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Monte Carlo Calculation of the Radial Distribution Function of Quantum Hard Spheres at Finite Temperatures*

P. A. WHITLOCK

Courant Institute of Mathematical Sciences, New York University, 251 Mercer Street, New York, New York 10012 and Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14863

AND

M. H. KALOS

Courant Institute of Mathematical Sciences, New York University, 251 Mercer Street, New York, New York 10012

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The Green's function Monte Carlo method is generalized to treat quantum systems at non-zero temperature. The algorithm that is developed absolutely requires importance sampling to make it feasible. The nature of the importance sampling transformation needed for an efficient algorithm is discussed in theory and practice. As a demonstration of the principles, we carry out a calculation of the two body contribution to the radial distribution function and the second virial coefficient of a hard sphere fluid. Accurate numerical results are obtained. It is also shown how improvement in the structure of the importance function can lead to dramatic improvements in computational efficiency. A method is described, and successfully applied, whereby an importance function may be determined in large part during the Monte Carlo, rather than *a priori*. Finally, we conjecture that importance sampling can also be applied to the sums over permutations for treating boson or fermion systems.

INTRODUCTION

The study of quantum fluids and crystals by Monte Carlo techniques has proved most valuable. Either for direct comparison with experiment or else in the elucidation of the properties of models, such investigations have contributed [1] to the theory of liquid and crystal phases of helium, hydrogen and deuterium, and of nuclear and neutron matter. Unfortunately practical methods exist only for the study of ground state problems. In most applications, systems at higher temperatures than zero are

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most interesting. Clearly only such states are experimentally accessible. In this paper we investigate the applicability to non-zero temperatures of the Green's function Monte Carlo method [2, 3] (GFMC) which has already been used for ground state problems. It will be demonstrated that GFMC is applicable in principle at all temperatures and that it can give accurate numerical results for the two-body problem providing that appropriate importance sampling is used.

The density matrix which describes equilibrium properties of quantum systems at finite temperatures is the solution of the Bloch equation [4]. To find a Monte Carlo technique suitable for integrating this equation, we note that the density matrix is the Green's function for the operator $H + \partial/\partial\beta$. The Green's function is sampled in a random walk so that the weight associated with the sampled points is proportional to the density matrix and from the density matrix the equilibrium properties of the system may be determined. Experience with ground state calculations [3] indicates that the calculation is impossible for large systems without the introduction of importance sampling into the Monte Carlo algorithm. Modification of the random walk by means of an importance function accelerates the computation and reduces the variance of the answer. Such importance sampling is also essential in the finite temperature problem discussed in this paper.

It is of course possible to study finite temperature systems using a path integral formulation [5]. To evaluate a diffusion process by path integrals, a truncated Wiener path is constructed which starts at some configuration of the system, $\mathbf{R}$ and ends at $\mathbf{R}'$ within a specified time. The presence of hard sphere or other potentials complicates the efficient construction of paths which avoid strongly repulsive potential regions and necessitates some form of biasing. We claim that an intelligent importance sampling scheme is also essential for the treatment of permutations.

As a demonstration of the theory the Green's function Monte Carlo method is applied to the diffusion of two indistinguishable spheres which interact by a hard sphere potential. In the course of defining the computational problem, it becomes clear that importance sampling is imperative for the variance to exist. The methodology used is essentially that described by Kalos, Levesque and Verlet (KLV) [3] pertaining to finite temperatures. Through the Monte Carlo calculation the radial distribution function of hard spheres and the direct and exchange second virial coefficients are determined and compared with previously obtained numerical estimates of these quantities. The KLV method is found to work well even with a poor choice of the importance function in the importance sampling and the efficiency of the Monte Carlo calculation increases when a better importance function is used. It is anticipated that the method will generalize satisfactorily to the many body problem.

Green's Function Monte Carlo Applied to the Bloch Equation

As we shall see, the density matrix is the solution of a partial differential equation—the Bloch equation. Through the use of suitable Green's functions the Bloch equation may be written as an integral equation. A random walk is then constructed whose

expected density is the solution of the integral equation and is therefore the density matrix [6].

In the coordinate representation, the density matrix may be defined as

$$\rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta) = \sum_k \Psi_k^*(\mathbf{R}_0)\, e^{-\beta E_k} \Psi_k(\mathbf{R}). \tag{1}$$

The quantities $\mathbf{R}$ and $\mathbf{R}_0$ are multidimensional vectors representing the configuration of the system, β equals $(k_B T)^{-1}$ and the Ψ_k, $k = 0, 1, 2...$, are complete eigenfunctions for Boltzmann statistics with eigenvalues E_k. Any quantity of physical interest in a system at equilibrium can be determined from the density matrix. For example in an N body Bose system contained in a volume V, the radial distribution function, $g(r, T)$, can be calculated from the diagonal part of the density matrix,

$$g(r, T) = \frac{V(N-1)}{N} \frac{\sum_P \int \rho_B(P\mathbf{R}, \mathbf{R}; \beta)\, \delta(r_n - r_m - r)\, d\mathbf{R}}{\sum_P \int \rho_B(P\mathbf{R}, \mathbf{R}; \beta)\, d\mathbf{R}} \tag{2}$$

where n and m represent some particle pair and P indicates a permutation of the particles.

That the density matrix, $\rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta)$ satisfies the Bloch equation may be shown by differentiating ρ_B with respect to β;

$$-\frac{\partial}{\partial \beta} \rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta) = \sum_k \Psi_k^*(\mathbf{R}_0)\, e^{-\beta E_k} E_k \Psi_k(\mathbf{R}) \tag{3a}$$

$$= H \rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta) \tag{3b}$$

$$= [-\nabla^2 + V(\mathbf{R})]\, \rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta). \tag{3c}$$

Units of $\hbar^2/2\mu = 1$ are implied in Eqs. (3); the Laplacian is in the full coordinate space and $V(R)$ is the full many-body potential. The Bloch equation has the form of a diffusion equation if β is identified with "time". The density matrix satisfies the further condition that when $\beta = 0$

$$\rho_B(\mathbf{R}, \mathbf{R}_0 ; 0) = \sum_k \Psi_k^*(\mathbf{R}_0)\, \Psi_k(\mathbf{R}) = \delta(\mathbf{R} - \mathbf{R}_0); \tag{4}$$

and thus it is seen that $\rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta)$ is a Green's function. $\rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta)$ describes the diffusion of the system from the configuration represented by $\mathbf{R}_0$ to that represented by $\mathbf{R}$ in a "time" β. The density matrix may be computed from Wiener path integrals as well as by a Monte Carlo procedure.

When hard sphere forces are present, the Green's function has the property that

$$\rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta) = 0 \quad \text{when} \quad \begin{cases} | r_i - r_j | \leqslant a & \text{for any } i \neq j \\ | r_{0i} - r_{0j} | \leqslant a & \text{for any } i \neq j, \end{cases} \tag{5}$$

where a is the hard sphere diameter. An integral relationship involving $\rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta)$ can be derived,

$$\rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta) = \int \rho_B(\mathbf{R}, \mathbf{R}'; \beta - \beta')\, \rho_B(\mathbf{R}', \mathbf{R}_0 ; \beta')\, d\mathbf{R}', \tag{6}$$

which holds for any $0 < \beta' < \beta$. This equation is the basis for using truncated paths in a Wiener integral. Equation (6) may be verified by inspection: the operator $[-\nabla^2 + V(\mathbf{R}) + (\partial/\partial\beta)]$ annihilates the factor $\rho_B(\mathbf{R}, \mathbf{R}'; \beta - \beta')$ in the integral and hence the right hand side. Furthermore if one takes the limit $\beta' \to 0$, the integral becomes simply $\rho_B(\mathbf{R}, \mathbf{R}'; \beta)$ in view of the boundary condition (4). In particular, for $\beta = 0$, the integral in (6) is $\delta(\mathbf{R} - \mathbf{R}_0)$.

The density matrix in the presence of hard sphere forces is not known and therefore cannot be sampled directly in a Monte Carlo calculation. It is possible, though, to sample $\rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta)$ recursively. This is achieved by dividing the domain D of $\mathbf{R}$ in which $\rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta) > 0$ into two parts, a subdomain D_0 and the rest of D. Let a partial Green's function, $\rho_0(\mathbf{R}, \mathbf{R}_0; \beta)$ be defined which is zero for $\mathbf{R}$ on or outside the boundary of D_0 ; i.e.

$$\left[-\nabla^2 + V(\mathbf{R}) + \frac{\partial}{\partial\beta}\right] \rho_0(\mathbf{R}, \mathbf{R}_0 ; \beta) = 0 \tag{7a}$$

$$\rho_0(\mathbf{R}, \mathbf{R}_0 ; 0) = \delta(\mathbf{R} - \mathbf{R}_0) \qquad R_0 \in D_0 \tag{7b}$$

$$\rho_0(\mathbf{R}, \mathbf{R}_0 ; \beta) = 0 \qquad \mathbf{R} \text{ or } \mathbf{R}_0 \notin D_0 . \tag{7c}$$

With these boundary conditions, both $\rho_0(\mathbf{R}, \mathbf{R}_0 ; \beta)$ and $\rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta)$ are symmetric upon interchange of $\mathbf{R}$ and $\mathbf{R}_0$, and Equations (7a) and (3c) may be rewritten as

$$\left[-\nabla'^2 + V(\mathbf{R}') + \frac{\partial}{\partial\beta'}\right] \rho_0(\mathbf{R}', \mathbf{R}_0 ; \beta') = 0 \tag{8a}$$

and

$$\left[-\nabla^2 + V(\mathbf{R}) - \frac{\partial}{\partial\beta'}\right] \rho_B(\mathbf{R}, \mathbf{R}'; \beta - \beta') = 0. \tag{8b}$$

If Eq. (8a) is multiplied by $\rho_B(\mathbf{R}, \mathbf{R}'; \beta - \beta')$ and Eq. (8b) is multiplied by $\rho_0(\mathbf{R}', \mathbf{R}_0; \beta')$, they may be subtracted and integrations performed with respect to $\mathbf{R}'$ over the domain D_0 and with respect to β' from 0 to β. With the help of Green's theorem and the boundary conditions on ρ_B and ρ_0, the following integral equation is derived

$$\rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta) = \rho_0(\mathbf{R}, \mathbf{R}_0 ; \beta) + \int_0^\beta \int_{\partial D_0} \rho_B(\mathbf{R}, \mathbf{R}'; \beta - \beta')[-\nabla'_n \rho_0(\mathbf{R}', \mathbf{R}_0 ; \beta')]\, d\beta'\, d\mathbf{R}', \tag{9}$$

where ∇'_n indicates the outer normal derivative on the boundary of D_0 with respect to $\mathbf{R}'$. The relation in Eq. (9) is used to generate the full Green's function, $\rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta)$, by Monte Carlo from a knowledge of $\rho_0(\mathbf{R}, \mathbf{R}_0 ; \beta)$.

