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Jastrow wave function and correlations of the Lennard-Jones Bose fluid

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We present results of Monte Carlo variational calculations for the ground state of the Lennard-Jones fluid. The Jastrow pseudopotential contains a correlation structure, that has been suggested to manifest the zero-point motion of rotons, at a distance of the order of first and second shell of neighbors. We find an improved ground-state energy, and its density dependence is in fair agreement with the "exact" result. The variational $g(r)$ and $S(k)$ are now in excellent agreement with the "exact" result. A comparison is made with the functional minimization approach. Computation of $S(k)$ at finite temperature is performed with Penrose's density matrix by the Monte Carlo method and by application of perturbation theory of classical liquids.

I. INTRODUCTION

As a result of numerous variational calculations and of Green's-function Monte Carlo calculations (GFMC) we know[1] that a substantial part of short-range correlations present in a Lennard-Jones (LJ) Bose fluid is described by a Jastrow wave function

$$\psi_J = \prod_{i<j} \exp[-\tfrac{1}{2}u(|\vec{r}_i - \vec{r}_j|)] \quad , \qquad (1)$$

and the most important feature of the "pseudopotential" $u(r)$ is its short-range behavior for $r \lesssim \sigma$ (σ is the length parameter of the LJ potential). This simply reflects the fact that the impenetrability of the atomic cores has a major role for many physical properties of the system.[2] This explains why still today the Jastrow wave function is very often used together with the McMillan parametrization,[3] $u = (b/r)^5$, for the pseudopotential.

A few years ago De Michelis and one of the present authors[4] considered a larger family of pseudopotentials and, in particular, they allowed the possibility that $u(r)$ becomes negative at intermediate distances. A slightly lower energy and an improved structure was found, but the large number of variational parameters present in the pseudopotential, taken together with the statistical errors of the computed energy inherent to the use of the Monte Carlo method, did not allow a unique determination of the best pseudopotential. The presence in the LJ potential both of an attractive part and of a repulsive part makes this problem particularly difficult, and for this reason it was decided to make a detailed study[5,6] of the pseudopotential $u(r)$ of Bose particles interacting with a repulsive interaction only. In Ref. 5 (hereafter called I) the quantum hard-sphere system was studied and in Ref. 6 the Yukawa repulsive interaction was considered.

In both cases the best energy is found when $u(r)$ has some structure at intermediate distances roughly in the region of the first maximum and of the following minimum of the radial distribution function $g(r)$. This structure in $u(r)$ not only lowers the energy but a significant improvement in $g(r)$ is obtained when the variational results are compared with the "exact" results[7] of GFMC calculations. On the basis of comparison of the shape of $u(r)$ with the result for the ground state of a simple excitation model of the system, it was concluded that the intermediate distance structure present in $u(r)$ reflects the zero-point motion of short-wavelength excitations, i.e., of those excitations corresponding to rotons in ^{4}He. Guided by these results we have considered again the Lennard-Jones fluid and in this paper we present the results of our Monte Carlo variational calculations for a wider family of "pseudopotentials" $u(r)$.

The necessity of parametrizing the pseudopotential $u(r)$ is inherent in our use of the Monte Carlo method to calculate $g(r)$. This is not needed with the approach that finds the best form of $u(r)$ using the Euler-Lagrange equation.[8–11] On the other hand, to implement this latter approach one is forced to introduce some approximation, for instance an approximate integral equation like the hypernetted chain equation that relates $g(r)$ to $u(r)$. The comparison of the result of such approximate functional optimizations of $u(r)$ with our Monte Carlo variational results for a rather wide family of trial pseudopotentials will shed light on the merits of the two approaches and on the role of the approximations in functional minimization computations.

The contents of the paper are the following. In Sec. II we give the results for the energy for different parametrizations of $u(r)$. The major part of the results are for the experimental equilibrium density of ^{4}He but few computations have also been performed at different densities. Spatial correlations are considered in Sec. III and our $u(r)$ is compared with the result of calculations based on the Euler-Lagrange equations and of the excitations model with and without inclusion of backflow in the wave function of rotons.

The effect of temperature on the structure factor $S(k)$ is computed in Sec. IV on the basis of Penrose's density matrix together with our wave function for the ground state. The computation is performed with the Monte Carlo method and with an application of the formalism of the perturbation theory of classical liquids in the "exponential" approximation. Finally in Sec. V we discuss our results.

II. GROUND-STATE ENERGY

The expectation value of the Hamiltonian

$$H=-\frac{\hbar^2}{2m}\sum_i \nabla_i^2+\frac{1}{2}\sum_{i\neq j} v(r_{ij}) \tag{2}$$

taken with the Jastrow wave function [Eq. (1)] can be written in terms of the radial distribution function $g(r)$ and the energy per particle reads

$$E_J\equiv\frac{\langle H\rangle}{N}=\frac{1}{2}\rho\int d^3r\left[v(r)+\frac{\hbar^2}{4m}\nabla^2 u(r)\right]g(r) \tag{3}$$

where $\rho=N/V$ is the average density. The usual Metropolis Monte Carlo method[7] is used to compute $g(r)$ from which E_J can easily be obtained by numerical integration. We have considered systems of 64 particles in a cubic box with the nearest image convention; for other details of the numerical method the reader is referred to I.

The Monte Carlo computation produces $g(r)$ for $r<\frac{1}{2}L$, where L is the box side. The tail correction to the energy, i.e., the contribution to the integral [Eq. (3)] from distances $r>\frac{1}{2}L$, and to the structure factor

$$S(q)=1+\rho\int d^3r[g(r)-1]e^{i\vec{q}\cdot\vec{r}} \tag{4}$$

have been computed with a $g(r)$ extended at $r>\frac{1}{2}L$ with the method used by Whitlock *et al.*[1] $g(r)$ is represented by a function $g(r)$ which describes damped oscillations, and the relative parameters are obtained by minimization of the deviation between $g(r)$ and the Monte Carlo $g(r)$ for $r<\frac{1}{2}L$ but beyond the first maximum of $g(r)$.

