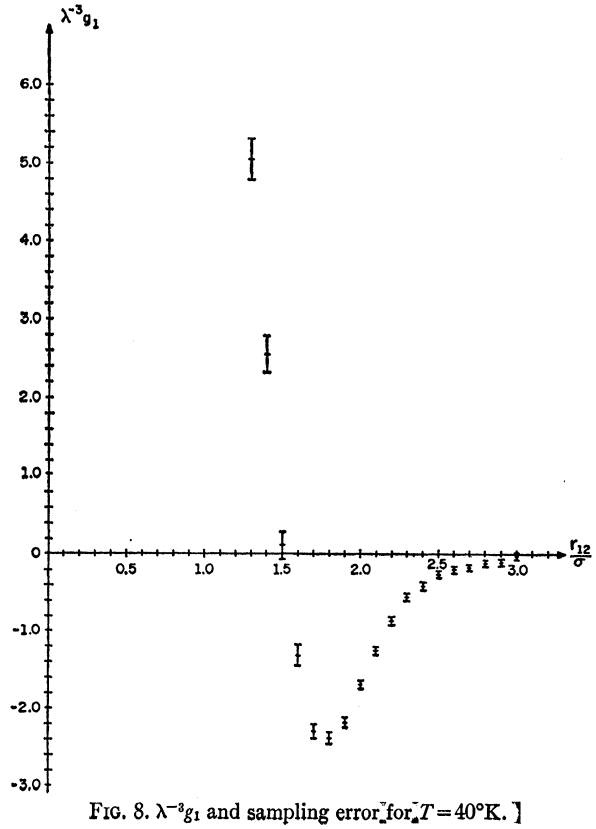

FIG. 8. $\lambda^{-3}g_1$ and sampling error for $T=40°K$.

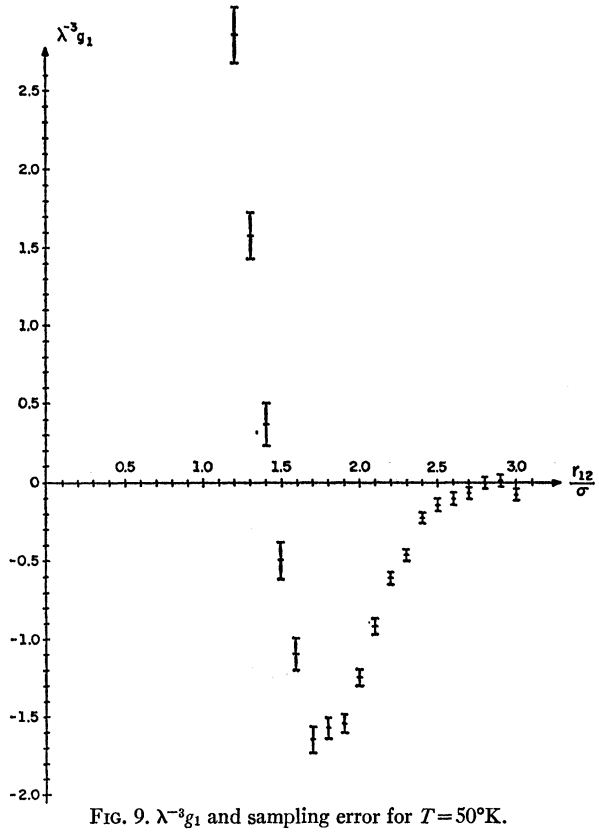

FIG. 9. $\lambda^{-3}g_1$ and sampling error for $T=50°K$.

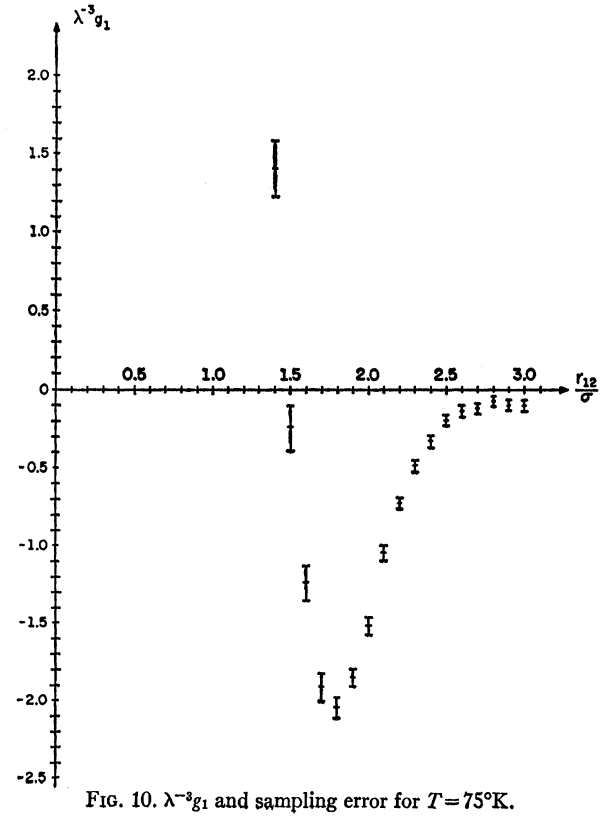

FIG. 10. $\lambda^{-3}g_1$ and sampling error for $T=75°K$.