The actual computation involves the sampling of a sequence of points and times; $(\mathbf{R}_1, \beta_1)$, $(\mathbf{R}_2, \beta_2)$,..., in the domain of $\rho_B(\mathbf{R}, \mathbf{R}_0; \beta)$. Initially, a subdomain D_0 is constructed about $\mathbf{R}_0$ in which the Green's function is known. Points $\mathbf{R}_1$ on the boundary of D_0 and a time interval β_1 are sampled using $-\nabla_n \rho_0(\mathbf{R}_1, \mathbf{R}_0; \beta_1)$ as the density function. In a similar manner, D_n is constructed about $\mathbf{R}_n$ and $-\nabla_n \rho_0(\mathbf{R}_{n+1}, \mathbf{R}_n;$

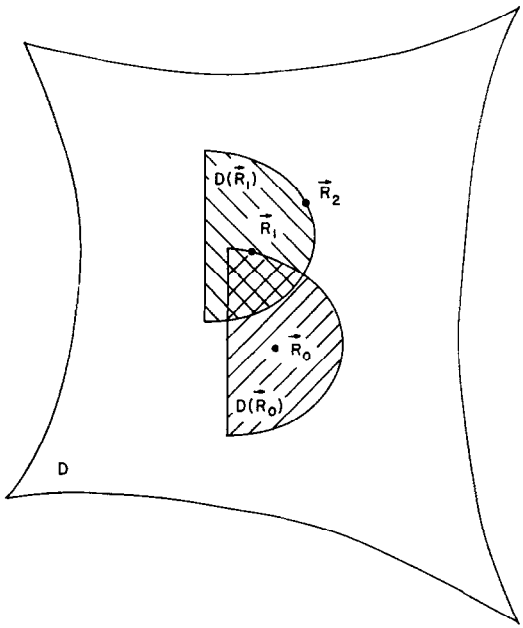

FIG. 1. A diagram of an idealized sequence of points and times, $(\mathbf{R}_n, \beta_n)$, sampled in the random walk constructed by a Green's Function Monte Carlo calculation. A subdomain $D(\mathbf{R}_n)$ is built about each $\mathbf{R}_n$ and a next $\mathbf{R}_{n+1}$ selected on the boundary of the subdomain.

$\beta_{n+1} - \beta_n)$ used to sample $\mathbf{R}_{n+1}$ and β_{n+1}. An idealized geometry for this process is shown in Figure 1. Let us define $Q(\mathbf{R}', \mathbf{R}_0; \beta')$ to be the density of arrivals at $(\mathbf{R}', \beta')$ at any step. $Q(\mathbf{R}', \mathbf{R}_0; \beta')$ satisfies the equation

$$Q(\mathbf{R}', \mathbf{R}_0; \beta') = \delta(\mathbf{R}' - \mathbf{R}_0)\,\delta(\beta') + \int_0^{\beta'} \int_{\partial D_0} [-\nabla'_n \rho_0(\mathbf{R}', \mathbf{R}''; \beta' - \beta'')]\, Q(\mathbf{R}'', \mathbf{R}_0; \beta'')\, d\mathbf{R}''\, d\beta''. \tag{10a}$$

This equation can also be written as

$$Q(\mathbf{R}', \mathbf{R}_0; \beta') = \delta(\mathbf{R}' - \mathbf{R}_0)\,\delta(\beta') + \int_0^{\beta'} \int_{\partial D_0} Q(\mathbf{R}', \mathbf{R}''; \beta' - \beta'')[-\nabla''_n \rho_0(\mathbf{R}'', \mathbf{R}_0; \beta'')]\, d\mathbf{R}''\, d\beta''. \tag{10b}$$

The quantity that is determined by the random walk is $\rho(\mathbf{R}, \mathbf{R}_0 ; \beta)$ which may be defined as

$$\rho(\mathbf{R}, \mathbf{R}_0 ; \beta) = \int_0^\beta \int_{D_0} \rho_0(\mathbf{R}, \mathbf{R}'; \beta - \beta')\, Q(\mathbf{R}', \mathbf{R}_0 ; \beta')\, d\mathbf{R}'\, d\beta'. \tag{11}$$

This quantity can be shown to be identical with the density matrix, $\rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta)$. By multiplying Equation (10b) by $\rho_0(\mathbf{R}, \mathbf{R}'; \beta - \beta')$ and then integrating R' over the domain D_0 and β' from 0 to β, an integral equation for $\rho(\mathbf{R}, \mathbf{R}_0 ; \beta)$ results which is the same as Eq. (9). Since the solution to Eq. (9) is unique, $\rho(\mathbf{R}, \mathbf{R}_0 ; \beta)$ and $\rho_B(\mathbf{R}, \mathbf{R}_6; \beta)$ are identical and the KLV Monte Carlo technique successfully describes "time" dependent diffusion.

In the discussion up to now, we have ignored the question of the symmetry of the wave functions and hence the symmetry of the density matrix with respect to particle interchange. Let us suppose that $\rho(\mathbf{R}, \mathbf{R}_0 ; \beta)$ is obtained using wave functions for distinguishable particles. Then we can construct ρ_B for a Bose system by setting

$$\rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta) = \sum_P \rho(P\mathbf{R}, \mathbf{R}_0 ; \beta) \tag{12}$$

where P is a particle permutation and the sum is over all possible such permutations.

In any physical problem we must be sure that the density matrix constructed has the required symmetry. That means, for Bose systems, that expectations with respect to ρ are computed by constructing random walks that start at $\mathbf{R}$ and return to $P\mathbf{R}$; one then averages over $\mathbf{R}$ and sums over P. The necessity for the permutation sum is a serious complication since in a many-body calculation there are very many permutations and their effect changes drastically with temperature. Also, it is known [7] that for hard sphere systems, the first permutations that become important as the temperature is lowered are cyclic permutations of three particles (rather than pair permutations). Thus the sum over permutations must be conducted in an intelligent way. This will be discussed in the next section.

The random walk simulates the diffusion of the system from one configuration R_0 to the permutation $P\mathbf{R}_0$. The decision as to which permutation will be the end point can be made prior to initiating the random walk or the decision can be made as the random walk evolves. Regardless of which method is used, the random walk proceeds from each point to a successor on the boundary of the subdomain. The overall Green's function is the sum of the partial Green's functions for every subdomain which occurs in the random walk and the function

$$\rho(P\mathbf{R}_0, \mathbf{R}_0 ; \beta) = \sum_n \rho_0(P\mathbf{R}_0, \mathbf{R}_n ; \beta - \beta_n) \tag{13}$$

is an unbiased Monte Carlo estimator for $\rho_B(P\mathbf{R}_0, \mathbf{R}_0 ; \beta)$.

To have the correct high temperature behavior as $\beta' \to \beta$, the Green's function within the subdomain, $\rho_0(\mathbf{R}, \mathbf{R}'; \beta - \beta')$, must be proportional to $(\beta - \beta')^{-(3N/2)}$ $\exp[-(\mathbf{R} - \mathbf{R}')^2/4(\beta - \beta')]$. Whenever $(\beta - \beta')$ becomes small and $\mathbf{R}$ is near $\mathbf{R}'$, singularities arise in $\rho_0(\mathbf{R}, \mathbf{R}'; \beta - \beta')$. Since $\rho_0(\mathbf{R}, \mathbf{R}'; \beta - \beta')$ is integrable but not

square integrable with respect to β, the Monte Carlo calculation which samples ρ_0 is an infinite variance Monte Carlo calculation; i.e., the overall Green's function is an average of very large and very small contributions from $\rho_0(\mathbf{R}, \mathbf{R}'; \beta - \beta')$. This is discussed further in an Appendix. Fortunately, the singular calculation may be transformed into a well behaved one by introducing importance sampling into the Monte Carlo procedure.

Theory of Importance Sampling Applied to the Bloch Equation

The Monte Carlo scheme we have described generates Green's function by sampling points in configuration space drawn from $\rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta)$. Clearly, the probability that the random walk will actually reach $P\mathbf{R}_0$ at β is zero. A somewhat more practical scheme is to use the estimator expressed by Eq. (13); that is, the sum over the steps of the walk of the probabilities that the random walk observed at some $(\mathbf{R}', \beta')$ will reach $P\mathbf{R}_0$ at time β. Use of the estimator will be totally ineffectual unless the walk populates reasonably densely a neighborhood of $(P\mathbf{R}_0, \beta)$. This will happen with very low probability, for example, in estimating exchange effects. Finally, as is shown in Appendix A, even when such a neighborhood is well sampled the estimator in in Eq. (13) has infinite variance and will exhibit extremely slow Monte Carlo convergence. However, importance sampling offers the possibility of altering the evolution of the "natural" diffusion process so as to choose suitably short paths which avoid hard sphere overlap or the occurance of strongly repulsive regions of configuration space and which permit the estimation of ρ_B at the required final position $P\mathbf{R}_0$ and "time" β. Such alteration of the diffusion process will have as a practical consequence the substantial reduction in Monte Carlo variance. That is, the infinite variance estimator will be replaced by a bounded score, and neighborhoods of $P\mathbf{R}_0$ and β will be well populated by the walk.