The pair interaction $v(r)$ is assumed to be of the Lennard-Jones form

$$v(r)=-4\epsilon[(\sigma/r)^6-(\sigma/r)^{12}] \tag{5}$$

with the de Boer-Michels parameters, $\epsilon=10.22$ K and $\sigma=2.556$ Å. The Monte Carlo variational calculation starts with an ansatz on the form of the pseudopotential $u(r)$ and then the parameters contained in $u(r)$ are determined by minimization of the expectation value [Eq. (3)] of the energy.

As discussed in the introduction, our main purpose was to determine if $u(r)$ contains an intermediate distance structure in addition to the short-range part which controls the close encounters between two particles. Therefore, we write the pseudopotential in the form

$$u(r)=u_0(r)+u'(r) , \tag{6}$$

where $u_0(r)$ is this short-range part and in $u'(r)$ we allow some intermediate distance contribution. One should keep in mind, however, that this division of $u(r)$ in two parts is only a convenient but not unique representation of $u(r)$. More precisely $u_0(r)$ represents any of the short-range functions which have been tested in previous variational calculations. These functions are characterized by being a decreasing function of distance and concave upwards.

Three forms for $u_0(r)$ have been used in the literature: the McMillan form[3]

$$u_0(r)=(b/r)^5 ; \tag{7}$$

the related form[4]

$$u_0=(b/r)^5\exp[-(r/r_0)^2] ; \tag{8}$$

and the form[2] that we call Kalos-Levesque-Verlet (KLV), modeled on the solution of the two-body problem for the Lennard-Jones potential (see the Appendix for its analytical form). The two last functions have a shorter range than McMillan's form and give a slightly better $S(k)$ whereas the energy is almost indistinguishable. Most of our computations have been performed with the KLV form for u_0; a few computations have also been performed with the other two forms of u_0.

We have considered three different forms for $u'(r)$. The first is a Gaussian and the second is the derivative of a Gaussian; we call, respectively, $u_1(r)$ and $u_2(r)$ the overall pseudopotential

$$u_1(r)=u_0(r)+C\exp[-(r-d)^2/D^2] , \tag{9}$$

$$u_2(r)=u_0(r)+C(r-d)\exp[-(r-d)^2/D^2] . \tag{10}$$

These forms of the pseudopotential have been used previously in the case of the hard sphere and of the Yukawa potential when $u_0(r)$ is the appropriate short-range function. In both those cases these functions have been found to give an improved description of the system: The energy is minimum for a nonzero value of C for a suitable choice of the length parameters d and D. A physical interpretation of the origin of the term added to $u_0(r)$ has been given as an effect of the zero-point motion of rotonlike excitations and this interpretation will be discussed further in the next section.

The third form of the pseudopotential, which we call $u_3(r)$, was introduced in Ref. 4 and it reads

$$u_3(r)=u_0(r)+C\exp[-(r-d)^2/D^2] -A\{E(\lambda-r)+E(r-\lambda)\exp[-(r-\lambda)^2/\Lambda^2]\}\ , \tag{11}$$

where $E(x)$ is the step function, $E(x)=1$ for $x>0$ and $E(x)=0$ for $x<0$. In Eq. (11), to the Gaussian has been added a term which is a negative constant for $r<\lambda$, and $r>\lambda$ goes to zero as a Gaussian. This added term allows the possibility that $u(r)$ becomes negative and this possibility was considered[4] in order to test a wave function that describes a self-bound state. The Lennard-Jones system we are considering forms a bound state, i.e., the energy of the system $E(\rho)$ has a minimum and its value at the minimum is negative at a certain density, the equilibrium density $\rho_{\rm eq}$. Let us consider N particles contained in a box of volume V. If the average density $\rho=N/V$ is less than $\rho_{\rm eq}$ the system forms a droplet, i.e., there is coexistence between a liquid phase at density $\rho_{\rm eq}$ and the vacuum (we are considering the system at $T=0$ K so that the vapor pressure is zero). In this respect a Jastrow wave function can have two kinds of behavior. Let us take into account the well-known analogy[3] between a quantum system described in the Jastrow approximation and an equivalent classical system, i.e., a system of classical particles interacting with a two-body potential $V^*(r)$ and at a temperature T^* such that $V^*(r)/k_BT^*=u(r)$. The analogy[12] is a consequence of the coincidence between ψ_J^2 of the quantum system with the Boltzmann factor of this equivalent classical system. From the known behavior of classical systems we conclude that, depending on the shape of $u(r)$ and on density, ψ_J^2 describes either a uniform state or a two-phase state, a high-density region coexisting with a low-density one. This last possibility arises only if $V^*(r)$, and therefore $u(r)$, has an attractive part which is strong enough. In this case we say that the Jastrow wave function describes a self-bound state because an equilibrium density is reached by means of the correlations present in ψ_J without need of imposing external constraints. A difference with respect to the exact wave function consists in the fact that even if ψ_J describes a two-phase state, the low-density phase corresponds to a finite, even if small, density and not to the vacuum as it should be.

The short-range pseudopotentials $u_0(r)$ do not describe a self-bound state because $u_0(r)$ are decreasing functions of r, the pseudoforce $\partial u_0/\partial\vec{r}$ is repulsive everywhere and the particles tend to occupy as uniformly as possible any allowed space. Only with the form $u_3(r)$ can the pseudoforce be attractive and large enough, if A is large, to give a self-bound state. The signature that this happens can be deduced by considering once again the classical analogy: The equivalent classical system is in the liquid state if the corresponding pressure p^* as a function of density for *fixed* V^*/k_BT^* has a van der Waals loop. Once $g(r)$ is known p^* can be computed by the virial relation

$$\pi\equiv\frac{p^*}{k_BT^*}=\rho\left[1-\tfrac{1}{6}\rho\int d^3r\,g(r)\,r\frac{du(r)}{dr}\right]\ . \tag{12}$$

We take the presence of a van der Waals loop in the compressibility factor π as the signature that a Jastrow wave function describes a self-bound state.