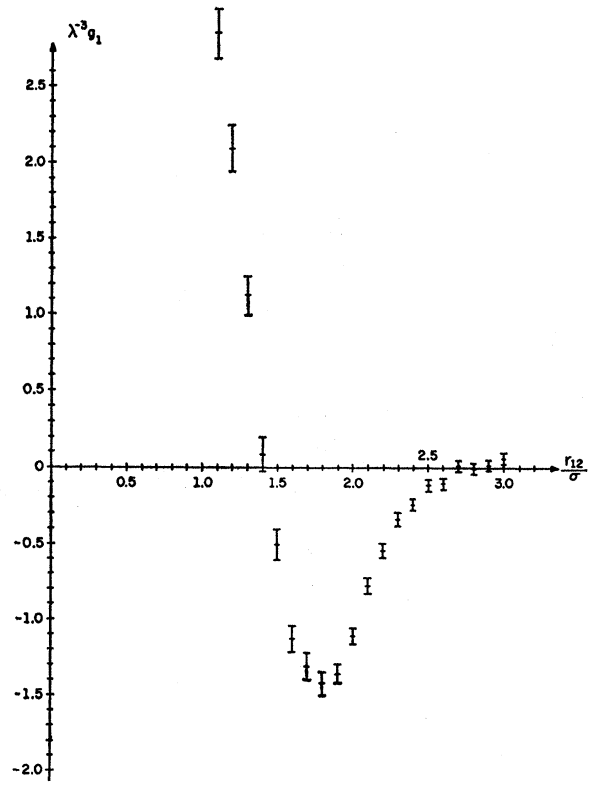

FIG. 11. $\lambda^{-3}g_1$ and sampling error for $T=100°K$.

for temperatures $T=5$, 10, 20, 30, 40, 50, 75, 100, and 273.18°K, and for values of r_{12} in the range $0.6\leq r_{12}/\sigma \leq 4.0$. The third virial coefficient $C(T)$ was computed for all but the lowest temperature, 5°K, using Eq. (2.8). A straightforward numerical integration was performed over r_{12} with $g_1(r_{12})$ approximated by $g_c(r_{12}; 20\,000)+g_e(r_{12}; 20\,000)$ and with the values of $W_2(r_{12})$ given in Ref. (1). The computations were performed on the Illiac II computer located at the University of Illinois. The details of the computation are summarized in Appendix B. A summary of the results for $g_1(r_{12}; 20\,000)=g_c(r_{12}; 20\,000)+g_e(r_{12}; 20\,000)$ over the range of temperature is shown in Fig. 3.

There are two sources of computational error which cause $g_1(r_{12}; 20\,000)$ and $C(T)$ to differ from the correct theoretical values of $g_1(r_{12})$ and the third virial coefficient for the interaction potential of Eqs. (2.10) and (2.11). These are the errors introduced by the p-fold integral approximation to the Wiener integrals and the Monte Carlo sampling error. The order p of the approximations $\mathbf{r}^{(p)}$ and $\mathbf{q}^{(p)}$ to the Wiener paths $\mathbf{r}(t)$ and $\mathbf{q}(t)$ was chosen for each temperature T so that $pT\geq 260°K$. Thus the accuracy of the multiple integral approximations at any temperature is at least equal to the accuracy of the two-term Wigner-Kirkwood approximation [first two terms in Eq. (3.37)] at 260°K. As an estimate of this accuracy, the third term in the Wigner-Kirkwood approximation to the second virial coefficient of He^4 at 260°K amounts to only 0.7% of the total. It will be seen that an error of this magnitude is negligible compared to the Monte Carlo sampling error.

As an estimate of the Monte Carlo sampling error, the sample standard deviations of the sample means, $g_c(r_{12}; 20\,000)$ and $g_e(r_{12}; 20\,000)$, were computed. The numerical results for $g_1(r_{12}; 20\,000)$ and the associated error estimates are shown plotted against r_{12}/σ for $T=5$, 10, 20, 30, 40, 50, 75, 100, and 273.18°K in Figs.

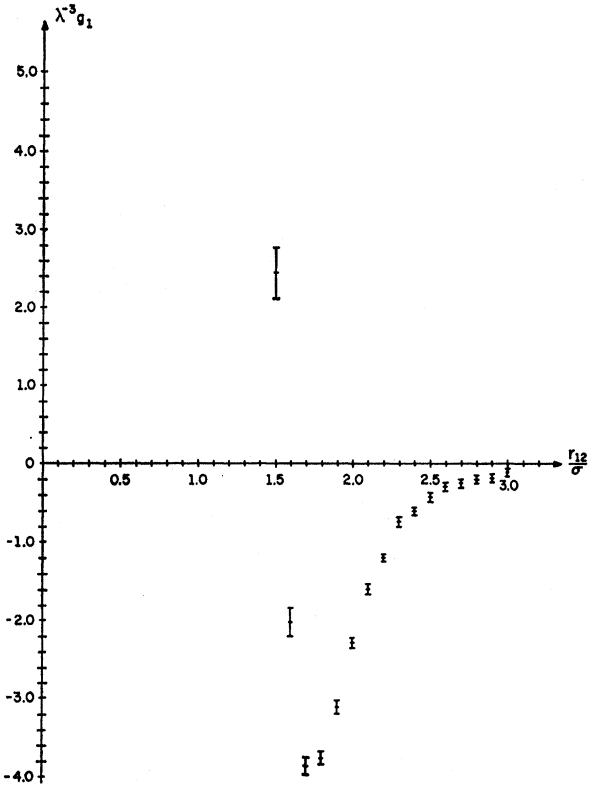

FIG. 12. $\lambda^{-3}g_1$ and sampling error for $T=273.18°K$.