Importance sampling improves the Monte Carlo calculation through the introduction and systematic use of estimates of the probability that the random walk observed at some $(\mathbf{R}', \beta')$ will terminate at $P\mathbf{R}_0$. This probability is $\rho_B(P\mathbf{R}_0, \mathbf{R}'; \beta - \beta')$ and an approximation to it is used to bias the random walk to produce a larger than *a priori* chance that the random walk will reach a neighborhood of $P\mathbf{R}_0$. The use of an importance function which approximates $\rho_B(P\mathbf{R}_0, \mathbf{R}_0 ; \beta)$ increases the computational efficiency and reduces the variance in the final result.

Designating the importance function by $\rho_I(P\mathbf{R}_0, \mathbf{R}_0 ; \beta)$ the integral equations, Eqs. (9–12), can be written in terms of ρ_I. A new quantity, $\tilde{Q}(\mathbf{R}', \mathbf{R}_0 ; \beta')$, may be defined

$$\tilde{Q}(\mathbf{R}', \mathbf{R}_0 ; \beta') = \frac{Q(\mathbf{R}', \mathbf{R}_0 ; \beta')\, \rho_I(P\mathbf{R}_0, \mathbf{R}'; \beta - \beta')}{\rho_I(P\mathbf{R}_0, \mathbf{R}_0 ; \beta)}, \tag{14}$$

and the integral equation for $\rho_B(P\mathbf{R}_0, \mathbf{R}_0 ; \beta)$ in terms of $\tilde{Q}(\mathbf{R}', \mathbf{R}_0 ; \beta')$ becomes

$$\rho_B(P\mathbf{R}_0, \mathbf{R}_0; \beta) = \int_0^\beta \int_{D_0} \left[\frac{\rho_0(P\mathbf{R}_0, \mathbf{R}'; \beta - \beta')\, \tilde{Q}(\mathbf{R}', \mathbf{R}_0; \beta')\, \rho_I(P\mathbf{R}_0, \mathbf{R}_0; \beta)}{\rho_I(P\mathbf{R}_0, \mathbf{R}'; \beta - \beta')}\right] d\beta'\, d\mathbf{R}'. \quad (15)$$

The Monte Carlo process now selects the initial point $\mathbf{R}_0$ and the final point $P\mathbf{R}_0$ from $\rho_I(P\mathbf{R}_0, \mathbf{R}_0; \beta)$. In the random walk for $\tilde{Q}$, the kernel $-\nabla'_n\rho_0(\mathbf{R}', \mathbf{R}''; \beta' - \beta'')$ is replaced by

$$-\nabla'_n\rho_0(\mathbf{R}', \mathbf{R}''; \beta' - \beta'')\, \rho_I(P\mathbf{R}_0, \mathbf{R}'; \beta - \beta')/\rho_I(P\mathbf{R}_0, \mathbf{R}''; \beta - \beta'') \quad (16a)$$

and the $\tilde{Q}$ equation is

$$\tilde{Q}(\mathbf{R}', \mathbf{R}_0; \beta') = \delta(R' - R_0)\, \delta(\beta') + \int_0^{\beta'} \int_{\partial D_0} \frac{\rho_I(P\mathbf{R}_0, \mathbf{R}'; \beta - \beta')}{\rho_I(P\mathbf{R}_0, \mathbf{R}''; \beta - \beta'')} \times [-\nabla'_n\rho_0(\mathbf{R}', \mathbf{R}''; \beta' - \beta'')]\, \tilde{Q}(\mathbf{R}'', \mathbf{R}_0; \beta'')\, d\mathbf{R}''\, d\beta''. \quad (16b)$$

A score, $\rho_0(P\mathbf{R}_0, \mathbf{R}_0; \beta)/\rho_I(P\mathbf{R}_0, \mathbf{R}_0; \beta)$ is recorded only when the Q walk terminates and it is weighted with the reciprocal of the *a priori* probability that the walk did terminate at that particular step.

It is necessary that the importance function have the correct high temperature behavior as $\beta \to \beta'$ so $\rho_I(\mathbf{R}, \mathbf{R}'; \beta - \beta')$ must be proportional to $(\beta - \beta')^{-3N/2} \exp(-(\mathbf{R} - \mathbf{R}')^2/4(\beta - \beta'))$. Since the score that is recorded is $\rho_0(P\mathbf{R}_0, \mathbf{R}_0; \beta)/\rho_I(P\mathbf{R}_0, \mathbf{R}_0; \beta)$, the singularities in the Monte Carlo calculation discussed in the Appendix have been removed and the estimator is bounded. As the importance function more closely resembles $\rho_B(P\mathbf{R}_0, \mathbf{R}_0; \beta)$, the estimation of the score is carried out with a variance which approaches zero. Rewriting Eq. (9) for ρ_B as follows

$$1 = \frac{\rho_0(P\mathbf{R}_0, \mathbf{R}_n; \beta - \beta_n)}{\rho_B(P\mathbf{R}_0, \mathbf{R}_n; \beta - \beta_n)} + \int_{\beta_n}^{\beta} \int_{\partial D_0} [-\nabla'_n\rho_0(\mathbf{R}', \mathbf{R}_n; \beta' - \beta_n)] \times \frac{\rho_B(P\mathbf{R}_0, \mathbf{R}'; \beta - \beta')}{\rho_B(P\mathbf{R}_0, \mathbf{R}_n; \beta - \beta_n)}\, dR'\, d\beta'; \quad (17)$$

the integral on the right is the probability that the $\tilde{Q}$ walk, biased by ρ_B, continues. If this integral is designated P_Q, then the score $\rho_0(P\mathbf{R}_0, \mathbf{R}_n; \beta - \beta_n)/\rho_B(P\mathbf{R}_0, \mathbf{R}_n; \beta - \beta_n) = 1 - P_Q$. When scoring is carried out with probability $(1 - P_Q)$ (the *a priori* probability that the walk should terminate at this step) and weighted by $(1 - P_Q)^{-1}$, the score is exactly 1. Since ρ_I is in general not the same as ρ_B, variation in the score must be expected. Even though ρ_I is not equal to ρ_B, it is clear that scoring should be considered only when the contribution from all future steps is small ($\rho_I(P\mathbf{R}_0, \mathbf{R}_n; \beta - \beta_n)$ is small). The total Green's function that is estimated by the random walks is

$$\rho_B(P\mathbf{R}_0, \mathbf{R}_0; \beta) = \left\langle \sum_n \frac{\rho_0(P\mathbf{R}_0, \mathbf{R}_n; \beta - \beta_n)\, \rho_I(P\mathbf{R}_0, \mathbf{R}_0; \beta)}{(1 - P_Q)\, \rho_I(P\mathbf{R}_0, \mathbf{R}_n; \beta - \beta_n)} \right\rangle \quad (18)$$

where the sum extends over those steps at which a scoring occurred.

A score is the weight associated with the point $\mathbf{R}_0$ in configuration space. When a quantity such as $g(r, T)$ is inferred from an ensemble of points, statistical fluctuations will occur in the values obtained. In principle, though, importance sampling could be used to obtain a zero variance estimate of $g(r, T)$ for some r, but it is doubtful whether this is practical to carry out.

The importance function ρ_I is the key to the efficient treatment of permutations as well. There are two possibilities: one is that ρ_I has the proper symmetry under permutation. If so, the random walk started at $\mathbf{R}_0$ and biased with $\rho_I(\mathbf{R}, \mathbf{R}_0 ; \beta)$ will move preferentially to the neighborhood of $P\mathbf{R}_0$ according to the contribution of the permutation P to the density at inverse temperature β and for configuration $\mathbf{R}_0$.

Alternatively—and this is the procedure we foresee as more practical—suppose that ρ_I is correct only for Boltzmann statistics and that the sum indicated in (12) must be carried out explicitly. That sum can itself be done by a Monte Carlo technique and we propose the following scheme. Define a joint probability density function for configurations $\mathbf{R}_0$ and permutations P by

$$h(\mathbf{R}_0 , P; \beta) = H^{-1}\rho_I(\mathbf{R}_0 , P\mathbf{R}_0 ; \beta) \tag{19}$$

$$H = \sum_P \int \rho_I(\mathbf{R}, P\mathbf{R}; \beta)\, d\mathbf{R}. \tag{20}$$

For any given ρ_I, h may be sampled by a suitable generalization of the Metropolis method. Such a procedure has recently been used by Ceperley, Chester, and Kalos [8].

Now suppose that a population of configurations and permutations $\{\mathbf{R}_0 , P\}$ has been generated according to (19) and that $\mathbf{R}_0$ and $P\mathbf{R}_0$ are used as initial and final points in the random walk in Equation (16b). Associated with such a walk is the weight

$$w(P\mathbf{R}_0 , \mathbf{R}_0 ; \beta) = \sum_n \frac{\rho_0(P\mathbf{R}_0 , \mathbf{R}_n ; \beta - \beta_n)}{(1 - P_Q)\, \rho_I(P\mathbf{R}_0 , \mathbf{R}_n ; \beta - \beta_n)}. \tag{21}$$

Note that this is like (18) except that the factor $\rho_I(P\mathbf{R}_0 , \mathbf{R}_0 ; \beta)$ has been omitted. $W(\mathbf{R}_0)$, the expected density (weighted with w) for all walks started at $\mathbf{R}_0$ is given by Eq. (21) multiplied by the density given in (19) which served as the source and summed over permutations, that is

$$W(\mathbf{R}_0) = \frac{1}{H} \sum_P \left\langle \rho_I(\mathbf{R}_0 , P\mathbf{R}_0 ; \beta) \sum_n \frac{\rho_0(P\mathbf{R}_0 , \mathbf{R}_n ; \beta - \beta_n)}{(1 - P_Q)\, \rho_I(P\mathbf{R}_0 , \mathbf{R}_n ; \beta - \beta_n)} \right\rangle \tag{22}$$

$$= H^{-1} \sum_P \rho(P\mathbf{R}_0 , \mathbf{R}_0 ; \beta) = H^{-1}\rho_B(P\mathbf{R}_0 , \mathbf{R}_0 ; \beta). \tag{23}$$

This is the Bose density matrix, according to Eq. (12).