We present now some of our variational results at the equilibrium density of ^{4}He when $u_0(r)$ is the KLV form with the value of its unique parameter a fixed at the optimum value,[2] $a=0.82$. Our computation with $u_0(r)$ gives an energy per particle, $E=(-5.81\pm0.09)$ K, in very good agreement with the previous result,[2] $(E=-5.82\pm0.06)$ K. All errors we quote are standard deviations from the averages. In Table I we give our results for the pseudopotential u_1. The center $r=d$ of the Gaussian is fixed in the neighborhood of the first minimum of $g(r)$, i.e., $r\sim2\sigma$, as the previous computations have suggested. The minimum energy obtains for a nonzero value of the amplitude C of the Gaussian. The effect on the energy is limited, of the order 0.2 K, but well outside the statistical errors. The origin of this decrease of E is the same as observed in the hard sphere[5] and in the Yukawa[6] system: The presence of the Gaussian not only enhances the oscillations of $g(r)$ but depresses $g(r)$ at short distances, $r<\sigma$, the first peak of $g(r)$ becoming sharper. As a consequence, the potential energy is lowered because the average $\langle r^{-12}\rangle$ decreases. The kinetic energy T is initially rather insensitive to the value of C because the positive contribution to T, due to the extra curvature brought by the Gaussian, is compensated by the decrease of the contribution to T coming from $\nabla^2u_0(r)$ because of the depression of $g(r)$ near the core. The length parameters d and D at the minimum have values $d=2\sigma$ and $D=0.6\sigma$ which correspond exactly to the values found[5] for the hard-sphere system of the equivalent radius $a=0.82\sigma$.

Also with the pseudopotential u_2 we find a lowering of the energy but in this case the effect is small-

TABLE I. Monte Carlo results at equilibrium density $\rho\sigma^3 = 0.365$ with pseudopotential u_1. E is the total energy and T the kinetic energy. S_{max} is the value (Ref. 16) of $S(k)$ at the first maximum, and n is the number of configurations per particle of Monte Carlo run.

C	d/σ	D/σ	E (K)	T (K)	S_{max}[a]	n
0			-5.81 ± 0.09	13.84	1.252	5.700
0.05	2.0	0.6	-5.90 ± 0.07	13.84	1.262	6.240
0.10	2.0	0.6	-5.98 ± 0.06	13.85	1.274	6.240
0.15	2.0	0.6	-5.80 ± 0.06	13.96	1.280	6.240
0.25	2.0	0.6	-5.71 ± 0.10	14.11	1.298	3.120
0.35	2.0	0.6	-5.62 ± 0.09	14.33	1.316	3.120
0.10	2.0	0.5	-5.98 ± 0.06	13.91	1.284	6.240
0.10	2.1	0.6	-5.84 ± 0.06	13.89	1.268	7.800
0.10	2.1	0.5	-5.99 ± 0.10	13.88	1.279	3.120
0.10	1.9	0.6	-5.90 ± 0.09	13.84	1.275	3.120
0.10	1.9	0.5	-5.83 ± 0.07	13.96	1.278	6.240

[a] Reference 16.

er, of the order of 0.1 K, and we do not report the results. It should be noticed that in the case of the Yukawa system it is found[6] that u_2 gives a significantly lower energy than u_1. We do not know the origin of such a different behavior but we suspect that it is due to the rather different shape of the short-range part u_0 in the two cases.

In Ref. 4 the pseudopotential $u_3(r)$ was considered, and numerous short Monte Carlo runs for different values of the length parameters d, D, λ, and Λ were performed. This permitted us to fix our attention on two different sets of parameters called α and β, the values of which can be found in Table II. Expression (8) was used for u_0 but the use of the KLV form of u_0 does not alter the results.[13] The α pseudopotential was found to give the lowest energy[14] whereas the β gives a higher energy but a good $g(r)$ when compared to the exact results. We have performed numerous new computations with the parameters of u_3 in the neighborhood of those corresponding to the α and β sets. The results of the longer Monte Carlo runs are given in Table II. In the first part, β-like pseudopotentials are considered and the minimum energy is -5.88 ± 0.06 K for the set of parameters that is labeled β' in the table. The gain in energy with respect to the u_0 pseudopotential is marginal but the short-range order is much improved: For instance, the height S_{max} of the first maximum[16] of the structure factor $S(k)$ is 1.31 as compared to the "exact" value $S_{\text{max}} = 1.32$ and to the value $S_{\text{max}} = 1.25$ corresponding to u_0. Moreover the β' pseudopotential describes a self-bound state as it can be seen from the slightly negative value of the pseudocompressibility factor π. The β' pseudopotential does not represent an absolute minimum, however, and in fact we find a significantly lower energy, $E = -6.10 \pm 0.05$ K, for the pseudopotential which we call α' in Table II and which has the same length parameters of the set α. Because of the large number of parameters contained in u_3 we cannot claim that this is the absolute minimum but, on the basis of the results of Table II and of numerous other short runs that we do not report here, we are rather confident that the pseudopotential α' is at least close to the optimum pseudopotential in the family of functions u_1, u_2, and u_3. As can be seen in Table II the α' pseudopotential gives a rather large positive value of π because the attractive part of u_3 has small amplitude and therefore this wave function does not describe a self-bound state. In fact that p^* as a function of ρ does not have a van der Waals loop.

A summary of the results of Jastrow variational calculation at the experimental equilibrium density is given in Table III. With the smooth pseudopotentials u_0 the kinetic energy turns out to be rather close to the "exact" value but a large discrepancy is present in the potential energy. With the new pseudopotential u_3 we get a slightly worse kinetic energy but this is compensated by the substantial improvement in the value of the potential energy. We notice also the good agreement with the result of an Euler-Lagrange variational calculation[10] that uses the Monte Carlo method together with a separability hypothesis.

A defect of previous Jastrow variational calculations

TABLE II. Monte Carlo results at $\rho\sigma^3 = 0.365$ with pseudopotential u_3. π is the pseudocompressibility factor (12).

