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Energy of a Boson Fluid with Lennard-Jones Potentials*

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A more powerful version of a numerical method published before is given which permits the integration of the Schrödinger equation for a large ensemble of particles. A new method for obtaining quantum expectation values is outlined. Numerical results are tabulated for the energy of the ground state of a system of 32 bosons interacting by Lennard-Jones potentials and with periodic boundary conditions. This is a commonly used model of liquid He^4. The present results are substantially lower and closer to experiment than variational estimates based on a Jastrow-type wave function.

I. INTRODUCTION

It is the purpose of this paper to show that it is possible to derive useful reliable numerical results for large quantum systems by Monte Carlo integration of the Schrödinger equation. The application is to a boson system interacting by Lennard-Jones pair potentials. A second aim is to present numerical results for the binding energy for the ground state of such a fluid.

The general outline of the method has been given before,[1,2] but it seems worthwhile to give a brief summary of the main ideas. A fundamental one is that the solutions of certain classes of integral equations can be developed rather easily by a Monte Carlo method, the generation of a numerical random walk. To see this, let R be a point in a space of arbitrary dimensionality and $\varphi(R)$ a function satisfying the conditions

$$\varphi(R) \geq 0 \text{ and } \int \varphi(R)\, dR = 1 . \quad (1)$$

Consider also a kernel $K(R, R')$ obeying

$$K(R,R') \geq 0, \quad \int K(R,R')\, dR < 1, \quad \text{for all } R'. \quad (2)$$

We define an algorithm for generating a sequence of random points $\{R\}$ as follows: Let the initial value of R be drawn at random from the probability distribution function $\varphi(R)$. Call R' the value of the coordinates at a later step in the sequence. At that stage let a new value R be selected at random from the distribution $K(R,R')$ conditional upon R'. Because of the normalization (2) there may be no next point and the sequence of values of R terminates.

Now let us calculate $\psi(R)$ the expected density with which points appear at any stage of the random walk in a unit volume near R. There are two contributions. The first point of the sequence may be in the neighborhood of R; this possibility contributes $\varphi(R)$ to the density. Secondly, a point may appear near R after a previous arrival at some R' and then a move —with probability $K(R, R')$ — to the neighborhood of R. This process contributes $\int K(R,R')\, \psi(R')\, dR'$ to the density of arrivals at R. In sum,

$$\psi(R) = \psi(R) + \int K(R,R')\, \psi(R')\, dR' . \quad (3)$$

Thus an observation of the density which arises when the random numerical procedure described above is carried out, provides a method of solution of integral equations of the type (3). In particular, if $\{R_i\}$ is the set of points which appears in M complete repetitions of the random walk, then, in the sense of the central limit theorem of statistics, the average value of any function $f(R)$ has the limiting value

$$\frac{1}{M} \sum_i f(R_i) \to \int f(R)\, \psi(R)\, dR \quad (4)$$

so that an arbitrary linear functional of the solution of Eq. (3) may be estimated.

Homogeneous integral equations may also be treated when $K(R, R')$ is replaced by $\lambda K(R, R')$. Introduce the eigenfunctions of the homogeneous equation

$$\psi_k(R) = \lambda_k \int K(R,R')\, \psi_k(R')\, dR', \quad k = 0, 1, \ldots \quad (5)$$

If one expands $\varphi(R)$, the inhomogeneous term of Eq. (3), in these eigenfunctions, it is possible to prove that the asymptotic density after many steps of the random walk is $\psi_0(R)$, corresponding to the lowest eigenvalue λ_0. The size of the population diminishes or grows accordingly as λ/λ_0 is less than or greater than one. The value of λ_0 may also be found at this stage of the calculation.

All of these techniques can be carried out in many dimensions and suggest themselves for the solution of certain many-body problems.