Finally, if we average, weighted with w, some function $f(\mathbf{R}_0)$ over all $\{\mathbf{R}_0 , P\}$, the expectation is

$$\langle f(\mathbf{R}) \rangle = \frac{\int f(\mathbf{R})\, \rho(\mathbf{R}, \mathbf{R}; \beta)\, d\mathbf{R}}{\int \rho(\mathbf{R}, \mathbf{R}; \beta)\, d\mathbf{R}}. \tag{24}$$

The sequence of operations consists in sampling $\{\mathbf{R}_0, P\}$ using (19), assigning a weight according to (21). This sequence permits the Monte Carlo calculation of expectations with respect to the diagonal part of the Bose density matrix. At the same time one can weight results obtained with P with the additional factor $(-1)^P$ to obtain results for Fermi statistics but we expect this simple strategem to give poor results at large β where even and odd permutations give contributions of similar absolute value.

There are several desirable properties of an appropriate importance function which guide us in its selection. The importance function must have the correct high temperature behavior in order that the last stages of the random walk ($\beta' \to \beta$) are correct. At low reduced temperatures, ρ_I should contain as much as can be conveniently arranged of the right physics of the system; and as $\beta \to \infty$, it should be symmetric with respect to permutations since the ground state density function is symmetric. The importance function may or may not be symmetrized for Bose statistics depending upon whether we propose to use it to guide the choice of permutations. In the practical selection of an importance function, the high temperature behavior must be correct but compromises are often necessary on the other desirable characteristics.

Application of the Theory to the Two-Body Problem

The simplest interesting system that can be considered is two indistinguishable spheres which interact by a hard sphere potential. The problem is equivalent to a point diffusing on the outside of an absorbing sphere as shown in Figure 2. For every $\mathbf{R}_0$

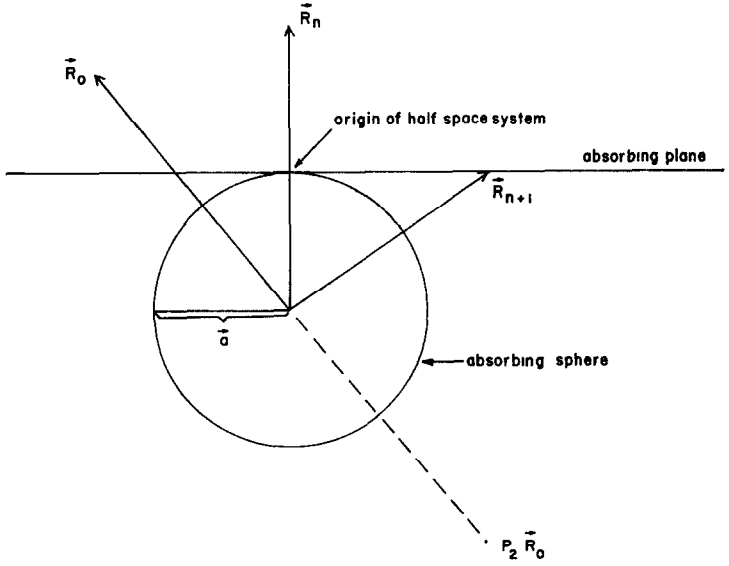

FIG. 2. A diagram showing a "marker" diffusing on the outside of an absorbing sphere. The marker started at $\mathbf{R}_0$ when $\beta = 0$ and now, at the nth step in the random walk, is at $\mathbf{R}_n$. A possible next step is to $\mathbf{R}_{n+1}$ on the boundary of the half space domain containing $\mathbf{R}_n$.

in the space, there corresponds a point reflected through the origin, $P_2\mathbf{R}_0$, which indicates the configuration of the system when the particles are interchanged; thus, there are two possible permutations. The density matrix, $\rho_B(\mathbf{R}, \mathbf{R}_0 ; \beta)$, describes the diffusion of a marker from $\mathbf{R}_0$ to $\mathbf{R}$ in "time" β.

From the density matrix, the radial distribution function may be calculated as shown in Equation (2). For two bodies, both the numerator and the denominator contain a contribution from the identity permutation and the pair exchange permutation, so the radial distribution function may be written as the sum of two terms

$$g(r, \beta) = g_{\text{dir}}(r, \beta) + g_{\text{exch}}(r, \beta). \tag{25}$$

The quantity $g_{\text{dir}}(r, \beta)$ derives from random walks which begin and end at $\mathbf{R}_0$,

$$g_{\text{dir}}(r, \beta) = \frac{V \int \rho_B(\mathbf{R}_0, \mathbf{R}_0 ; \beta)\, \delta(r_n - r_m - r)\, d\mathbf{R}_0}{\sum_P \int \rho_B(P\mathbf{R}, \mathbf{R}; \beta)\, d\mathbf{R}}. \tag{26a}$$

Note that the factor $(1 - 1/N)$ in Eq. (2) becomes 1 for two bodies in relative coordinates. Evaluation of the denominator in (2) over a large volume yields asymptotically $V/(4\pi\beta)^{3/2}$ for two bodies since the value of the direct permutation of $\rho_B(P\mathbf{R}, \mathbf{R}; \beta)$ approaches the constant value $(4\pi\beta)^{-3/2}$ as $\mathbf{R} \to \infty$ and the exchange contribution quickly dies off as $\mathbf{R} \to \infty$. The expression for g_{dir} becomes

$$g_{\text{dir}}(r, \beta) = (4\pi\beta)^{3/2} \rho_B(\mathbf{R}, \mathbf{R}; \beta). \tag{26b}$$

In a similar manner, we find

$$g_{\text{exch}}(r, \beta) = (4\pi\beta)^{3/2}\, \rho_B(-\mathbf{R}, \mathbf{R}; \beta). \tag{27}$$

In the high temperature limit, $g_{\text{dir}}(r, \beta)$ goes to the classical pair correlation function and $g_{\text{exch}}(r, \beta)$ approaches zero.

To evaluate the radial distribution functions in the two body system, the KLV method may be applied to the diffusion process. The implementation of the method involves dividing space into two regions; one region is the subdomain D_0 in which the partial Green's function, ρ_0, is defined. The subdomain used here is a half space whose boundary is an absorbing plane tangent to the sphere. This is not the only possible choice for the subdomain, but it does have desirable characteristics. For example, the mean time to absorption is much greater for the half-space than for a spherical domain. The total elapsed time in a random walk is the sum of the times to leakage for each subdomain so fewer steps are needed with planar boundaries.

The Green's function in the half-space with an absorbing plane boundary is

$$\rho_0(\mathbf{R}, \mathbf{R}_0 ; \beta) = \frac{\exp[-(\mathbf{R} - \mathbf{R}_0)^2/4\beta]}{(4\pi\beta)^{3/2}} \{1 - \exp[((\mathbf{R} - \mathbf{R}_0)^2 - (\mathbf{R} - \mathbf{R}_I)^2)/4\beta]\} \tag{28}$$

where $\mathbf{R}, \mathbf{R}_0$ are contained in the half-space and $\mathbf{R}_I$ is the image of $\mathbf{R}_0$ reflected through

the absorbing plane. This approximation for the two body problem was used by Uhlenbeck and Beth [9] in evaluating the direct radial distribution function at high temperatures. Upon substituting Eq. (28) into the expression for g_{dir}, Eq. (26), the Uhlenbeck and Beth expression for g_{dir} becomes

$$g_{\text{dir}}(r, \beta) = 1 - \exp\left[-\frac{a^2}{\beta}\left(\frac{r}{a} - 1\right)^2\right] \tag{29}$$

where a is the hard sphere diameter.

Once $\rho_0(\mathbf{R}, \mathbf{R}_0 ; \beta)$ is known for the subdomain, a random walk is constructed in which the kernel $(-\partial\rho_0(\mathbf{R}', \mathbf{R}_n ; \beta' - \beta_n)/\partial n)$ serves as the source for future diffusion. The random walk is initiated by setting $\mathbf{R}_0 = \mathbf{R}$ at $\beta = 0$ and defining a half space containing $\mathbf{R}_0$ whose absorbing plane boundary is tangent to the sphere and perpendicular to $\mathbf{R}_0$. The point $(\mathbf{R}_1, \beta_1)$ is selected from the distribution $(-\partial\rho_0(\mathbf{R}_1, \mathbf{R}_0 ; \beta_1)/\partial n)$ on the plane. The random walk continues from each $\mathbf{R}_n$ as follows: a half space containing $\mathbf{R}_n$ is constructed and a β_{n+1} and B_{n+1} on the plane boundary are sampled from $-\partial\rho_0(\mathbf{R}_{n+1}, \mathbf{R}_n ; \beta_{n+1} - \beta_n)/\partial n$. This is sketched in Fig. 2. The process of moving to the plane and the construction of a new half space is iterated until β_n is greater than β. There is no other mechanism for termination in this direct Monte Carlo procedure. An outline of this procedure, including the estimation of ρ_B by Eq. (13), is provided in Appendix B.

A direct sampling of $\rho_0(\mathbf{R}, \mathbf{R}_0 ; \beta)$ in Equation (28) with no importance sampling leads to a singular Monte Carlo computation. As $\mathbf{R}_n$ approaches $P\mathbf{R}_0$, the values of β_n will be chosen uniformly in the vicinity of β and can be arbitrarily close to β. This will lead to enormous contributions to the final score and $g(R)$ will be calculated with infinite variance (shown in detail for the N particle case in Appendix A). One benefit of importance sampling here is to transform the singular Monte Carlo calculation into a well-behaved one.

Importance Sampling in the Two-Body Problem

As has been described, an importance function which approximates the density function is needed. The first such function used in the importance sampling of the two body problem is

$$\rho_I(\mathbf{R}, \mathbf{R}_0 ; \beta) = \frac{\exp[-(\mathbf{R} - \mathbf{R}_0)^2/4\beta]}{(4\pi\beta)^{3/2}}\{1 - \exp[-(R^2 - a^2)(R_0^2 - a^2)/4a^2\beta]\}. \tag{30}$$

The particular functional form of $\rho_I(\mathbf{R}, \mathbf{R}_0 ; \beta)$ was chosen for several reasons. As $\beta \to 0$, the expression in Equation (30) has the proper high temperature behavior. Also, $\rho_I(\mathbf{R}, \mathbf{R}_0, \beta)$ approximates the Uhlenbeck-Beth function in Eq. (28) as $\mathbf{R}, \mathbf{R}_0 \to a$. This guarantees that the importance function vanishes on the surface of the sphere. Lastly, the dependence of $\rho_I(\mathbf{R}, \mathbf{R}_0 ; \beta)$ on the spatial variables allows the integrals over the surface of the plane, ∂D_0, to be carried out. No additional knowledge gained

from other calculations of the pair correlation function was built into the importance function. In particular, no consideration was given to the low temperature limit behavior of ρ_I.