	C	d/σ	D/σ	A	λ/σ	Λ/σ	E (K)	T (K)	π	$S_{\max}$[a]	n
	0			0			-5.81 ± 0.09	13.84	4.55	1.252	5.700
β	0.25	2.0	0.6	0.6	1.25	1.15	-5.58 ± 0.08	14.41	0.21	1.304	4.700
	0.15	2.0	0.6	0.7	1.25	1.15	-5.53 ± 0.08	14.38	-1.22	1.277	4.680
	0.25	2.0	0.6	0.7	1.25	1.15	-5.71 ± 0.08	14.43	-0.25	1.304	5.860
	0.35	2.0	0.6	0.7	1.25	1.15	-5.64 ± 0.07	14.67	0.75	1.318	6.240
	0.45	2.0	0.6	0.7	1.25	1.15	-5.57 ± 0.10	14.85	1.71	1.337	3.120
	0.15	1.9	0.6	0.7	1.25	1.15	-5.54 ± 0.08	14.39	-1.36	1.278	4.680
	0.25	1.9	0.6	0.7	1.25	1.15	-5.78 ± 0.07	14.38	-0.49	1.298	6.150
	0.35	1.9	0.6	0.7	1.25	1.15	-5.69 ± 0.08	14.51	0.395	1.316	4.680
	0.15	1.8	0.6	0.7	1.25	1.15	-5.57 ± 0.11	14.26	-1.51	1.277	3.120
β'	0.25	1.8	0.6	0.7	1.25	1.15	-5.88 ± 0.06	14.26	-0.71	1.294	7.800
	0.35	1.8	0.6	0.7	1.25	1.15	-5.84 ± 0.06	14.34	0.92	1.304	7.800
	0.10	1.8	0.6	0.5	1.50	1.0	-5.63 ± 0.11	13.97	-0.37	1.257	3.120
α	0.20	1.8	0.6	0.5	1.50	1.0	-5.84 ± 0.08	13.96	0.43	1.273	4.680
	0.25	1.8	0.6	0.5	1.50	1.0	-5.92 ± 0.08	13.97	0.83	1.274	4.680
	0.30	1.8	0.6	0.5	1.50	1.0	-5.89 ± 0.08	14.03	1.24	1.286	4.680
	0.20	1.8	0.6	0.4	1.50	1.0	-5.96 ± 0.08	13.93	1.57	1.274	4.680
	0.25	1.8	0.6	0.4	1.50	1.0	-6.02 ± 0.05	13.93	1.96	1.279	9.360
	0.40	1.8	0.6	0.4	1.50	1.0	-5.85 ± 0.11	14.13	3.19	1.298	3.124
	0.20	1.8	0.6	0.3	1.50	1.0	-5.85 ± 0.07	13.93	2.72	1.273	6.240
α'	0.30	1.8	0.6	0.3	1.50	1.0	-6.10 ± 0.05	13.96	3.52	1.289	9.360
	0.40	1.8	0.6	0.3	1.50	1.0	-5.94 ± 0.09	14.08	4.33	1.298	3.120
	0.20	1.8	0.6	0.2	1.50	1.0	-5.93 ± 0.10	13.90	3.86	1.280	3.120
	0.30	1.8	0.6	0.2	1.50	1.0	-6.03 ± 0.09	13.98	4.67	1.291	3.120
	0.40	1.8	0.6	0.2	1.50	1.0	-5.86 ± 0.10	14.11	5.48	1.300	3.120

[a]Reference 16.

is that the equilibrium density is lower than the experimental value ρ_{eq}, with the McMillan u_0 the equilibrium density being $0.9\rho_{\text{eq}}$. We have not determined the equilibrium density with the new pseudopotentials but few computations (see Table IV) have been performed at the density $\rho\sigma^3 = 0.328 = 0.9\ (\rho_{\text{eq}}\sigma^3)$ and we find an energy -5.97 K that is higher than density ρ_{eq}. A careful minimization of the energy with respect to the values of the parameters of u_3 could slightly lower this value of E but we do not believe that it can become as low as the value -6.10 K found at ρ_{eq}. We take this as evidence that the

TABLE III. Summary of Jastrow variational results at equilibrium density $\rho\sigma^3 = 0.365$ and comparison with the GFMC "exact" result. $g_{\max}$ is the value of $g(r)$ at the first maximum. $S_{\max}$ corresponds to the extended (Ref. 16) $g(r)$.

Pseudopotential	E (K)	T (K)	V (K)	$S_{\max}$	$g_{\max}$
"Exact" (GFMC)[a]	-6.85 ± 0.03	13.62 ± 0.12	-20.47 ± 0.12	1.32	1.34
McMillan[a]	-5.68	13.67	-19.35	1.23	1.26
Present result (best u_3)	-6.10 ± 0.05	13.96 ± 0.02	-20.06 ± 0.04	1.31	1.33
Funct. minimization[b]	-6.02 ± 0.10			1.28	1.30
Funct. minimization (HNCE[c])	-5.77				1.31

[a]Reference 1. [b]Reference 10. [c]Reference 11.

TABLE IV. Monte Carlo results at different densities with pseudopotential u_3. $S_{\max}$ corresponds to the extended (Ref. 16) $g(r)$.

C	d/σ	D/σ	A	λ/σ	Λ/σ	E (K)	T (K)	$S_{\max}$	n
					$\rho\sigma^3=0.438$				
0			0			-4.52 ± 0.10	18.55	1.309	6.240
0.3	1.8	0.6	0.3	1.5	1.0	-4.77 ± 0.08	18.74	1.352	7.800
0.4	1.8	0.6	0.4	1.5	1.0	-4.74 ± 0.08	18.85	1.362	7.800
0.3	1.8	0.5	0.3	1.41	0.94	-4.91 ± 0.13	18.87	1.362	3.120
0.4	1.8	0.5	0.4	1.41	0.94	-4.82 ± 0.12	19.05	1.375	3.120
0.3	1.694	0.565	0.3	1.41	0.94	-4.91 ± 0.08	18.63	1.349	7.800
0.4	1.694	0.565	0.4	1.41	0.94	-4.89 ± 0.10	18.71	1.360	6.240
		"exact"[a]				-6.39 ± 0.03	18.61	1.456	
					$\rho\sigma^3=0.328$				
0			0			-5.94 ± 0.06	11.84	1.247	6.240
0.25	1.8	0.6	0.25	1.5	1.10	-5.97 ± 0.06	11.84	1.252	6.240
0.30	1.8	0.6	0.30	1.5	1.10	-5.96 ± 0.06	11.91	1.257	6.240
		"exact"[a]				-6.62 ± 0.015	11.43		

[a] Reference 1.

equilibrium density with u_3 is closer to ρ_{eq} than with the previous variational calculations.