Here we consider the integration of the Schrödinger equation for the fundamental state of a system of N bosons. Using units in which $\hbar^2/2m = 1$, this is

$$[-\textstyle\sum_i \nabla_i^2 + V(x_1, \ldots, x_N)]\,\psi(x_1, \ldots, x_N)$$
$$= E\,\psi(x_1, \ldots, x_N) \quad . \tag{6}$$

To cast this as an integral equation, it is necessary to use an appropriate Green's function. We give a summary of how this may be done in a particularly simple case, that of Ref. 1.

We discuss the problem in which the potential energy V is never positive and may be written $V = -\lambda\, W_0$ so that the lowest energy is negative; $E = -B < 0$. Let R be the vector that stands for $(x_1, x_2, \ldots, x_N)$. Equation (6) is rearranged as

$$(-\nabla^2 + B)\,\psi(R) = \lambda\, W_0(R)\,\psi(R) \quad . \tag{7}$$

Green's function for the operator $(-\nabla^2 + B)$ is known[1]; call it $G_0(R, R')$. The integral equation equivalent to (7) is then

$$\psi(R) = \lambda \int G_0(R, R')\, W_0(R')\,\psi(R')\, dR' \,. \tag{8}$$

$G_0(R, R')\; W_0(R')$ satisfies the conditions of Eq. (2) so that the discussion pertaining to homogeneous integral equations applies, providing one is willing to use as eigenvalue the strength of the potential required to give a fixed energy.

Clearly, however, Eq. (2) is not satisfied if $V(R)$ can be positive and particularly if it is unbounded from above. We are compelled to consider the use of Green's functions for more general operators,

$$[-\nabla^2 + W(R)]\, G_W(R, R') = \delta(R - R'),\quad W(R) \geqslant 1 \tag{9}$$

The ground state of a boson system requires G_W which is positive everywhere, and it is easy, by integrating Eq. (9), to show that G_W also satisfies the other condition of Eq. (2). The function $W(R)$ determines the probability of the disappearance of a point in the course of a random move from R' to R.

The actual form of $W(R)$ which must be used is to some extent arbitrary, but it must contain any strongly repulsive part of the potential energy of the system. For hard-core or Lennard-Jones forces, G_W is not known explicitly. However, all that is needed is a method of randomly selecting a point R, given a point R_0, that is, an algorithm for sampling $G_W(R, R_0)$. We show below that G_W is the solution of a class of integral equations in which known Green's functions appear as kernel. The discussion given above for inhomogeneous integral equations applies so that a random walk whose expected density satisfies such an integral equation samples G_W. This can be carried out so that G_W either vanishes at infinity (in R), or that G_W is a multiply periodic function of R. Certain theoretical and technical developments are strongly motivated by computational considerations, particularly the necessity to evaluate the total potential energy of the system as rarely as possible during the random walk. Thus, although the method can be shown to have as a limiting case a Wiener integral, it is computationally much more efficient in the form given here.

Each step of sampling G_W constitutes an iteration of the integral equation equivalent to the Schrödinger equation. Although the method appears somewhat elaborate from this description, it is possible to carry out hundreds of such iterations on a fast modern digital computer to ensure the convergence to the ground-state wave function of a 32- or 256-body system of bosons interacting with a variety of potentials.

II. SAMPLING GREEN'S FUNCTION FOR $-\nabla^2 + W(R)$

Sampling of Green's function G_W is accomplished with the use of the following theorem: We suppose that with every point R there is associated a surface $\mathcal{S}(R)$ with R inside. Let G_U be Green's function for the operator $[-\nabla^2 + U(R)]$ which vanishes on the surface $\mathcal{S}(R_0)$ and

$$[-\nabla^2 + U(R)]\,G_U(R, R_0) = \delta(R - R_0), \tag{10}$$

$$\begin{aligned} G_U(R, R_0) &= 0, \quad \text{for } R \text{ on } \mathcal{S}(R_0) \\ &= 0, \quad \text{for } R \text{ outside } \mathcal{S}(R_0). \end{aligned} \tag{11}$$