Upon incorporating the importance function given in Eq. (30) into the integral equations, the marginal distribution function in β becomes

$$M(\beta) = \int_{\beta_n}^{\beta_f} \int_{\partial D_0} \frac{\rho_I(P\mathbf{R}_0, \mathbf{R}; \beta_f - \beta)}{\rho_I(P\mathbf{R}_0, \mathbf{R}_n; \beta_f - \beta_n)} [-\nabla_n \rho_0(\mathbf{R}, \mathbf{R}_n; \beta - \beta_n)]\, d\mathbf{R}\, d\beta$$

$$= \frac{Z_n}{(4\pi(\beta_f - \beta_n))^2\, \rho_I(P\mathbf{R}_0, \mathbf{R}_n; \beta_f - \beta_n)}$$

$$\times \int_{\beta_n}^{\beta_f} \left\{ \frac{\left[\exp\left[\frac{-((X_f - X_n)^2 + (Y_f - Y_n)^2)}{4(\beta_f - \beta_n)} \right] \times \exp\left[\frac{-Z_f^2}{4(\beta_f - \beta)} - \frac{Z_n^2}{4(\beta - \beta_n)} \right] \right]}{(\beta_f - \beta)^{1/2} (\beta - \beta_n)^{3/2}} \right.$$

$$\left. - \frac{\left[\exp\left[\frac{(X_f + ((\beta_f - \beta)/(\beta - \beta_n))\, X_n)^2 + (Y_f + ((\beta_f - \beta)/(\beta - \beta_n))\, Y_n)^2}{4(\beta_f - \beta)((\mathbf{R}_f/a)^2 + (\beta_f - \beta)/(\beta - \beta_n))} - \frac{\mathbf{R}_f^2}{4(\beta_f - \beta)} - \frac{\mathbf{R}_n^2}{4(\beta - \beta_n)} \right] \right]}{(\beta_f - \beta)^{1/2} (\beta - \beta_n)^{3/2} \left(\left(\frac{\mathbf{R}_f}{a} \right)^2 + \frac{\beta_f - \beta}{\beta - \beta_n} \right)} \right\} d\beta \tag{31}$$

where $\mathbf{R}_f$ is synonymous with $P\mathbf{R}_0$ and β_f indicates the final time. The integrand in Eq. (31) is sampled for a β [10] and the probability of scoring is determined,

$$P_s(P\mathbf{R}_0, \mathbf{R}_n; \beta_f - \beta_n) = \text{probability of scoring} = \frac{\rho_0(P\mathbf{R}_0, \mathbf{R}_n; \beta_f - \beta_n)}{\rho_I(P\mathbf{R}_0, \mathbf{R}_n; \beta_f - \beta_n)}. \tag{32}$$

If the half-space contains $P\mathbf{R}_0$, then it is possible to terminate the random walk and record a score. If the half-space does not contain $P\mathbf{R}_0$ or a decision not to score is made based upon the value of P_s, a next $\mathbf{R}$ is sampled from the kernel

$$\frac{-\nabla_n \rho_0(\mathbf{R}, \mathbf{R}_n; \beta - \beta_n)\, \rho_I(P\mathbf{R}_0, \mathbf{R}; \beta_f - \beta)}{\rho_I(P\mathbf{R}_0, \mathbf{R}_n; \beta_f - \beta_n)(1 - P_s)} \tag{33}$$

where $(1 - P_S)$ is employed as a weight or as a branching ratio. An outline of the Monte Carlo procedure with importance sampling is presented in Appendix B. The

two Monte Carlo methods, with and without important sampling may be contrasted. In the latter case, the random walk terminates only when β_n is greater than β_f and the estimator for $g(r, \beta)$ has infinite variance. The introduction of importance sampling alters the evolution of the diffusion process by choosing suitably short paths which avoid the absorbing sphere and enforces $\beta_n < \beta_f$. This permits the estimation of $\rho(P\mathbf{R}_0, \mathbf{R}_0; \beta_f)$ with a bounded estimator and hence finite variance. Termination

neighborhood of $P\mathbf{R}_0$ and the expected contribution from future steps is small.

The total Green's function which is estimated by the random walk is

$$\rho(P\mathbf{R}_0, \mathbf{R}_0; \beta_f) = \sum_n \frac{\rho_0(P\mathbf{R}_0, \mathbf{R}_n; \beta_f - \beta_n)\, \rho_I(P\mathbf{R}_0, \mathbf{R}_0; \beta_f)}{P_s(P\mathbf{R}_0, \mathbf{R}_n; \beta_f - \beta_n)\, \rho_I(P\mathbf{R}_0, \mathbf{R}_n; \beta_f - \beta_n)} \tag{34}$$

where the sum extends only over the steps at which a scoring occurred. The sum in Eq. (34) is an unbiased estimator for the actual Green's function, $\rho_B(P\mathbf{R}_0, \mathbf{R}_0; \beta_f)$.

Results and Discussion

The results of the Monte Carlo calculation on the two body Bloch Equation for the direct radial distribution function, g_{dir}, and the exchange radial distribution function, g_{exch}, are given in Tables I and II, respectively. The quoted values represent 10,000 random walks each; the quoted error is a measure of the range of scores recorded within the 10,000 walks. Also given in the Tables are exact numerical values of g_{dir} and g_{exch} calculated by Larsen [11]. It is obvious that the method works best at high temperatures and at large distances. Indeed at $\lambda_T/a = 1.4$ (λ_T is the thermal wave length and a is the hard sphere diameter), the Green's function Monte Carlo method is sufficiently sensitive so that it may be used to detect the difference of g_{dir} from 1 as the two particles recede from one another. At lower temperatures, the Monte Carlo results are still good but the errors have increased. As explained earlier, the importance function, Eq. (30), was not optimized for low temperature behavior and its behavior is surely wrong at such temperatures. It is interesting that reasonable results can be obtained at reduced temperatures which correspond to approximately. 2° K. On the other hand, the inferior qualities of the importance function adversely affect the calculation of the exchange radial distribution function at high temperatures. Since it must guide the diffusion around the sphere, the inappropriate behavior leads to a poor choice of path. Of course, if no importance sampling were used, the probability of circumventing the sphere would be very small. Even an inferior choice of ρ_I is better than none.

In Table III, the Green's function Monte Carlo values for the second virial coefficients are presented in comparison with Boyd, Larsen and Kilpatrick's numerical values [12] and some asymptotic expansions [12]. The direct virial coefficient may be determined from the direct radial distribution function,

$$\frac{B_{\text{dir}}}{B_{\text{clas}}} = -3 \int_0^\infty (g_{\text{dir}} - 1)\, R^2\, dR \tag{35}$$

TABLE I

Direct Radial Distribution Function for Hard Spheres

$\lambda_T/a = 1.4$[a]			$\lambda_T/a = 10$		
R[b]	Monte Carlo estimate[c]	Numerical result[d]	R[b]	Monte Carlo estimate[c]	Numerical result[d]
1.125	$.08668 \pm .17 \times 10^{-3}$	.086503	1.25	$.04948 \pm .00063$	.050402
1.25	$.27278 \pm .40 \times 10^{-3}$	.272861	1.75	$.2342 \pm .0022$	.236874
1.375	$.48164 \pm .65 \times 10^{-3}$	.481210	2.25	$.4060 \pm .0030$	.408308
1.50	$.66520 \pm .79 \times 10^{-3}$	.665109	2.75	$.5456 \pm .0043$	.547489
1.625	$.80437 \pm .86 \times 10^{-3}$	.803755	3.25	$.6580 \pm .0038$	.658482
1.75	$.89640 \pm .66 \times 10^{-3}$	.895494	3.75	$.7488 \pm .0034$	.746257
2.0	$.97785 \pm .20 \times 10^{-3}$	.977751	4.25	$.8174 \pm .0028$	.81467
2.25	$.996802 \pm .33 \times 10^{-4}$	.996774	4.75	$.8678 \pm .0021$	.867636
2.50	$.999676 \pm .37 \times 10^{-5}$	.999682	5.25	$.9061 \pm .0016$	.907420
2.75	$.999979 \pm .27 \times 10^{-6}$	.999979	5.75	$.9381 \pm .0011$	.936739

[a] $\lambda_T/a = [4\pi\beta/a^2]^{1/2}$.
[b] R is dimensionless. When $R = 1$, the hard spheres are touching.
[c] These values correspond to 10,000 samples at each R. The error shown is one standard deviation.
[d] S. Y. Larsen [11].

where $B_{\text{clas}} = 2\pi a^3/3$ and $R = r/a$. The integration was performed by Monte Carlo with the choice of R guided by the function

$$P_{\text{dir}}(R) = \exp[-(R-1)^2/4\beta_f]\, R^2\, dR. \tag{36}$$

Again the Monte Carlo results are most impressive at high temperatures and can accurately reproduce the deviation of the direct virial coefficient from the classical value.

In a similar manner, the exchange virial coefficient may be determined from the exchange radial distribution function;

$$\frac{B_{\text{exch}}}{B_{\text{clas}}} = -3\int_0^\infty g_{\text{exch}} R^2\, dR. \tag{37}$$

The choice of R during the Monte Carlo integration was guided by the function

$$P_0(R) = (R-1)\, e^{-(R-1)^2/4\alpha\beta_f}. \tag{38}$$

The variable α was chosen such that $P_0(R)$ would have its maximum at the value of R for which $g_{\text{exch}}(R)$ has its maximum. Data generated by the GFMC calculation of g_{exch} was used to determine the appropriate values of α.