4–12, respectively. The length of the error bar associated with $\lambda^{-3}g_1(r_{12}; 20\,000)$ is equal to twice the sum of the sample standard deviations of $\lambda^{-3}g_c(r_{12}; 20\,000)$ and $\lambda^{-3}g_e(r_{12}; 20\,000)$.

Although the Monte Carlo sampling connected with the Wiener integration and with the Riemann integration of $G(r_{12},\mathbf{Q})$ over the position $\mathbf{Q}$ of the third particle is done as a single process, it is convenient to consider the sampling error to be a sum of separate contributions from these two sources. The sampling error in the integration with respect to $\mathbf{Q}$ depends on the variation of $G(r_{12},\mathbf{Q})\Gamma^{-1}(\mathbf{Q})$ as a function of $\mathbf{Q}$. Since $G(r_{12},\mathbf{Q})$ contains functions of the form $e^{-\beta V(\mathbf{Q}\pm r_{12}/2)}$ which have an increasing variation in $\mathbf{Q}$ as β increases, it is to be expected that the sampling error due to the $\mathbf{Q}$ integration will increase with decreasing temperature.

A factor of β also multiplies the exponent of the functional integrand of the Wiener integration so that the

variance of the Monte Carlo procedure for computing the multiple integral approximation to the Wiener integral will also increase as T decreases as a result of the increase in β. The variance of the multiple integral approximation is further influenced by the fact that the Wiener random functions $\mathbf{r}(t)$ and $\mathbf{q}(t)$ in Eqs. (4.8) and (4.9) are multiplied by the thermal wavelength λ. Since λ increases with decreasing temperature, the variance again increases as T decreases. A final contribution to the same behavior of increasing variance with decreasing T results from the fact noted above that p was increased with decreasing T in order to maintain the accuracy of the multiple integral approximation to the Wiener integrals. The multiplicity, $6(p-1)$, of the integral thus increases with decreasing T resulting in an increasing variance for the Monte Carlo procedure.

The standard deviation of the multiple integral results also depends upon the choice of the initial vector $\mathbf{r}_0^{(p)}$ of the Markov chain $\{\mathbf{r}_t^{(p)}\}$. Because of the one-step memory inherent in the chain, the choice of an initial vector $\mathbf{r}_0^{(p)}$, which is improbable with respect to the probability density $P(\mathbf{r}^{(p)})d\mu_{rp}$, Eqs. (4.35) and (4.41) can cause a large variation in the integrand as the vectors $\mathbf{r}_t^{(p)}$ move from $\mathbf{r}_0^{(p)}$ toward the region of maximum $P(\mathbf{r}^{(p)})d\mu_{rp}$. An attempt was made to reduce the error caused by a bad choice of $\mathbf{r}_0^{(p)}$ for each pair of values of r_{12} and T. At high temperatures $P(\mathbf{r}^{(p)})d\mu_{rp}$ assigns the highest probability to vectors in the neighborhood of $\mathbf{r}^{(p)}\equiv 0$, provided that $P(\mathbf{r}^{(p)})$ is slowly varying over the range of $\mathbf{r}_{12}+\mathbf{r}^{(p)}$. Thus for the highest temperature and largest r_{12}, the initial vector was taken to be $\mathbf{r}_0^{(p)}\equiv 0$. At lower temperatures, the initial vector for the largest value of r_{12} was taken to be the last vector $\mathbf{r}_M^{(p)}$ generated by the Markov chain for the same value of r_{12} at the next higher temperature. For successively smaller values of r_{12}, the initial vector was taken to be the last vector generated at the same temperature and the next higher value of r_{12}.

The quantities $g_c(r_{12};M)$ were also computed with $M<20\,000$ at several pairs of values for r_{12} and T. The standard deviations in these quantities were observed to decrease as $M^{-1/2}$, as would be expected of a well-formulated Monte Carlo procedure.

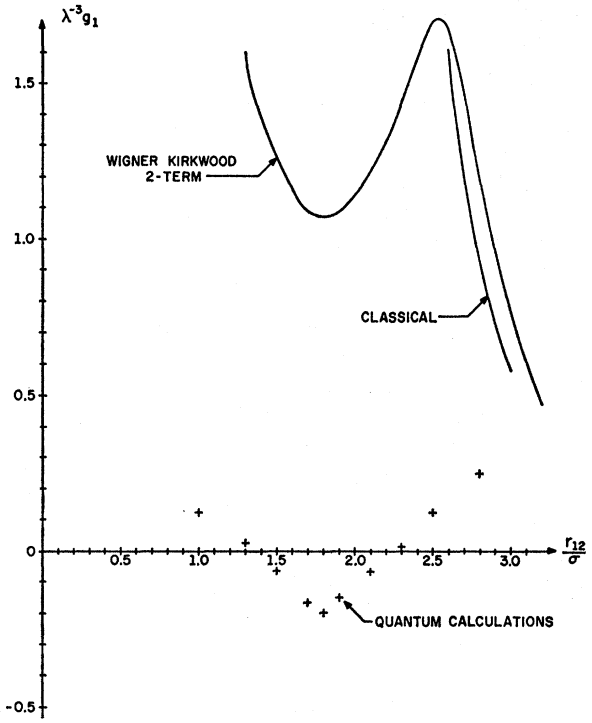

FIG. 13. Comparison of $\lambda^{-3}g_1$ with classical and semi-classical values for $T=5°K$.