We have also performed a few computations at density $\rho\sigma^3=0.438=1.2\ (\rho_{\text{eq}}\sigma^3)$ with the pseudopotential u_3 and we have found an energy $E=-4.91\pm0.08$ K. This value should be compared[1] with $E=-4.50$ K obtained with the McMillan u_0 and with $E=-4.52\pm0.10$ K obtained with the KLV $u_0(r)$. Three sets of length parameters have been tested, one equal to the α', one scaled with the ratio $(\rho_{\text{eq}}/\rho)^{1/3}$ and one combination of the two. In all cases the energy is lowered (see Table IV) and the lowest energy is obtained with the set scaled with $(\rho_{\text{eq}}/\rho)^{1/3}$. The strength of the intermediate distance structure increases with density. This is in agreement with the behavior found for the Yukawa system.[6]

We conclude that all three new pseudopotentials (u_1, u_2, and u_3) that we have tested give a better representation of the ground state of the Lennard-Jones system that the previous parametrizations of $u(r)$, the form u_3 being the best. The lowering of the ground-state energy at the equilibrium density is ~ 0.3 K and this is roughly one third of the difference between the previous Monte Carlo variational result and the "exact" one. The equilibrium density appears to be closer to the experimental value and the lowering of the energy is larger when the density increases. In this respect one should also keep in mind that we have not made an extensive search of the optimum u_3 at the higher density and this could give a still lower energy. The length parameters of the intermediate distance structure of the pseudopotential at different densities are found to scale with $(\rho_{\text{eq}}/\rho)^{1/3}$ in agreement with previous results[6,15] for other systems.

III. CORRELATIONS AND PSEUDOPOTENTIAL

A common defect of Jastrow variational computations[7] is the underestimate of the short-range order present in the system as shown by the peaks of $g(r)$ and of $S(k)$ that turn out to be smaller than the result of the "exact" computation or of the ^{4}He experimental data. However with the intermediate distance structure allowed by the $u(r)$ that we have tested in this work and in the previous ones,[4–6] the short-range order given by the Jastrow wave function is comparable with the one given by the exact computation. The degree of short-range order given by ψ_J is sensitive to the strength of the intermediate distance present in $u(r)$ as can be seen in Tables I and II where the value[16] of $S(k)$ at its main maximum $S_{\max}$ is given as a typical measure of short-range order. An improvement is found for all three pseudopotentials u_1, u_2, and u_3, and it involves not only the height of the peaks of $g(r)$ and $S(k)$ but also the overall shape. It is very satisfying that the distribution function obtained with the pseudopotential that gives the *lowest* energy, i.e., $u_3(r)$ with the set α' of the parameters, is among the best that we have obtained. This $g(r)$ is compared in Fig. 1 with the "ex-

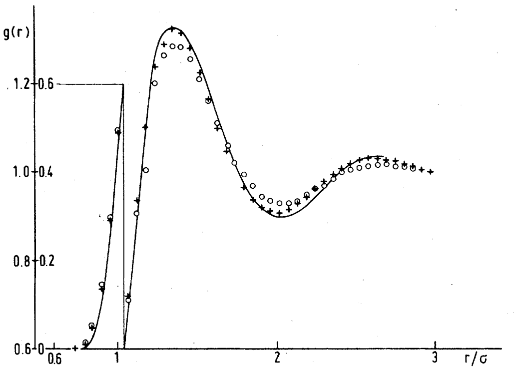

FIG. 1. Radial distribution function at equilibrium density $\rho\sigma^3 = 0.365$. Solid line: smoothed "exact" result (Ref. 1). Open dots: our variational result with KLV u_0. Crosses: our result with $\alpha' - u_3$ pseudopotential.

act" one and with the one obtained with the KLV form $u_0(r)$. The discrepancy between the "exact" $g(r)$ and the one corresponding to $u_0(r)$ is to a large extent removed with the new wave function and only minor differences remain. From the figure one can notice that also near the core, where $u_0(r)$ essentially coincides with the $\alpha' - u_3$, there is an improvement, the $g(r)$ being depressed for $r < \sigma$ by the presence of the intermediate distance structure in the pseudopotential. As already discussed in the previous section this fact is at the basis of the lowering of the energy obtained with such wave function.

In Fig. 2 the "exact" structure factor $S(k)$ is compared with the one given by the McMillan $u_0(r)$ and with the result for the $\alpha' - u_3$. Again we notice the excellent agreement between the latter's $S(k)$ and the exact one. The height of the main peak of $S(k)$ is still underestimated and displaced to larger k value but the remaining difference is very small and comparable with the uncertainty of the calculations. Some other pseudopotentials that do not give the lowest energy give an even better agreement for $S(k)$ and in Fig. 3 the result for the β' pseudopotential is shown. The pseudopotentials u_1 and u_2 give a slightly less accurate structure than u_3 and in Fig. 3 the result for u_1 that gives the lowest energy is reported.

From the point of view of the variational approach the Jastrow wave function that really matters is the one that minimizes the energy. However, the ψ_J that reproduces the "exact" $g(r)$ is also significant. In fact, if we ask for the ψ_J for which the overlap $\langle \psi_J | \psi_0 \rangle$ with the "exact" ψ_0 is maximum, we find that this takes place for that pseudopotential $u(r)$ for which the variational $g(r)$ equals the "mixed" $g(r)$,[1] i.e., the radial distribution function constructed with $\psi_0 \psi_J$. This mixed average is exactly what is directly obtained in a GFMC computation and therefore such $u(r)$ can be determined by looking for the pseudopotential for which the variational and the mixed $g(r)$ are equal. These are also equal to the "exact" $g(r)$ if the difference between ψ_J and ψ_0 is small enough so that this difference can be treated as a perturbation.[1] In view of the excellent agreement that we find for $S(k)$ with the $\beta' - u_3$, this is a good candidate for $u(r)$.