Then set

$$\begin{aligned} Q_W(R, R_0) = {} & \delta(R - R_0) + [U(R) - W(R)] \\ & \times \int G_U(R, R')\, Q_W(R', R_0)\, dR' \\ & + \int \left(-\frac{\partial G_U}{\partial n}(R, R') \right) Q_W(R', R_0)\, dR' \,, \end{aligned} \tag{12}$$

$$G_W(R, R_0) = \int G_U(R, R')\, Q_W(R', R_0)\, dR' \,. \tag{13}$$

The integration in Eq. (13) and the first integral of Eq. (12) are extended over those R' for which R lies on the interior of $\mathcal{S}(R')$. The second integral of Eq. (12) is taken over those R' for which R lies on $\mathcal{S}(R')$. The proof is straightforward; apply the operator $[-\nabla^2 + U(R) + W(R) - U(R)]$ to Eq. (13) to get

$$\begin{aligned} [-\nabla^2 + W]\,G_W(R, R_0) = {} & \int [-\nabla^2 + U(R)]\,G_U(R, R') \\ & \times Q_W(R', R_0)\, dR' + [W(R) - U(R)] \\ & \times \int G_U(R, R')\, Q_W(R', R_0)\, dR' \,. \end{aligned} \tag{14}$$

The first integral of Eq. (14) has a contribution from the interior of $\mathcal{S}(R')$ where $[-\nabla^2 + U]G_U = \delta(R - R')$ and another from the discontinuity of the normal derivative of G_U at $\mathcal{S}(R')$. Thus

$$[-\nabla^2 + W(R)]\,G_W(R, R_0) = Q_W(R, R_0) + \int \frac{\partial G_U}{\partial n}(R, R')$$

$$\times Q_W(R', R_0)\, dR' + [W(R) - U(R)] \times \int G_U(R, R') Q_W(R', R_0)\, dR' . \qquad (15)$$

Using Eq. (12), we have

$$[-\nabla^2 + W(R)] G_W(R, R_0) = \delta(R - R_0) .$$

If $U(R) \geqslant W(R)$, then every term in (12) is positive and may be used as a density function in a random walk. Note that $G_U(R, R')$ describes a diffusion process in which a point begins at R' and is followed until it crosses $\mathcal{S}(R')$ for the first time, which takes place with probability per unit area on $\mathcal{S}(R')$ of $-\partial G_U/\partial n$. The probability per unit volume of being absorbed at a point on the interior of $\mathcal{S}(R')$ before crossing for the first time is $U(R) G_U(R, R')$. Thus, Eq. (12) for Q is the same as the equation for the density of arrivals in a random walk in which steps are made from R' to a point on $\mathcal{S}(R')$ chosen with density $-\partial G_U/\partial n$, or to a point inside $\mathcal{S}(R')$ with density UG_U. Such interior points continue in the random walk for Q_W with probability $1 - W(R)/U(R)$; points moved to the surface $\mathcal{S}(R')$ always continue the random walk. If $W(R) \geqslant 1$, then it is always possible to guarantee that the density G_U integrates to a quantity less than one so that no branching is required in the last step (13) of the random walk that develops Q_W. This convenient property can always be arranged.

According to Eq. (13), every point drawn from Q_W (that is, every point in the random walk for Q_W) contributes to G_W. But, on rewriting the equation as

$$W(R) G_W(R, R_0) = \frac{W(R)}{U(R)} \int U(R) G_U(R, R') Q_W(R', R_0)\, dR' , \qquad (16)$$

we observe that a point moved to the interior of $\mathcal{S}(R')$ with density UG_U contributes to WG_W with probability W/U, i.e., precisely when it terminated the random walk for Q_W.

This method may be applied in one particularly simple way. The surface $\mathcal{S}(R_0)$ is taken as a sphere (in configuration space) centered at R_0 and U as a constant which bounds $W(R)$ from above over that sphere. The radius may be chosen so as to maximize the probability of terminating the walk at any step.

For a Lennard-Jones potential, the sharply rising repulsive potential suggests that a bound may be found by examining the effect of moving together the closest pair of all. In fact, this does not give a rigorous bound, but practically, departures are extremely rare. A value of W exceeding the bound has never turned up in several million samples.