B. Numerical Comparisons with Theory and Experiment

It can be seen from Fig. 3 that the position of the minimum in $g_1(r_{12})$ remains fairly constant at $r_{12}\simeq 1.8\sigma$ over the entire temperature range. The position of the minimum in $g_1(r_{12})$ can be interpreted in terms of a crude argument about the spatial arrangement of three particles. If one takes the most probable arrangement of particles as a linear arrangement with each particle falling at the minimum of the potentials due to its two nearest neighbors, then for the Lennard-Jones (12-6) potential there should be maximum probability of finding a particle at distances of 1.12σ and 2.24σ

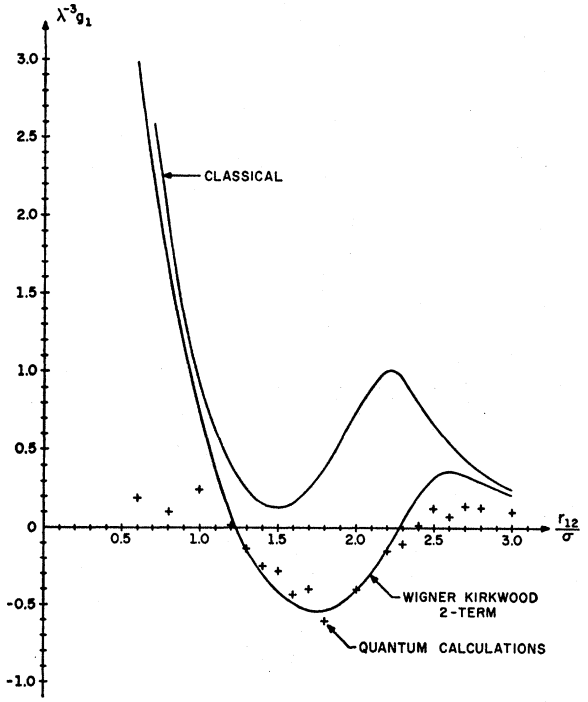

FIG. 14. Comparison of $\lambda^{-3}g_1$ with classical and semi-classical values for $T=10°K$.

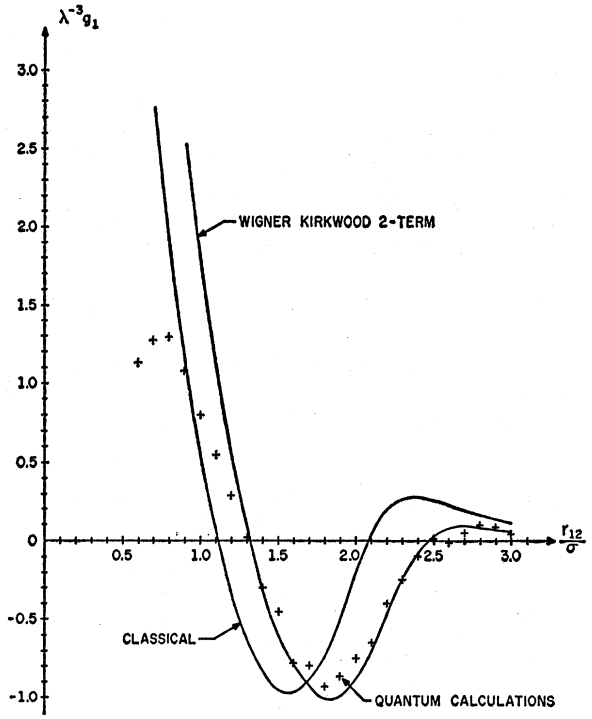

FIG. 15. Comparison of $\lambda^{-3}g_1$ with classical and semi-classical values for $T=20°K$.

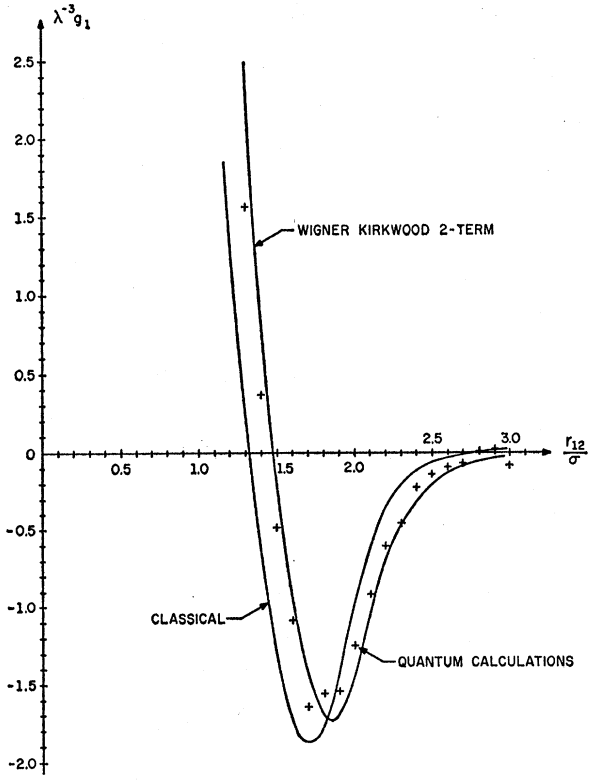

FIG. 16. Comparison of $\lambda^{-3}g_1$ with classical and semi-classical values for $T=50°K$.