TABLE II

Exchange Pair Correlation Function for Hard Spheres

	$\lambda_T/a = 2.93761$			$\lambda_T/a = 10$	
R[a]	Monte Carlo estimate[b]	Numerical result[c]	R[a]	Monte Carlo estimate[b]	Numerical result[c]
1.125	$.785 \times 10^{-3} \pm .021 \times 10^{-3}$	$.778 \times 10^{-3}$	1.25	$.03068 \pm .00050$	.030112
1.25	$2.237 \times 10^{-3} \pm .064 \times 10^{-3}$	2.276×10^{-3}	1.75	$.1277 \pm .0017$	.128927
1.50	$4.56 \times 10^{-3} \pm .11 \times 10^{-3}$	4.481×10^{-3}	2.25	$.1911 \pm .0025$	.193442
1.625	$4.66 \times 10^{-3} \pm .11 \times 10^{-3}$	4.749×10^{-3}	2.75	$.2183 \pm .0028$	.218570
1.75	$4.63 \times 10^{-3} \pm .16 \times 10^{-3}$	4.545×10^{-3}	3.25	$.2184 \pm .0027$	.215374
2.0	$3.419 \times 10^{-3} \pm .080 \times 10^{-3}$	3.366×10^{-3}	3.75	$.2004 \pm .0023$	.194707
2.25	$2.044 \times 10^{-3} \pm .067 \times 10^{-3}$	2.027×10^{-3}	4.25	$.1672 \pm .0018$	.165175
2.5	$1.037 \times 10^{-3} \pm .023 \times 10^{-3}$	1.041×10^{-3}	4.75	$.1360 \pm .0013$	.133021
2.75	$.477 \times 10^{-3} \pm .013 \times 10^{-3}$	$.467 \times 10^{-3}$	5.25	$.10285 \pm .00092$	.102371
2.875	$.3114 \times 10^{-3} \pm .0065 \times 10^{-3}$	$.298 \times 10^{-3}$	5.75	$.07598 \pm .00064$	.075591

[a] R is dimensionless and equals r/a. When $R = 1$, the hard spheres are touching.
[b] These values correspond to 10,000 samples at each R. The error shown is one standard deviation.
[c] S. Y. Larsen [11].

In Table III, the absolute value of the ratio of the exchange virial coefficient to the classical virial coefficient is reported. In contrast to the direct virial coefficient, B_{exch} is determined most precisely at the lowest temperatures. At temperatures higher than $\lambda_T/a = 2.0$, a value for the exchange virial coefficient cannot be reliably extracted by this Monte Carlo calculation. This is of course due to the poor guidance given by the importance function in the region of high temperatures for the exchange of the two hard spheres.

Improved Importance Sampling

While the results that were achieved with the importance function introduced previously are impressive, especially for the direct radial distribution function and virial coefficient, the difficulty in determining high temperature exchange results is unsatisfactory. Therefore an alternate importance function was devised which would be more realistic in the exchange region. Following a suggestion by Lieb [13] the function

$$\rho_I' = \left(\frac{1}{4\pi\beta}\right)^{3/2} \exp[-S^2(r, r')/4\beta] \left\{1 - \exp\left[\frac{-(r-a)(r'-a)}{\beta}\right]\right\} \tag{39}$$

was tried as an importance function. In this equation $S(r, r')$ is the shortest distance

TABLE III

Second Virial Coefficients for Hard Spheres

$B_{dir}/B_{classical}$				$B_{exch}/B_{classical}$[c]			
$\lambda_T/$[a]	Monte Carlo estimate[a]	Numerical value[b]	High temp. expansion[b]	λ_T/a	Monte Carlo estimate[a]	Numerical value[b]	Low temp. expansion[b]
.050	$1.05410 \pm .40 \times 10^{-3}$		1.0538	2.0	$6.90 \times 10^{-4} \pm .38 \times 10^{-4}$	7.333×10^{-4}	
.40	$1.4727 \pm .0042$		1.4761	2.9375	$4.79 \times 10^{-2} \pm .12 \times 10^{-2}$	4.80×10^{-2}[d]	
.80	$2.055 \pm .011$		2.0599	4	$.4719 \pm .0075$	.47582	
1.2	$2.770 \pm .021$		2.7577	6	$4.496 \pm .054$	4.5127	
1.4	$3.151 \pm .026$	3.14	3.1517	8	$16.81 \pm .18$	16.507	17.943
2	$4.537 \pm .049$	4.49	4.5260	10	$41.34 \pm .43$	40.715	41.661
2.9375	$7.12 \pm .10$	7.1[d]					
4	$11.04 \pm .19$	11.06					
6	$20.46 \pm .45$	21.03					
8	$34.91 \pm .93$	34.63					
10	54.2 ± 1.6	51.95					

[a] These values correspond to 10,000 samples at each (λ_T/a).
[b] M. E. Boyd, S. Y. Larsen & J. E. Kilpatrick [12].
[c] The absolute value of B_{exch} is reported for spin zero.
[d] S. Y. Larsen [11].

between r and r' which does not intersect the absorbing sphere. For the case where r and r' are within sight of each other, the shortest distance is just $| r - r' |$; but when one of the points is in the shadow of the sphere, $S(r, r')$ is composed of two tangent lines and an arc on the sphere. The motivation for choosing this importance function is that the shortest path from r to r' will be the most likely in the random walk, especially at high temperatures. The new importance function is identical to the half space Green's function, Eq. (28), for r and r' within sight of each other. The improvement in using Eq. (39) is expected to be most dramatic in the calculation of exchange quantities.

Rather than rederive all the sampling techniques which would be needed to use the new ρ_I', the Monte Carlo was modified in a way which retained the techniques developed for the original ρ_I and then corrected the sampling using ρ_I'. A new $(\mathbf{R}_n, \beta_n)$ are selected from a distribution based on ρ_I; the multiplicity [10] associated with this point is adjusted to reflect that we should be sampling ρ_I'

$$M' = M \frac{\rho_I(\mathbf{R}_f, \mathbf{R}_n; \beta_f - \beta_n)\, \rho_I'(\mathbf{R}_f, \mathbf{R}_{n-1}; \beta_f - \beta_{n-1})}{\rho_I'(\mathbf{R}_f, \mathbf{R}_n; \beta_f - \beta_n)\, \rho_I(\mathbf{R}_f, \mathbf{R}_{n-1}; \beta_f - \beta_{n-1})}, \tag{40}$$

where M' is the adjusted multiplicity, M is the multiplicity based on ρ_I and $(\mathbf{R}_{n-1}, \beta_{n-1})$ is the previous point in the random walk. Upon making this change in the GFMC code, an improvement in the calculation of the exchange correlation function is definitely observed. In Table IV a comparison of the g_{exch} which results when the importance function in Equations (30) and (39) are used is given for a range of temperatures. At each temperature the final internuclear separation, R, is that which corresponds to the maximum in g_{exch}. The values labelled efficiency, ϵ, are designed to measure quantitatively the improvement of one Monte Carlo calculation over another. For the same number of random walks, 10,000 in this case, the efficiency is the variance estimated in the Monte Carlo calculation multiplied by the elapsed time of the computation. Thus the efficiency measures the composite effect of improving variance while possibly changing the computation time for each trial. As the temperature increases ("time" decreases), the ratio of the efficiencies increases; and the ratio can be made arbitrarily large at high enough temperatures.

Through the use of an improved importance function, accurate and precise values of both the exchange and direct correlation are possible. With the function in Eq. (39), there is no restriction on where the exchange radial distribution function may be easily determined.

The philosophy above was to find an analytical importance function which contained as much as the actual physics of the problem as could be contrived and thereby improving the performance of the Monte Carlo code. This is not the only way to approach the development of useful importance functions. Each time a random walk

function $\rho_B(\mathbf{R}, \mathbf{R}'; \Delta p)$. If space and time are discretized into cells, the outcome of a series of random walks can yield information about the importance function in tabular form. This can be visualized as follows: suppose N_b walks start in the cell Y_b and N_f

TABLE IV

Comparison of the Behavior of the *GFMC* Code with the Original and the Improved Analytical Importance Functions

λ_T/a	R	$g_{\text{exch}}(R)$ from original importance function	ϵ^b	$g_{\text{exch}}(R)$ from improved importance function	ϵ^b	Numerical result[a]
1.4	1.25	$4.3 \times 10^{-7} \pm 1.2 \times 10^{-7}$	1.4×10^{-11}	$5.07 \times 10^{-7} \pm .18 \times 10^{-7}$	7.5×10^{-14}	5.37×10^{-7}
2	1.4375	$1.516 \times 10^{-4} \pm .085 \times 10^{-4}$	7.4×10^{-9}	$1.578 \times 10^{-4} \pm .031 \times 10^{-4}$	1.5×10^{-9}	1.605×10^{-4}
2.93761	1.625	$4.70 \times 10^{-3} \pm .11 \times 10^{-3}$	1.3×10^{-6}	$4.716 \times 10^{-3} \pm .072 \times 10^{-4}$	5.9×10^{-7}	4.749×10^{-3}
4	1.875	$2.367 \times 10^{-2} \pm .038 \times 10^{-2}$	1.6×10^{-5}	$2.398 \times 10^{-2} \pm .028 \times 10^{-2}$	7.4×10^{-6}	2.3726×10^{-2}
6	2.25	$8.68 \times 10^{-2} \pm .11 \times 10^{-2}$	1.3×10^{-4}	$8.673 \times 10^{-2} \pm .098 \times 10^{-2}$	7.1×10^{-5}	8.7012×10^{-2}
8	2.5625	$1.571 \times 10^{-1} \pm .019 \times 10^{-1}$	3.7×10^{-4}	$1.551 \times 10^{-1} \pm .018 \times 10^{-1}$	2.6×10^{-4}	1.56886×10^{-1}
10	2.9375	$2.188 \times 10^{-1} \pm .026 \times 10^{-1}$	7.2×10^{-4}	$2.223 \times 10^{-1} \pm .029 \times 10^{-1}$	6.9×10^{-4}	2.20065×10^{-1}

[a] S. Y. Larsen [11].