Green's function for $(-\nabla^2 + U)$ which vanishes on a sphere of radius r can be written in terms of Bessel functions of imaginary argument,

$$G_U(R, R_0), = \frac{1}{2\pi}\left(\frac{\nu U}{2\pi\rho}\right)^{\nu} K_\nu(\rho)\left(1 - \frac{K_\nu(\rho_0) I_\nu(\rho)}{I_\nu(\rho_0)}\right), \qquad (17)$$

$$\nu = \tfrac{3}{2}N - 1, \quad \text{for an } N\text{–body system,}$$

$$\text{and } \rho = \sqrt{(U)}\, |R - R_0| \leqslant \sqrt{(U)}\, r = \rho_0 . \qquad (18)$$

In the limit $r \to 0$, the method becomes particularly simple, since then

$$G_U(R, R_0) \to 1 - Ur^2/6N . \qquad (19)$$

Furthermore, if W is continuous, then

$$U \to W(R_0) .$$

The product of successive Green's functions becomes $\exp[-\int W(R(t))\, dt]$ with the integral taken along the path of a diffusive walk, that is, when $r \to 0$, the method reduces to a Wiener integral.[3] The practical objection to the latter is that for the quantum-mechanical many-body problem W derives from the potential energy function. This depends (at least) upon all pairs whose separation is within range of the pair potential. Computationally it is the most time consuming part of the calculation. Converging to the ground state and obtaining nearly statistically independent estimates drawn from it require a random walk that may extend far in configuration space. An efficient calculation will generally be characterized by long steps, with calculation of the full W being done as rarely as possible. Thus r should be chosen reasonably large. For Lennard-Jones or other potential energy function repulsive at close distances, too large a radius implies a large bounding U which tends to inefficient sampling.

With the computational requirements clearly in mind, another, even stronger, use of the basic theorem is possible. Large values of W are associated with closely spaced particle pairs. It is likely that only a few of all pairs which contribute to W determine the large value. In that case, a bounding funcion $U(R) \geqslant W$ can be calculated in much less time than W. Of course, G_U is then unknown, but it in turn can be sampled by finding G_X for $X \geqslant U$. It is practical to take X constant over a sphere as above. The bulk of the random walk is then devoted to sampling G_U; only when this terminates is W itself calculated. If $(U-W)/U$ is usually close to 1, the efficiency of sampling G_W is little degraded. A drawback of this refinement is the necessity for keeping track of which pairs are or may become close. The scheme can be further developed using a hierarchy of many levels of bounding potentials, but this has not been carried through. The efficiency of the method depends strongly on details of the computer program, and has not been optimized in any sense. Nevertheless, a scheme of this kind has been constructed which results in a saving of a factor of 20 in computer time for a 256-body calculation.

The methods discussed above naturally give Green's function $G_W(R, R_0)$, which vanishes at infinity in R. For some problems this is appropriate. However, in treating an extensive system like a quantum fluid in terms of a finite number of particles, the most satisfactory method has proved to be the widely used procedure of assuming that the particles are contained in a box (usually a cube) and that the properties of the system are periodic. In our problem this means that the wave function, and therefore G_W, must be constructed so as to be periodic. This is easily done as follows.

Denote by $R(I)$ all the points in space for which results must be the same as at $R = R(0)$ in a basic box. If R is in a $3N$-dimensional space, then I is a vector of $3N$ integers, each of which ranges from $-\infty$ to ∞. The points $R(I)$ are developed from R by displacements along coordinate axes. The extension of G (which vanishes at infinity) so as to be periodic is

$$G_P(R, R_0) = \sum_L G\big(R, R_0(L)\big) \ , \tag{20}$$

for

$$\begin{aligned} G_P\big(R(I),\ R_0\big) &= \sum_L G\big(R(I),\ R_0(L)\big) \\ &= \sum_L G\big(R(0), R_0(L-I)\big) = G_P(R, R_0). \end{aligned} \tag{21}$$