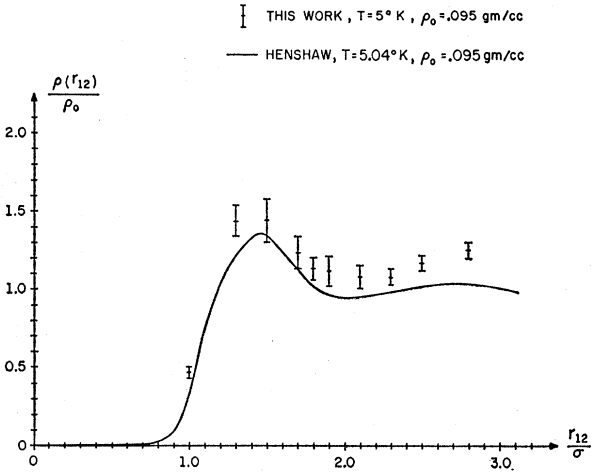

FIG. 17. The pair distribution function for average density $\rho_0=0.095$ g/cc.

from a reference particle. Correspondingly, there should be a minimum probability of finding a particle midway between these two positions or at 1.69σ. If $W_2(r_{12})$ is slowly varying near this minimum of the pair distribution function, then the corresponding minimum in $g_1(r_{12})$ should fall at approximately the same value of r_{12}. The calculated position of the minimum, 1.8σ, agrees well enough with this result to indicate that the minimum can be interpreted physically as the gap between the first and second shells of atoms about the reference atom.

Classical and two-term Wigner-Kirkwood approximations for $g_1(r_{12})$ have also been calculated using respectively the first and first two terms of Eq. (3.37) for $\langle 1,2,3|e^{-\beta H_3}|1,2,3\rangle$. The integration over the position of the third particle was carried out by a straightforward iterated Simpson's rule approximation. Comparisons between the Classical, Wigner-Kirkwood, and quantum calculations are shown in Figs. 13–16. The classical values of $g_1(r_{12})$ have previously been calculated by Henderson,[23] and the results presented agree with his calculations wherever there is overlap. In observing these comparisons, it should be noted that when $g_1(r_{12})$ is used to calculate a physically measurable quantity, it is multiplied by $W_2(r_{12})$ which goes to zero rapidly with decreasing r_{12} for $r_{12}/\sigma<1$. Thus, values of $g_1(r_{12})$ for $r_{12}\lesssim 0.8\sigma$ are not significant.

The two-term Wigner-Kirkwood approximation is fairly accurate down to about $T=10°K$. The position of the minimum in $g_1(r_{12})$ corresponding to the inter-shell gap remains approximately constant for the Wigner-Kirkwood data while a significant shift toward smaller values of r_{12} with decreasing temperature occurs in the classical position of this minimum. At 5°K the Wiener integral method gives results which differ markedly from the two-term Wigner-Kirkwood approximation. Results were obtained for only a few values of

[23] D. Henderson, Mol. Phys. **10**, 73 (1965).

r_{12} at $T=5°K$, due to the amount of computation time involved in the Monte Carlo procedure for large values of the order p of the Wiener integral approximation ($p=52$ at $T=5°K$). Considering the *a posteriori* information on the accuracy of the two-term Wigner-Kirkwood approximation, it would seem that reasonably accurate results could be obtained with $pT\gtrsim 30°K$ rather than $pT\gtrsim 260°K$ so that it would be possible to repeat the 5°K computation in one tenth the time.

There seems to be no experimental data on the pair distribution function in He^4 gas at low temperatures. The pair distribution function for liquid helium, however, has been measured by neutron diffraction for several values of the density.[24] Figures 17 and 18 show

$$W_2(r_{12})[1+ng_1(r_{12})]\cong\frac{n_2(r_{12})}{n^2}=\frac{\rho(r_{12})}{\rho_0}$$

for $T=5°K$ and number densities n corresponding to mass densities $\rho_0=0.095$ gm/cc and $\rho_0=0.184$ gm/cc, respectively, compared with Henshaw's data for these same densities. Since only three particle effects have been taken into account in the computation, agreement cannot be expected beyond the second peak in the distribution function. To indicate the variation of $\rho(r_{12})/\rho_0$ with temperature smooth curves have been fitted to the numerical results for

$$W_2(r_{12})[1+ng_1(r_{12})]\cong\rho(r_{12})/\rho_0$$

for temperatures 10, 20, and 40°K for the density $\rho_0=0.184$ gm/cc. The resulting curves are shown in Fig. 19.