Also at higher density we find a significant improvement in the structure and in Fig. 4 some results at density $\rho\sigma^3 = 0.438$ are shown: the "exact" $S(k)$, our variational result for the KLV u_0, and for the best u_3 pseudopotential. In this case however our variational result with u_3 is not as good as at the equilibrium density, and a sizable difference remains with respect to the "exact" $S(k)$. A reason for this might be that we have not really searched for the minimum energy at this density but we have simply

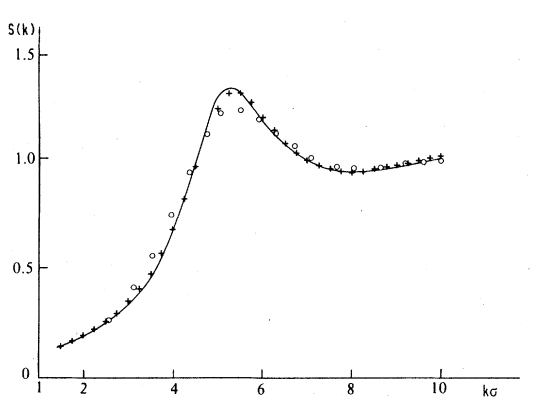

FIG. 2. Structure factor at $\rho\sigma^3 = 0.365$. Solid line: "exact" result (Ref. 1). Open dots: variational (Ref. 1) $S(k)$ with McMillan's u_0. Crosses: our result with $\alpha' - u_3$.

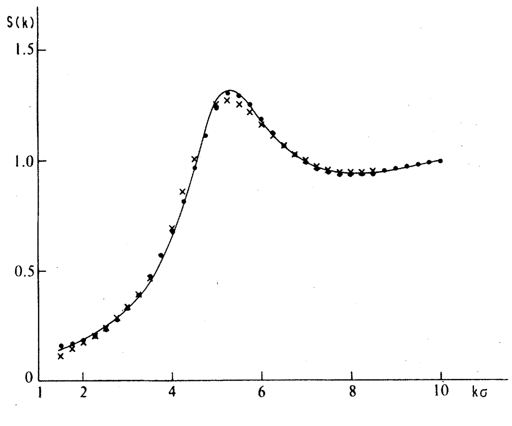

FIG. 3. Structure factor at $\rho\sigma^3 = 0.365$. Solid line: "exact" result (Ref. 1). Dots: our result with $\beta' - u_3$. Crosses: our result with $u_1(C = 0.1,\ d/\sigma = 2,\ D/\sigma = 0.6)$.

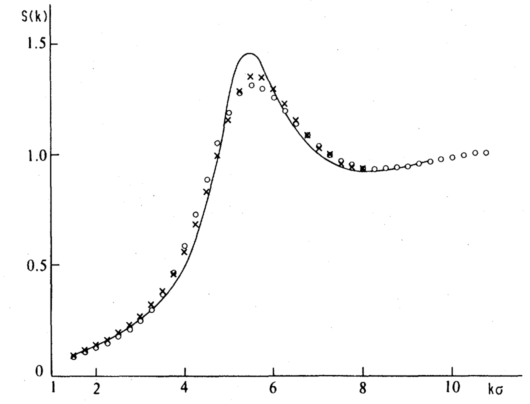

FIG. 4. Structure factor at $\rho\sigma^3 = 0.438$. Solid line: "exact" result (Ref. 1). Open dots: our variational result with KLV u_0. Crosses: our result with u_3 ($C = 0.3$, $d/\sigma = 1.694$, $D/\sigma = 0.565$; $A = 0.3$, $\lambda/\sigma = 1.41$, $\Lambda/\sigma = 0.94$).

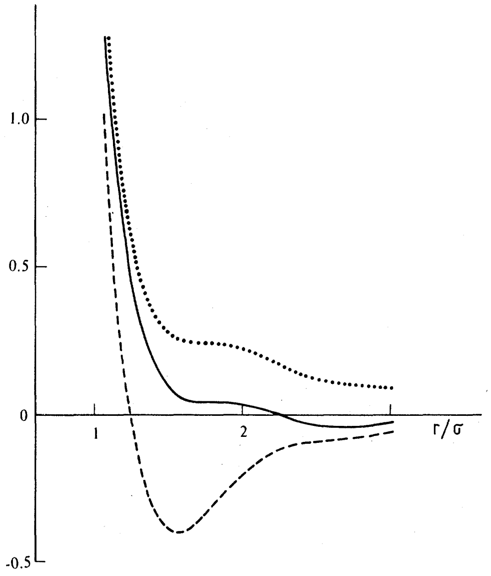

FIG. 5. Solid line: pseudopotential $\alpha' - u_3$. Dashed line: pseudopotential $\beta' - u_3$. Dotted line: best pseudopotential of Ref. 8.

taken the best pseudopotential at the equilibrium density. However, in part the effect could also be real because we know[5, 17] that three-body correlations in the wave function are important and their importance is expected[5] to increase at higher density.

The present Jastrow variational results give the best structure obtained so far. Previous Monte Carlo variational calculations with smooth pseudopotentials did not give a good representation of the short-range order and the $S(k)$ for McMillan's u_0 given in Fig. 2 is typical in this respect. An improvement was found on the basis of Euler-Lagrange functional optimization but these results are not as good as ours. For instance, an implementation[10] of this approach that uses the Monte Carlo method with the approximation of separability of different wave vectors gives the maximum of $S(k)$ at $k\sigma = 5.5$ with $S_{\max} = 1.28$ at the equilibrium density. The "exact" $S(k)$ has the maximum at $k\sigma = 5.3$ with $S_{\max} = 1.32$ and our variational result gives the maximum at $k\sigma = 5.4$ with $S_{\max} = 1.31$.