That is, by adding "image" sources at $R_0(I)$ to the source at R_0, G is constructed to be periodic. Analytically, the extension from G to G_P is a serious complication. However, sampling G_P is only a little more difficult than sampling G, for we may select at random any of the terms of Eq. (20) according to the probability that an R sampled from $G\big(R, R_0(L)\big)$ is in fact in our basic cell. But the chance that this is true is exactly the same as the chance that R' drawn from $G(R', R_0)$ is in box $(-L)$. That is, whenever a point moves out of the basic box, we may move it back by suitable displacements and suppose it to have come from an image source outside the box. In effect, when a particle leaks out of any face of the box, it must be allowed to leak back in the opposite face. This procedure is familiar in Monte Carlo or molecular-dynamics treatments of classical systems. It is the only device needed to ensure periodic behavior of the solution.

III. MONTE CARLO INTEGRATION OF THE SCHRÖDINGER EQUATION

Using the techniques afforded by Sec. II we may take up the question of integration of the Schrödinger equation. With units in which $\hbar^2/2m = 1$, an N-body system is described by

$$\begin{aligned} \Big[-\sum_i \nabla_i^2 + V(x_1, \cdots, x_N)\Big]\psi(x_1, \cdots, x_N) \\ = E\psi(x_1, \cdots, x_N) \ . \end{aligned} \tag{6}$$

Let R be a vector in $3N$-dimensional configuration space that stands for $x_1 \cdots x_N$. Then (6) is replaced by

$$\big[-\nabla^2 + V(R)\big]\ \psi(R) = E\ \psi(R), \tag{22}$$

with the Laplace operator being carried out in the full space.

There are several alternative ways to rewrite Eq. (22) as an integral equation. The following one which is particularly simple to apply may be used when V is bounded from below:

$$V(R) \geqslant -V_b \ . \tag{23}$$

For any constant potential Z, add $(V_b + Z)\psi(R)$ to both sides of Eq. (22) to get

$$\big[-\nabla^2 + V(R) + V_b + Z\big]\psi(R) = (E + V_b + Z)\psi(R), \tag{24}$$

$$\psi(R) = (E + V_b + Z) \int G_W(R, R')\psi(R')\, dR' \ , \tag{25}$$

where $W(R)$ is given by

$$W(R) = V(R) + V_b + Z \geqslant Z \ . \tag{26}$$

Iteration of the last integral equation converges to the ground-state wave function $\psi_0(R)$; the value of E which makes the population asymptotically stable is E_0, the energy of the ground state. For if the integral equation (25) is expressed as

$$\psi = (H + V_b + Z)^{-1}(E + V_b + Z)\psi \ , \tag{27}$$

then

$$\psi_0 \propto \lim_{n\to\infty} \big[(H + V_b + Z)^{-1}(E + V_b + Z)\big]^n \phi(R) \ , \tag{28}$$

provided that $\langle \psi_0 \mid \phi \rangle \neq 0$. Z should be small compared with $E_0 + V_b$ so as not significantly to slow convergence.

The completeness of the eigenfunctions of H gives the property that

$$\begin{aligned} \lim_{n\to\infty} \big[(H + V_b + Z)^{-1}(E + V_b + Z)\big]^n \delta(R - R_0) \\ \propto \psi_0(R)\psi_0(R_0). \end{aligned} \tag{29}$$

In its dependence upon R the last equation is simply a special case of Eq. (28). In either case, the distribution of points which have undergone many steps of G_W, that is, of $(H + V_b + Z)^{-1}$, is given by $\psi_0(R)$. But we have a second way of obtaining $\psi_0(R_0)$. Define

$$q(R_0) \equiv \lim_{n\to\infty} \int [(H+V_b+Z)^{-1}(E+V_b+Z)]^n \times \delta(R-R_0)dR \ . \tag{30}$$