Two factors influence the comparison between Henshaw's neutron diffraction data for liquid He^4 and the numerical results of this work. The first is the choice

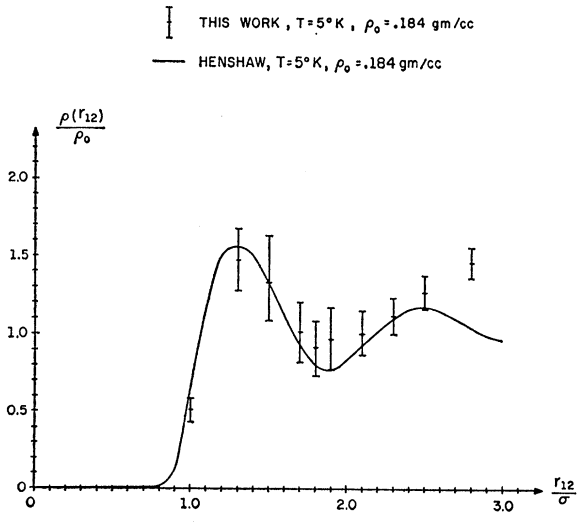

FIG. 18. The pair distribution function for average density $\rho_0=0.184$ g/cc.

D. G. Henshaw, Phys. Rev. **119**, 14 (1960).

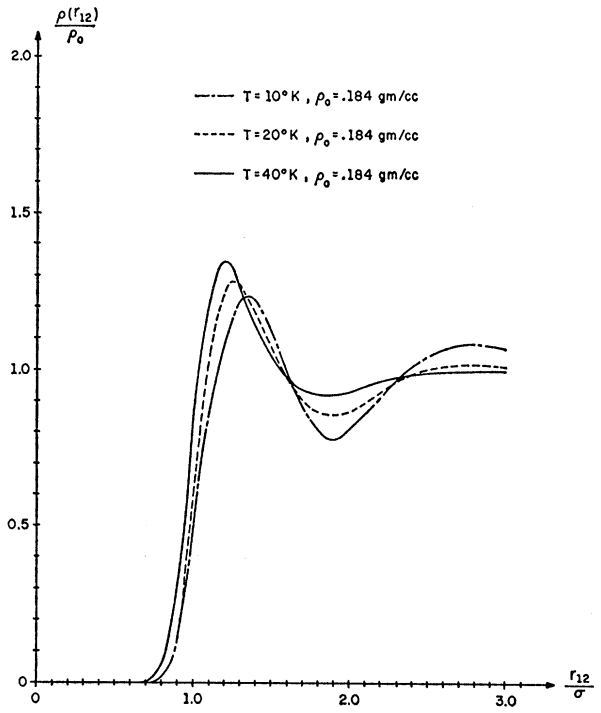

FIG. 19. The pair distribution function as a function of temperature for $\rho_0=0.184$ g/cc.

of the Lennard-Jones (12-6) potential [Eq. (2.10)] as the correct intermolecular potential for helium. The second is the validity of the cluster expansion for temperatures and densities at which helium is a liquid. The influence due to each of these factors cannot be separated without recomputing $W_2(r_{12})$ and $g_1(r_{12})$ for a different intermolecular potential. However, barring

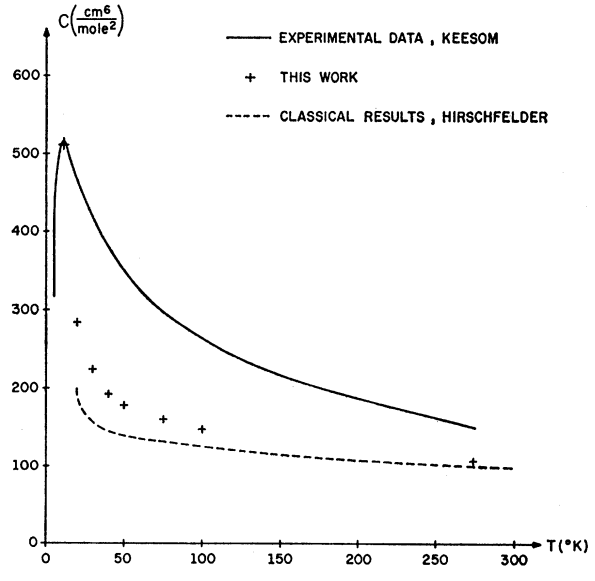

FIG. 20. Comparison of calculated third virial coefficient with classical and experimental values.

compensating errors in these two approximations, Figs. 17 and 18 indicate that both approximations are fairly good for the pair distribution of liquid He^4 at 5°K.