The pseudopotentials that give the lowest energies have a more or less pronounced structure at intermediate distances, in the region of the first maximum and of the following minimum of $g(r)$. As can be seen in Fig. 5 the $\alpha' - u_3$ pseudopotential becomes slightly negative, it has a local minimum in the region of the first maximum of $g(r)$, and the absolute minimum is roughly at the position of the second maximum of $g(r)$. Between the two there is a maximum corresponding to the minimum of $g(r)$. Such structure is less pronounced[15] with the u_1 pseudopotential when only a shoulder remains, whereas the $\beta' - u_3$ has a well developed negative minimum corresponding to the fact that it gives a self-bound state. The energies given by these rather different pseudopotentials do not differ by more than 0.2 K and this is a manifestation of the insensibility of the energy to changes of the wave function away from the region of the repulsive cores. Very subtle correlations are present however because the value of the energy can rapidly deteriorate for change in $u(r)$ much smaller than the difference, for instance, between the $\alpha' - u_3$ and the best u_1. Our experience is that the only changes of $u(r)$ at intermediate distance that lower the energy are those that enhance the short-range order of the fluid.

Results of functional minimization of the energy are in qualitative agreement with our result since this approach also gives a pseudopotential with some structure at intermediate distance. In Fig. 5 the $u(r)$ obtained by hypernetted chain (HNC) functional minimization[8] is shown [this is very similar to $u(r)$ obtained by Campbell and Pinski[10]]. The shoulder of $u(r)$ is present at $r \sim 1.7-1.8$ (the same result is found in Ref. 11) and this is a smaller distance than the one we find. We believe that this is the reason why we find a better $S(k)$. A large difference is present between this $u(r)$ and ours at larger diatances, but this is due to the fact that our parametrization of $u(r)$ does not include the r^{-2} phonon term[18] whereas the functional minimization approach has built in such a term.

The presence in $u(r)$ of some structure at intermediate distances in systems with a completely different pair interaction such as the hard sphere or Yukawa interaction indicates that this structure does not directly reflect the form of the pair interaction. The fact that in first approximation its position scales with $\rho^{-1/3}$ in different systems[15] points to a collective effect. In fact it has been suggested in I that this structure reflects the zero-point motion of short-wave length excitations, i.e., of rotons in the case of ^{4}He. If one starts with Feynman's description[19] of the phonon-roton excitations as density fluctuations in a dense medium, the model ground state for such elementary excitations has the form of a Jastrow wave function $\prod \exp[-\frac{1}{2}\nu_0(r_{ij})]$ where ν_0 is

$$\nu_0(r) = \frac{1}{N}\sum_{\vec{k}} [S^{-1}(k) - 1] e^{i\vec{k}\cdot\vec{r}} \ . \tag{13}$$

In Fig. 6 $\nu_0(r)$ is plotted when the experimental $S(k)$ is used in Eq. (13). The main peak of $S(k)$, that is related to rotons on the basis of Feynman's form for the excitation energy, $\epsilon(k) = \hbar^2 k^2/2mS(k)$, induces a structure in $\nu_0(r)$ at distance of order $r/\sigma \sim 1.5-2.0$.

In a better approximation one can take into account the backflow associated with rotons with the Feynman-Cohen (FC) wave function[19] for the excited states, and this gives a model ground-state wave function with two- and three-body correlations. If we consider only the Jastrow contribution, it has the form $\prod \exp[-\frac{1}{2}\nu_{\rm FC}(r_{ij})]$ where

$$\nu_{\rm FC}(r) = \frac{1}{N}\sum_{\vec{k}} \mathfrak{N}_k^{-1} \exp\{ i[\vec{k}\cdot\vec{r} + 2g_{\vec{k}}(\vec{r})]\} \ , \tag{14}$$

$$g_{\vec{k}}(r) = A_k \vec{k}\cdot\vec{r}/r^3 \ , \tag{15}$$

$$\mathfrak{N}_k = S(k) + kA_k I_9(k) + k^2 A_k^2 I_{10}(k) \ . \tag{16}$$

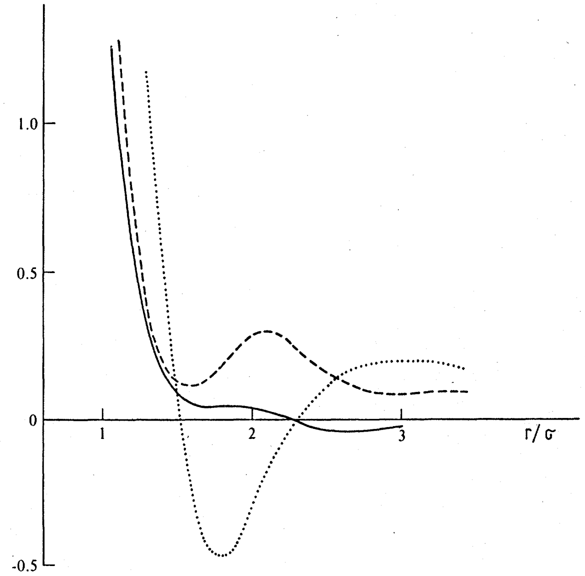

FIG. 6. Solid line: pseudopotential $\alpha' - u_3$. Dashed line: $\nu_0(r)$ [Eq. (13)]. Dotted line: $\nu_{\rm FC}(r)$ [Eq. (14)].

Here A_k is the backflow parameter in the Feynman-Cohen wave function and I_9 and I_{10} are three- and four-particle integrals appearing in that theory.[19] Equation (14) is the generalization to higher order in A_k of the first-order expression given in I. We have computed $\nu_{\rm FC}(r)$ using for A_k, I_9, and I_{10} the values determined by Padmore and Chester[20] and $\nu_{\rm FC}$ is plotted in Fig. 6. A_k and I_9 have been computed[20] only in the neighborhood of the roton minimum, and in order to compute $\nu_{\rm FC}$, we had to extrapolate these functions to zero when $k \to \infty$. We have verified that this extrapolation does not affect $\nu_{\rm FC}$ in the region of interest. From Fig. 6 one notices that $\nu_{\rm FC}$ and ν_0 are similar in that both have a minimum followed by a maximum at intermediate distances, and differ from one another by no more than the $\beta' - u_3$ differs from the $\alpha' - u_3$ as shown in Fig. 5. On the basis of the similarity between such model wave functions and the variational one, in particular, because of the presence of an intermediate distance structure in both cases, we attribute this feature of the wave function to the zero-point motion of rotons.