[b] The efficiency is the variance estimated in the Monte Carlo calculation multiplied by the elapsed time of computation.

walks arrive at Y_f, the volume which contains $(\mathbf{R}_f, \beta_f)$. Our estimate of the actual density function $\rho_B(Y_f \leftarrow Y_b)$ is

$$\rho_B(Y_f \leftarrow Y_b) = \frac{N_f}{N_b} \rho_I(Y_f \leftarrow Y_b) \tag{41}$$

and the ratio of the actual density function to the importance function is N_f/N_b. The ratio N_f/N_b for each volume in space accessed in a random walk can easily be recorded and the information used as an improved importance function. The usage of the tabular data is similar in approach to the way the improved analytical importance function was introduced above. A point $(\mathbf{R}_n, \beta_n)$ is chosen from a probability distribution function appropriate to the original importance function Eq. (30) and the multiplicity associated with this point is corrected by multiplying it by the tabulated ratios in the volumes containing the point and the previous point (cf. Eq. (40)). The process can be a self-learning one in which the table is updated as more and more random walks are conducted using the table. Eventually a very accurate representation of the density matrix could be achieved as more data are generated.

The one serious drawback to the generation and use of a numerical importance function as described is the dimensionality of the table necessary to contain it. For each pair of final point and time $(\mathbf{R}_f, \beta_f)$, there is a separate table containing the space and times the steps in a random walk will acess. This is necessary because the ratio, N_f/N_b, recorded pertains to the number of walks passing through cell Y_b which reach cell Y_f (the cell which contains R_f) in time $\beta_f - \beta$. In theory, it would be necessary to assemble a three dimensional table in $(\mid R \mid, \theta, \Delta\beta)$ for all the combinations of $(\mathbf{R}_f, \beta_f)$. In practice, though, random walks which wish to reach $\mathbf{R}_f$ in a time $\beta_f' < \beta_f$ can use the data generated for $(\mathbf{R}_f, \beta_f)$.

As a demonstration of the feasibility of using a numerical importance function, a table of data was generated for $R_f = 1.875$ and $\lambda_T/a = 6$ from a series of 10^5 random walks importance sampled in the original way, Eq. 30. Exchange radial distribution functions at several values of λ_T/a less than 6 and $R_f = 1.876$ were calculated and are reported in Table V; each value represents the result of 5000 random walks. Table V compares the performance of the GFMC code with the analytical improved importance function, Eq. (39), the original importance function, Eq. (30), and the numerical function. At values of λ_T/a near 6, the numerical function behaves as well as the improved analytical function in calculating $g_{\text{exch}}(R)$ as measured by the efficiency. At higher temperatures (smaller λ_T/a), the data in the numerical function table is less complete and this is reflected in the increasing standard error in the g_{exch} result as compared with the analytical calculation. In all cases, however, the GFMC calculation which employs the numerical importance function is better than the original calculations. It can be anticipated that if the numerical data had been collected from a series of random walks which were biased by Eq. (39), even better improvements in efficiency would emerge upon subsequent use of the data.

The dimensionality problem will prevent the use in exactly the mode used here for many-body problems. Any reasonable division into "cells" in a $3N$ dimensional

TABLE V

Comparison of the Exchange $g(R)$ Calculated Using Various Importance Functions

$\lambda_T^{\frac{1}{2}}/a$	$g(R)$ from original ρ_I, Eq. (30)	ϵ	$g(R)$ from improved ρ_I, Eq. (39)	ϵ	$g(R)$ from numerical ρ_I	ϵ
2	$4.9 \times 10^{-5} \pm .36 \times 10^{-5}$	6.9×10^{-10}	$5.60 \times 10^{-5} \pm .16 \times 10^{-5}$	1.7×10^{-10}	$5.29 \times 10^{-5} \pm .28 \times 10^{-5}$	2.8×10^{-10}
2.9375	$3.94 \times 10^{-3} \pm .13 \times 10^{-3}$	9.8×10^{-7}	$3.949 \times 10^{-3} \pm .075 \times 10^{-3}$	2.9×10^{-7}	$4.018 \times 10^{-3} \pm .097 \times 10^{-3}$	3.8×10^{-7}
4	$2.241 \times 10^{-2} \pm .054 \times 10^{-2}$	1.6×10^{-5}	$2.374 \times 10^{-2} \pm .044 \times 10^{-3}$	8.5×10^{-6}	$2.380 \times 10^{-2} \pm .038 \times 10^{-3}$	6.0×10^{-6}
6	$8.01 \times 10^{-2} \pm .16 \times 10^{-2}$	1.4×10^{-4}	$7.49 \times 10^{-2} \pm .13 \times 10^{-2}$	6.1×10^{-5}	$7.96 \times 10^{-2} \pm .12 \times 10^{-2}$	5.9×10^{-5}

space will result in samples too sparse in any cell to be statistically reliable. But it should prove possible to use the data generated during the Monte Carlo in a global way to determine best parameters for some assumed importance function.

Conclusion

An extension of the Green's function Monte Carlo method of Kalos, Levesque and Verlet has been outlined for finite temperature, quantum many body systems. The method involves writing the Bloch equation for the system as an integral equation and sampling the Green's function in a Monte Carlo calculation to solve the integral equation. The Green's function of the system is the density matrix and knowledge of the density matrix allows the calculation of quantities of physical interest. The computation has borne out our assertion that the successful application of the GFMC method requires the introduction of importance sampling to eliminate the occurrence of infinite variances and to increase computational efficiency. Of considerable importance in the many body quantum system is the correct handling of particle permutations. Two general methods are proposed. One which requires sampling permutations should be feasible. Although we did not use it, it would clearly have worked successfully in the two-body problem.

Feasibility was investigated by applying the GFMC method to the case of two bodies interacting by a hard sphere potential. The straight forward Green's function Monte Carlo calculation is seen to have infinite variance, and importance sampling is absolutely necessary. We implemented this into an algorithm, using deliberately an importance function whose description of the exchange term was seriously inaccurate. The results proved rather good in spite of this deficiency. The acceptibility of the result was judged by comparing radial distribution functions and virial coefficients generated by the GFMC calculation with accurate numerical results [11]. Of particular note is that the Monte Carlo calculation can accurately predict the deviation of the direct virial coefficient from the classical values at high temperatures. Very small departures of the direct radial distribution function from unity have been accurately calculated.

Additional Monte Carlo calculations demonstrated that a better choice of the importance function significantly reduced the variance of the final result. With the improved importance function, accurate high temperature exchange results were determined. We also explored the use of a numerical importance function obtained by accumulating information in tabular form from a series of the same random walks that solve the Bloch Equation. This experiment successfully demonstrated the feasibility of fixing values or parameters of an importance function as an outcome of the Monte Carlo.

The results reported here indicate, insofar as a two-body calculation can, that the Green's function Monte Carlo method can be applied to the calculation of equilibrium properties of quantum systems. We plan next to develop the algorithm into a form suited for many-body problems and to apply the result to a small number of hard spheres.

APPENDIX A

We prove here the assertion that the use of the Green's Function random walk without importance sampling together with the use of Eq. (13) to estimate ρ_B for the hard-sphere problem leads to infinite variance. The consequences of this result will be discussed briefly. The proof is given for the general (N-body) problem; its validity for the 3-dimensional case considered in detail in the body of the paper follows easily.

A direct Green's Function Monte Carlo calculation of the density matrix uses the integral equation

$$\rho(\mathbf{R}, \mathbf{R}_0 ; \beta) = \int_0^B \int_D \rho_0(\mathbf{R}, \mathbf{R}'; \beta - \beta')\, Q(\mathbf{R}', \mathbf{R}_0 ; \beta')\, d\mathbf{R}'\, d\beta' \tag{A1}$$

to relate the density matrix $\rho(\mathbf{R}, \mathbf{R}_0 ; \beta)$ to the set of points $\{\mathbf{R}_n , \beta_n\}$ in a random walk sampled from the density $Q(\mathbf{R}', \mathbf{R}_0 ; \beta')$. Then, a Monte Carlo estimator for ρ_B is formed by summing all the contributions from $\rho_0(\mathbf{R}, \mathbf{R}'; \beta - \beta')$ in the course of the random walk,

[redacted]

The variance of the mean of the density matrix in Eq. (A2) can be related to the variance of the Green's Function in the subdomain, ρ_0 , by

$$\mathrm{var}\{\rho\} = \frac{1}{K} \mathrm{var}\{\rho_0\} \tag{A3}$$

in which K is the number of histories averaged to estimate the mean of $\rho(P\mathbf{R}_0 , \mathbf{R}_0 ; \beta_f)$. The variance of the sum of subdomain Green's Functions is

$$\mathrm{var}\{\rho_0\} = \langle \rho_0{}^2 \rangle - \langle \rho_0 \rangle^2 \tag{A4}$$

where the angular brackets denote the expectation value of $\rho_0(\mathbf{R}, \mathbf{R}'; \beta - \beta')$ for the subdomain evaluated with respect to the population of $\{\mathbf{R}', \beta\}$ given by the Q equation. The quantity $\langle \rho_0 \rangle$ is finite since it is the original density function. We now show that $\langle \rho_0{}^2 \rangle$ is infinite.

Let D_c be the largest $3N$-dimensional cube of any orientation that has $P\mathbf{R}_0$ as its center and which does not permit any hard sphere overlap. Denote its side as $2r_l$. We need a lower bound for $\rho_0(P\mathbf{R}_0 , \mathbf{R}; \beta_f - \beta)$ for $\mathbf{R}$ contained within the cube; such a bound can be devised by using a multidimensional image expansion. Let $\mathbf{L}$ be a $3N$ dimensional vector whose components are $\pm 2m_k r_l$ where $m_k = 0, 1, 2,...$; then

$$\rho_0(P\mathbf{R}_0 , \mathbf{R}; \beta_f - \beta) = \frac{1}{(4\pi(\beta_f - \beta))^{3N/2}} \sum_{\mathbf{L}} (-1)^{\Sigma_k m_k} \exp\left[- \frac{(P\mathbf{R}_0 - \mathbf{R} - \mathbf{L})^2}{4(\beta_f - \beta)} \right]. \tag{A5}$$