Using Eq. (2.8), the third virial coefficient $C(T)$ was evaluated for all temperatures at which $g(r_{12})$ was calculated except for 5°K. C(5°K) was not calculated partly due to the large sampling errors in $g_1(r_{12})$ at 5°K, but primarily due to the fact that values of $g_1(r_{12})$ for $r_{12}>2.8\sigma$ give a large contribution to the integral for C(5°K) and no numerical results were obtained for this range of r_{12}. Figure 20 shows the numerical results for $C(T)$ compared to the values adopted by Keesom[25] for the experimental third virial coefficient and the values calculated classically from the Lennard-Jones (12-6) potential.[16]

Over almost all of the temperature range the computed values fall consistently below the experimental results. Since Eq. (2.8) does not depend on the neglect of higher-order terms in the cluster expansion, the cause of this difference is evidently the choice of the pairwise additive Lennard-Jones (12-6) potential as the correct three particle potential for helium. Some recent calculations by Sherwood, De Rocco, and Mason[26] indicate that nonadditive three-body forces may have a sizeable effect on the third virial coefficient of He^4. The ways in which $g_1(r_{12})$ and $C(T)$ differ from the experimental values can be reconciled qualitatively. Figures 17 and 18 indicate that the calculated $g_1(r_{12})$ is fairly consistently larger than the experimental $g_1(r_{12})$. On performing the integration over $d2$ in Eq. (2.8), this would lead to a $C(T)$ which would be smaller than its experimental value, as is verified in Fig. 20.

C. Conclusion

The comparisons of Sec. V B point to two conclusions regarding the physics of the He^4 system. The first is that quantum mechanical calculations based on the cluster expansion and assuming a pairwise additive Lennard-Jones (12-6) potential can produce a reasonable qualitative fit to the pair distribution function in liquid He^4. Secondly, the consistent deviation of the calculated third virial coefficient from the experimental values over the full temperature range indicates that the choice of the latter potential for the three-body interaction in He^4 is not good enough to yield quantitative agreement with experiment.

From the mathematical viewpoint, it has been shown that the Wiener integral may be a useful computational tool. The upper bounds of Sec. III B indicate that the expression of a quantity in terms of Wiener integrals can yield qualitative and semiquantitative information on the size and behavior of that quantity. Finally, the numerical evaluation of a Wiener integral expression has been shown to be computationally feasible in a situation where the amount of computation involved in integrating the original partial differential equation giving rise to the Wiener integral would be prohibitive.

[25] W. H. Keesom, *Helium* (Elsevier Publishing Co., Inc., New York, 1942), Chap. 2.

[26] A. E. Sherwood, A. G. De Rocco, and E. A. Mason, J. Chem. Phys. 44, 2984 (1966).

APPENDIX A: LEMMA FOR THE PROOF OF EQ. (4.58)

Lemma:

$$\rho^*(\mathbf{x}'|\mathbf{x})w(\mathbf{x})=\rho^*(\mathbf{x}^T|\mathbf{x}'^T)w(\mathbf{x}'^T). \tag{4.58}$$

Proof: From Eqs. (4.48) and (4.50) it follows that

$$\rho^*(\mathbf{x}^T|\mathbf{x}'^T)w(\mathbf{x}'^T)=\left(\frac{p}{\pi}\right)^{(p-1)/2}(2\pi)^{1/2}\left(\frac{p}{2\pi}\right)^{p/2}$$
$$\times\exp\Big[-p\sum_{i=1}^{p-1}(x_i{}^T-\tfrac{1}{2}(x_{i-1}{}^T+x_{i+1}{}'^T))^2$$
$$-\tfrac{1}{2}p\sum_{i=1}^{p}(x_i{}'^T-x_{i-1}{}'^T)^2\Big]. \tag{A1}$$

By the definition of $\mathbf{x}^T$, $x_i{}^T=x_{p-1}$, $i=0, 1, \cdots, p$, so Eq. (A1) becomes

$$\rho^*(x^T|x'^T)w(x'^T)=\left(\frac{p}{\pi}\right)^{(p-1)/2}(2\pi)^{1/2}\left(\frac{p}{2\pi}\right)^{p/2}$$
$$\times\exp\Big[-p\sum_{i=1}^{p-1}(x_{p-i}-\tfrac{1}{2}(x_{p-i+1}+x_{p-i-1}'))^2$$
$$-\tfrac{1}{2}p\sum_{i=1}^{p}(x_{p-i}'-x_{p-i+1}')^2\Big]. \tag{A2}$$

Setting $l=p-i$, one finds that

$$\rho^*(\mathbf{x}^T|\mathbf{x}'^T)w(\mathbf{x}'^T)=\left(\frac{p}{\pi}\right)^{(p-1)/2}(2\pi)^{1/2}\left(\frac{p}{2\pi}\right)^{p/2}$$
$$\times\exp\Big[-p\sum_{l=1}^{p-1}x_l{}^2+p\sum_{l=1}^{p-1}x_lx_{l+1}+p\sum_{l=2}^{p-1}x_lx_{l-1}'$$
$$-p\sum_{l=1}^{p-1}\tfrac{1}{4}(x_{l+1}+x_{l-1}')^2-\frac{p}{2}\sum_{l=0}^{p-1}(x_l')^2$$
$$+p\sum_{l=1}^{p}x_l'x_{l+1}'-\frac{p}{2}\sum_{l=1}^{p}(x_l')^2\Big], \tag{A3}$$

and making use of the fact that $x_0=x_p=x_0'=x_p'=0$.