According to Eq. (29),

$$q(R_0) \propto \psi_0(R_0) \ .$$

This has the following consequence: Let R_m be drawn from a population whose density is $\psi_0(R)$. Starting from R_m, let the iteration proceed further. The asymptotic total population [i.e., $q(R_m)$] is proportional to $\psi_0(R_m)$. The joint distribution for values of $q(R_0)$ is thus $\psi_0^2(R_m)$. Various observables can be recorded in this way. For example, the pair distribution function is obtained by recording a histogram of pair distances in the configuration R_m weighted by $q(R_m)$. More generally, we estimate any expectation by

$$\langle F \rangle = \int F(R)\psi^2(R)\,dR \Big/ \int \psi^2(R)\,dR \cong \textstyle\sum_m F(R_m)q(R_m) \Big/ \sum_m q(R_m) \ . \tag{31}$$

Note that the convergence to q is faster than might at first be supposed, since on integrating over all R the contributions of low excited states with odd reflection symmetries vanish.

A disadvantage of this method is that if V_b is large, then the convergence is rather slow. This situation is ameliorated considerably if one separates V into "attractive" and "repulsive" parts V_- and V_+, respectively,

$$V(R) = V_+(R) - V_-(R), \tag{32}$$

where $V_\pm$ may be chosen as

$$V_\pm = \max(\pm V, \ 0) \ . \tag{33}$$

Now let B be an estimate of $-E_0$, the total binding energy of the ground state. Add $[V_-(R)+B]\psi(R)$ to both sides of Eq. (22):

$$B^{-1}[-\nabla^2 + V_+(R) + B]\psi(R) = [V_-(R) + B + E]\psi(R)/B, \tag{34}$$

$$\psi(R) = B^{-1} \int G_W(R,R')[V_-(R') + B + E]\psi(R')\,dR' \ , \tag{35}$$

where now $W = [V_+(R) + B]/B \geq 1$. (36)

Again, the value of E which makes the iteration of Eq. (35), or its random-walk equivalent, asymptotically stable is the ground-state energy. In practice, B is adjusted as the calculation proceeds to be the latest value of E, so $B = E$ in using Eq. (35). At any stage, Monte Carlo integration of both sides of Eq. (34) gives a numerical estimate of E.

The operator that appears on the right-hand side of Eq. (35) is not self-adjoint, so that the developments of Eqs. (29) and (30) obviously cannot be used. But Eq. (35) is easily symmetrized as follows: $G_W(R,R')$ is a symmetric function.[4] Multiply Eq. (35) by

$$Y(R) = [V_-(R) + B + E_0]^{1/2}, \tag{37}$$

and let $\chi(R) = Y(R)\psi(R);$ (38)

then,

$$\chi(R) = \int Y(R)G_W(R,R')Y(R')\chi(R')\,dR' \equiv \mathcal{Y}\chi(R) \ . \tag{39}$$

Let $\chi_k(R)$ be the eigenfunctions

$$\chi_k(R) = \lambda_k \mathcal{Y}\chi_k(R) \ . \tag{40}$$

The operator here is symmetric and therefore self-adjoint; the functions χ_k are complete.[5] Thus,

$$\sum \chi_k(R)\chi_k(R_0) = \delta(R - R_0), \tag{41}$$

and

$$\lim_{n\to\infty} \mathcal{Y}^n \delta(R - R_0) = \chi_0(R)\chi_0(R_0) = Y(R_0)\psi_0(R_0)\chi_0(R), \tag{42}$$

$$q'(R_0) \equiv \lim_{n\to\infty} [Y(R_0)]^{-1} \int [\mathcal{Y}^n \delta(R - R_0)]\,dR \ , \tag{43}$$

$$q'(R_0) = \psi_0(R_0) \ . \tag{44}$$

Thus when E_0 is known from the earlier calculation which provided samples R_m drawn from ψ_0, it is possible to carry through the methods outlined above to get quantum expectations with respect to ψ_0^2.