The sum on $\mathbf{L}$, which is absolutely convergent, may be reordered to include successive-

ly larger terms in $|L|$. The first two terms are $\mathbf{L} = 0$ and $|L| = 2r_l$ ($\sum |m_l| = 1$) and together these give a lower bound for $\rho_0(P\mathbf{R}_0, \mathbf{R}; \beta_f - \beta)$. That is, let

$$\mathbf{X} = \mathbf{R} - P\mathbf{R}_0 \tag{A6}$$

be a set of cartesian coordinates parallel to the edges of D_c. Then

$$\rho_0(P\mathbf{R}_0, \mathbf{R}; \beta_f - \beta) > \frac{1}{(4\pi(\beta_f - \beta))^{3N/2}} \left\{\exp[-X^2/4(\beta_f - \beta)] - \sum_{|L|=1} \exp\left[-\sum_k (X_k - 2m_k r_l)^2/4(\beta_f - \beta)\right]\right\} \tag{A7}$$

where in each term of the sum exactly one $m_k = \pm 1$. Thus for $\mathbf{R} \in D_c$, i.e., $|X_k| \leqslant r_l$, Equation (A7) becomes

$$\rho_0(P\mathbf{R}_0, \mathbf{R}; \beta_f - \beta) > \frac{1}{(4\pi(\beta_f - \beta))^{3N/2}} \{\exp[-X^2/4(\beta_f - \beta)] - 6N \exp[-r^2/4(\beta_f - \beta)]\}. \tag{A8}$$

Now consider D_s, the $3N$-dimensional sphere of radius r_l inscribed in D_c. Within this domain and in the time interval $\beta_f - \Delta\beta < \beta' < \beta_f$, the density, $Q(P\mathbf{R}_0, \mathbf{R}; \beta_f - \beta)$ with which the points $(\mathbf{R}', \beta')$ will populate the neighborhood of $P\mathbf{R}_0$ is positive and bounded away from zero. Let $Q_0 > 0$ be a lower bound to that density; then the square of the estimator derived from Eq. (13) averaged over all space and β satisfies

$$\begin{aligned} \langle \rho_0^2(P\mathbf{R}_0, \mathbf{R}_0; \beta_f)\rangle &> Q_0 \int_{\beta_f - \Delta\beta}^{\beta_f} \int_{D_S} \rho_0^2(P\mathbf{R}_0, \mathbf{R}; \beta_f - \beta)\, d\mathbf{R}\, d\beta \\ &> Q_0 \int_0^{\Delta\beta} \frac{1}{(4\pi\beta')^{3N}} \int_{D_S} \{\exp[-X^2/4\beta'] - \exp[-r_l^2/4\beta']\}^2\, d\mathbf{X}\, d\beta'. \end{aligned} \tag{A9}$$

The integral indicated on the right-hand side of Eq. (A9) factors into three contributions

$$I = Q_0 \int_0^{\Delta\beta} \frac{1}{(4\pi\beta')^{3N}} (I_1 - I_2 + I_3)\, d\beta' \tag{A10}$$

where

$$I_1 = \int_0^{r_l} \exp[-X^2/2\beta']\, X^{3N-1}\, dX,$$

$$I_2 = 2 \exp[-r_l^2/4\beta'] \int_0^{r_l} \exp[-X^2/4\beta']\, X^{3N-1}\, dX,$$

and

$$I_3 = \exp[-r_i^2/2\beta'] \int_0^{r_i} X^{3N-1}\, dX$$

$$= \frac{r_i^{3N}}{3N} \exp[-r_i^2/2\beta'].$$

Since I_3 is positive the inequality of Eq. (A9) is preserved if I_3 is omitted.

By introducing the change of variables $V = X^2/2\beta'$, the integrals I_1 and I_2 are transformed into

$$I_1 = \frac{(2\beta')^{3N/2}}{2} \int_0^{V_i} e^{-V} V^{(3N/2)-1}\, dV \tag{A11}$$

and

$$I_2 = (2\beta')^{3N/2} \exp\left[-\frac{r_i^2}{4\beta'}\right] \int_0^{V_i} e^{-V/2} V^{(3N/2)-1}\, dV \tag{A12}$$

where $V_i = r_i^2/2\beta'$. Now, $r_i^2/2\Delta\beta < V_i < \infty$; therefore

$$I_1 > I_{10}\beta'^{3N/2} \equiv \frac{(2\beta')^{3N/2}}{2} \int_0^{r_i^2/2\Delta\beta} e^{-V} V^{3N/2-1}\, dV \tag{A13a}$$

and

$$I_2 < I_{20}\beta'^{3N/2} \equiv (2\beta')^{3N/2} \exp\left[-\frac{r_i^2}{4\beta'}\right] \int_0^{\infty} e^{-V/2} V^{(3N/2)-1}\, dV. \tag{A13b}$$

I_{10} and I_{20} are positive and finite; and the β' integral deriving from I_2 in Eq. (A10) exists. On the other hand

$$Q_0 \int_0^{\Delta\beta} \frac{I_1}{(4\pi\beta')^{3N/2}}\, d\beta' > Q_0 \frac{I_{10}}{(4\pi)^{3N}} \int_0^{\Delta\beta} (\beta')^{-3N/2}\, d\beta' \tag{A14}$$

which diverges. Since the other terms in Eq. (A9) are finite, $\langle \rho_0^2 \rangle$ is infinite.

The result still applies if we use ρ_0 for domains larger than D_c ; in particular, it applies for the half space bounded by a plane as in the example used in the body of this paper. That is, if $D \in D_c$, then Eq. (9) shows immediately that

$$\rho_0(P\mathbf{R}_0\,, \mathbf{R}; \beta_f - \beta) > \rho_{0c}(P\mathbf{R}_0\,, \mathbf{R}; \beta_f - \beta)$$

when ρ_0 and ρ_{0c} vanish on the boundaries of D and D_c respectively.

It is possible to do a Monte Carlo calculation whose estimator has an infinite variance. An integral which is analagous to that in Eq. (A9) is $\int_0^1 dw$ where w is sampled from $p(w) = (3N/2 + 1)\, w^{3N/2}$ and the recorded score is $f(w) = [p(w)]^{-1}$. Such a Monte Carlo calculation is characterized by a limit distribution for the random variable $[\bar{w} - \langle w \rangle]/K^{-(3N/2+1)}$ where K is the number of samples and $\bar{w}$ is the sample

mean. The distribution of $\bar{w}$ becomes asymptotically narrower about the population mean, $\langle w \rangle$, but the width decreases much slower than the usual $K^{-1/2}$. In addition the distribution is very broad—having no second moment—so large fluctuations in the mean are expected. In contrast, importance sampling permits the calculation of the same integral with an effective $f(w)$ which is bounded and for which the ordinary Central Limit Theorem holds. Thus, it was considered imperative to use importance sampling in the Green's Function Monte Carlo method outlined herein.

Appendix B

This appendix contains a concise representation of the sequence of steps needed to generate a single history in the Green's Function Monte Carlo method with and without importance sampling. Averages over many histories yield an estimate of the density matrix which is used in Eq. (26) or (27) to give the radial distribution function.

Green's Function Monte Carlo without Importance Sampling

1. Set $\mathbf{R}_0 = \mathbf{R}$
   $\beta_0 = 0$
   $n = 0$.
2. Construct half space containing $\mathbf{R}_0$.
3. Set $\rho(P\mathbf{R}_0, \mathbf{R}_0; \beta) = \rho_0(P\mathbf{R}_0, \mathbf{R}_0; \beta)$.
4. Sample point R_{n+1} on the bounding plane and "time" β_{n+1} from density function
$$-\frac{\partial \rho_0(\mathbf{R}_{n+1}, \mathbf{R}_n; \beta_{n+1} - \beta_n)}{\partial n}.$$
5. If $\beta_{n+1} > \beta$, terminate history.
6. Set $n = n + 1$ and construct half space containing $\mathbf{R}_n$.
7. Set $\rho(P\mathbf{R}_0, \mathbf{R}_0; \beta) = \rho(P\mathbf{R}_0, \mathbf{R}_0; \beta) + \rho_0(P\mathbf{R}_0, \mathbf{R}_n; \beta - \beta_n)$. Go to 4.

Green's Function Monte Carlo with Importance Sampling

1. Set $\mathbf{R}_0 = \mathbf{R}$
   $\beta_0 = 0$
   $m = 0$
   score $= 0$.
2. Construct half space containing $\mathbf{R}_0$.
3. Evaluate probability of scoring:
$$P_S(0) = \frac{\rho_0(P\mathbf{R}_0, \mathbf{R}_0; \beta)}{\rho_I(P\mathbf{R}_0, \mathbf{R}_0; \beta)}.$$

4. Sample a β'' from $B_1(\beta')$, the first term of integrand of Eq. (31) of text, written concisely as

$$M(\beta) = \int_{\beta''}^{\beta} [B_1(\beta') - B_2(\beta')]\, d\beta'.$$

5. Set branching multiplicity to be

$$M = \int_{\beta''}^{\beta} B_1(\beta')\, d\beta' \left[1 - \frac{B_1(\beta'')}{B_2(\beta'')}\right] \frac{1}{1 - P_S(0)} + \xi\,[15].$$

6. If $M = 0$, go to 9. (Note: this branch has terminated.)

7. Iterate step 8 M times.

8. Set $m = m + 1$
   $\beta_m = \beta''$.
   $\mathbf{R}_m$ is sampled from kernel of Eq. (31).
   Each point $(\mathbf{R}_m , \beta_m)$ is a branch of the random walk.

9. Set $m = m - 1$.

10. If $m = 0$, go to 15.

11. Construct half space containing $\mathbf{R}_m$.

12. Calculate

$$P_S(\beta_m) = \frac{\rho_0(P\mathbf{R}_0 , \mathbf{R}_m ; \beta - \beta_m)}{\rho_I(P\mathbf{R}_0 , \mathbf{R}_m ; \beta - \beta_m)}.$$

13. If $P_S(\beta_m) < \xi\,[15]$, go to 4.

14. Set score = score $+ \dfrac{\rho_0(P\mathbf{R}_0 , \mathbf{R}_m ; \beta - \beta_m)\, \rho_I(P\mathbf{R}_0 , \mathbf{R}_0 ; \beta)}{P_S(\beta_m)\, \rho_I(P\mathbf{R}_0 , \mathbf{R}_m ; \beta - \beta_m)}$.
   Go to 9.

15. All branches of the random walk have completed; terminate history.

$$\text{Set } \rho(P\mathbf{R}_0 , \mathbf{R}_0 ; \beta) = \rho_0(P\mathbf{R}_0 , \mathbf{R}_0 ; \beta) + \frac{1}{(1 - P_S(0))} \times \text{score}.$$

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FOOTNOTES AND REFERENCES

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