this becomes

$$\rho^*(x^T|x'^T)w(x'^T)=\left(\frac{p}{\pi}\right)^{(p-1)/2}(2\pi)^{1/2}\left(\frac{p}{2\pi}\right)^{p/2}$$
$$\times\exp[-p\sum_{l=1}^{p-1}(x_l')^2+p\sum_{j=1}^{p-1}x_j'x_{j-1}'+p\sum_{j=1}^{p-1}x_j'x_{j+1}$$
$$-p\sum_{l=1}^{p-1}\tfrac{1}{4}(x_{l+1}+x_{l-1}')^2-p\sum_{l=1}^{p-1}x_l^2+\sum_{j=1}^{p}x_jx_{j-1}], \quad \text{(A4)}$$

where $j=l+1$. Equating the dummy subscripts and combining the sums, one obtains

$$\rho^*(\mathbf{x}^T|\mathbf{x}'^T)w(\mathbf{x}'^T)=\left(\frac{p}{\pi}\right)^{(p-1)/2}(2\pi)^{1/2}\left(\frac{p}{2\pi}\right)^{p/2}$$
$$\times\exp[-p\sum_{l=1}^{p-1}(x_l'-\tfrac{1}{2}(x_{l+1}+x_{l-1}'))^2$$
$$-\tfrac{1}{2}p\sum_{l=1}^{p}(x_l-x_{l-1})^2]=\rho^*(\mathbf{x}'|\mathbf{x})w(\mathbf{x}), \quad \text{(A5)}$$

which completes the proof.

APPENDIX B: DETAILED COMPUTATIONAL PROCEDURE FOR $g_c(r_{12};M)$, $g_e(r_{12};M)$, AND $C(T)$

The step-by-step procedure for computing the approximation $g_c(r_{12};M)$ to $g_c(r_{12})$ is as follows:

(1) Generate M independent Wiener path approximations consisting of $3p$-dimensional vectors $\mathbf{q}_t^{(p)}$, $t=1, 2, \cdots, M$ drawn from a probability distribution $d\mu_{qp}$ by Eq. (4.38), $\mathbf{q}_0=\mathbf{q}_p=0$,

$$\mathbf{q}_i=\frac{\mathbf{q}_{i-1}(1-i/p)}{1-(i-1)/p}+\xi_i\left[\frac{(1/p)(1-i/p)}{1-(i-1)/p}\right]^{1/2}, \quad i=1, 2, \cdots, p-1 \quad \text{(B1)}$$

where the ξ_i are three-dimensional random variables, the coordinate variables of which are independent and normally distributed with mean 0 and variance 1.

(2) Generate an M-step Markov chain $\{\mathbf{r}_t^{(p)}|t=1, 2, \cdots, M\}$ with stationary probability

$$\frac{D_{12}(r^{(p)})}{W_2(\mathbf{1},\mathbf{2})}d\mu_{rp}$$

by first generating $\bar{\mathbf{r}}_t^{(p)}$, using the procedure described by Eq. (4.64), and setting $\mathbf{r}_t^{(p)}=\bar{\mathbf{r}}_t^{(p)}$ if $D_{12}(\bar{\mathbf{r}}_t^{(p)})\geq D_{12}(\mathbf{r}_{t-1}^{(p)})$, while if $D_{12}(\bar{\mathbf{r}}_t^{(p)})<D_{12}(\mathbf{r}_{t-1}^{(p)})$ set

$$\mathbf{r}_t^{(p)}=\bar{\mathbf{r}}_t^{(p)} \text{ with probability } \frac{D_{12}(\bar{\mathbf{r}}_t^{(p)})}{D_{12}(\mathbf{r}_{t-1}^{(p)})} \quad \text{(B2)}$$

and

$$\mathbf{r}_t^{(p)}=\mathbf{r}_{t-1}^{(p)} \text{ with probability } 1-\frac{D_{12}(\bar{\mathbf{r}}_t^{(p)})}{D_{12}(\mathbf{r}_{t-1}^{(p)})}. \quad \text{(B3)}$$

(3) Generate M independent random vectors $\mathbf{Q}_t=(Q_x,Q_y,0)_t$, $t=1, 2, \cdots, M$ according to the probability $\Gamma_c(\mathbf{Q})d^2\mathbf{Q}$.

(4) Form the average

$$g_c(r_{12};M)=\frac{1}{M}\sum_{t=1}^{M}L_c(\mathbf{r}_t^{(p)},\mathbf{q}_t^{(p)},\mathbf{Q}_t)\Gamma_c^{-1}(\mathbf{Q}_t). \quad \text{(B4)}$$

Equations (4.71), (4.35), (4.36), (2.9), and (4.75) are pertinent to the above procedure.

The procedure for computing the approximation $g_e(r_{12};M)$ to $g_e(r_{12})$ is the same as that for $g_c(r_{12};M)$ except that steps (3) and (4) are modified.

(3′) Generate M independent random vectors $\mathbf{Q}_t=(\rho_Q,\theta_Q,0)_t$, $t=1, 2, \cdots, M$ according to a probability $\Gamma_e(\mathbf{Q})d^2\mathbf{Q}$.

(4′) Form the average

$$g_e(r_{12};M)=\frac{1}{M}\sum_{t=1}^{M}A(\mathbf{r}_t^{(p)},\mathbf{q}_t^{(p)},\mathbf{Q}_t)\Gamma_e^{-1}(\mathbf{Q}_t). \quad \text{(B5)}$$

Equations (4.93), (4.90), (4.91), and (4.88) are additionally needed for the computation.