IV. NUMERICAL RESULTS FOR THE ENERGY OF A 32-BODY SYSTEM

A computer program which embodies the theory of Secs. II and III has been written and run successfully for Lennard-Jones potentials of the form

$$V(R) = V(x_1, \ldots, x_N) = \sum_{i<j} v(|x_i - x_j|) \ , \tag{45}$$

$$v(x) = 4\epsilon[(\sigma/x)^{12} - (\sigma/x)^6] \ . \tag{46}$$

The particles are confined in a cubical box whose dimensions are fixed by selecting a density of the system. As is common in calculations of this kind, the potential is cut off at a particle separation of half the length of a side of the cube. For a system of 32 particles at the experimental equilibrium density of 0.022 atoms per cubic angstrom, this cutoff occurs at $x = 2.22\sigma$, a rather small value. As we shall see below, the large energy correction to an infinite cutoff can be made unambiguously.

The calculations were started, somewhat unwisely, with particles in a regular (fcc) lattice configuration. Relaxation to the ground state is rather slow, but it provided the impetus and test of much of the theoretical advance outlined in Secs. II and III. In particular, the improvement in convergence following the use of a few-pair "model" potential was dramatic.

The calculation is entirely feasible for a system of 256 particles on a CDC 6600, as tests have shown. To avoid devoting too much time to the preliminary convergence to the ground state, such calculations will use a Jastrow-type wave function with configurations generated by the molecular-dynamics method of Schiff and Verlet.[6]

We present here results for a system of 32 particles with the following parameters [cf. Eq. (46)]:

$$\sigma = 2.556\ \text{Å}, \quad \epsilon = 10\ ^\circ\text{K}, \quad \hbar^2/2m = 6.0166\ \text{Å}^2/\ ^\circ\text{K}\ .$$

Table I shows the results. The energy values called E_1 are those given directly without a correction for the potential cutoff. Corrections were carried out as follows: In a large set of configurations, the average and mean-square change in potential which results from doubling the cutoff range was obtained. In doing this, periodic behavior is assumed outside the cell. The values in the column $\Delta_1 E$ show the average decrease in potential energy. σ_1 gives the rms value of the change. We note that this is very small; that is, the effect of changing the cutoff is nearly independent of the coordinates of those configurations likely to appear in ψ. Not surprisingly, then, the effect of the extra potential is simply to add $\Delta_1 E$ to the energy. Additional calculations demonstrated that a further doubling of the cutoff adds close to $\Delta_1 E/8$, just what is expected from the integral of a potential falling off as r^{-6} and a constant ψ. On this basis the extrapolation to infinite cutoff is $\Delta_2 E = \Delta_1 E/7$. The energy value with both corrections is shown in the last column. The statistical errors given are the estimated standard deviation.

These results give a minimum energy of

$$E = (-6.25 \pm 0.05)\ ^\circ\text{K}, \quad \epsilon = 10.0$$

at a density of $\rho = 0.0210\ \text{Å}^{-3}$.

This may be compared with the results of McMillan[7] and of Schiff and Verlet[6] of 5.95 °K, but it should be noted that the potential used in the work reported here is slightly weaker than that reported before. Schiff and Verlet used $\epsilon = 10.22$. Correction for the difference may be made from perturbation theory using the estimates of $\langle V \rangle$ obtained from the Jastrow wave function. It amounts to $-0.38\ ^\circ$K, giving a value of

$$E = -6.63\ ^\circ\text{K}, \quad \epsilon = 10.22\ .$$

This is substantially larger, and considerably closer to the experimental value of −7.14, but this conclusion must be regarded as tentative until results with a larger ensemble of particles are obtained.

TABLE I. Energy values and corrections for potential truncation for a 32-particle system with periodic boundary conditions.

Density (atoms/Å^3)			Energy per particle °K		
	E_1	$\Delta_1 E$	σ_1	$\Delta_2 E$	Total energy
0.020	-4.80 ± 0.07	-1.21	0.013	-0.17	-6.18 ± 0.07
0.022	-4.50 ± 0.05	-1.47	0.016	-0.22	-6.19 ± 0.05
0.024	-3.66 ± 0.06	-1.75	0.018	-0.25	-5.66 ± 0.06

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[7] W. L. McMillan, Phys. Rev. 138, A442 (1965).