IV. CORRELATIONS AT FINITE TEMPERATURE

The radial distribution function $g(r,T)$ at finite temperature T is obtained from the diagonal part of the density matrix $\langle R|\sigma|R\rangle$ $[R \equiv (\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)]$. As long as phonons and rotons can be considered as independent excitations and an excited state corresponding to a single excitation has the form

$$\psi_{\vec{k}} = F_{\vec{k}}\psi_0 \ , \tag{17}$$

the density matrix can be explicitly constructed and its diagonal part reads[18,21,22]

$$\langle R|\sigma|R\rangle = \psi_0^2 \exp\left[\sum_{\vec{k}} |F_{\vec{k}}|^2 (1 + e^{\epsilon_k/k_B T})^{-1}\right] \ . \tag{18}$$

In the Feynman approximation one has $F_{\vec{k}} = \rho_{\vec{k}}/(NS_0(k))^{1/2}$ where $\rho_{\vec{k}}$ is the density fluctuation component $\rho_{\vec{k}} = \sum_i \exp(i\vec{k}\cdot\vec{r}_i)$ and $S_0(k)$ is the ground-state structure factor, and the thermal factor in Eq. (18) has the form of a Jastrow term. It can be written in the form

$$\langle R|\sigma|R\rangle = \psi_0^2 \exp\left[-\sum_{i<j} [\nu_T(r_{ij}) - \nu_0(r_{ij})]\right] \ , \tag{19}$$

where

$$\nu_T(r) = \frac{1}{N}\sum_{\vec{k}} \left[S_0^{-1}(k) \tanh\left[\frac{\epsilon_k}{2k_B T}\right] - 1\right] e^{i\vec{k}\cdot\vec{r}} \tag{20}$$

and $\nu_0(r)$ is this function at $T = 0$ K as given in Eq.

(13). If we use an approximate form for the ground state, like a Jastrow wave function, then the calculation of $g(r,T)$ is the same as the calculation of $g(r)$ in the ground state, the only difference being that in place of the pseudopotential $u(r)$ there is a temperature-dependent one: $u_T(r)=u(r)+\nu_T(r)-\nu_0(r)$. The Monte Carlo method can be used at this point to compute $g(r,T)$. The feasibility of this approach has been already tested.[23] Since the temperature-dependent term $\nu_T-\nu_0$ is a weak perturbation compared to $u(r)$, it is also possible to use one of the perturbation theories of classical liquids.[24] This possibility arises because of the equivalence of the present problem with one of a fictitious classical liquid interacting with the pair interaction $v^*(r)=u(r)+\nu_T(r)-\nu_0(r)$ as discussed in Sec. II. We have tested this approach also and now we present some of our results.

The function $\nu_T(r)$ contains the contribution from all wave vectors, i.e., from all excitations of the system. Then the difference $\nu_T-\nu_0$ contains a long-range term of the form r^{-2} due to long-wavelength phonons and this term exactly cancels[18] the r^{-2} term contained in ψ_0 and due to the zero-point motion of the same phonons. Since, in place of the exact ψ_0, we use a Jastrow wave function that does not contain this phonon contribution, we subtract from ν_T the phonon contribution ν_T^{ph}, i.e., the expression (20) with $\hbar ck$ replacing ϵ_k and $\hbar k/2mc$ replacing $S_0(k)$. At temperature above 1.5 K the energy spectrum ϵ_k is found experimentally to depend on temperature and we use this $\epsilon_k(T)$ in Eq. (21). A justification for this has been given in Ref. 22.

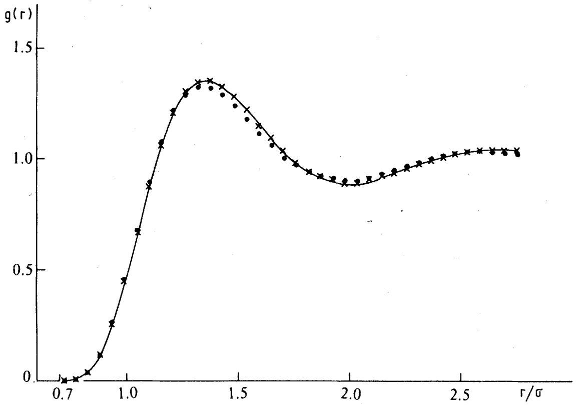

FIG. 7. $g(r)$ at $T=0$ K (dots, variational result with $\alpha'-u_3$ pseudopotential) and at $T=2.05$ K: Monte Carlo result (crosses) and perturbation theory (solid line).

As an exemplification of our computations we present the results at density $\rho=2.298\times10^{20}$ at/cm^3 [$\rho\sigma^3=0.3845=1.054\;(\rho_{\text{eq}}\sigma^3)$]. We have performed a Monte Carlo computation for the ground state with the $\alpha'-u_3$ pseudopotential. This gives an energy $E=-5.90$ K (for comparison the McMillan u_0 gives $E=-5.52$ K) and $g(r)$ is shown in Fig. 7. A second computation has been performed with the pseudopotential

$$u_T(r)=u(r)+\Delta_T(r)\ , \tag{21}$$

where $u(r)$ is again the $\alpha'-u_3$ pseudopotential and

$$\Delta_T(r)=\frac{1}{2\pi^2\rho}\int_0^\infty dkk\,\frac{\sin kr}{r}\left\{S_0^{-1}(k)\left[\tanh\left(\frac{\epsilon_k}{2k_BT}\right)-1\right]-\frac{2mc}{\hbar k}\left[\tanh\left(\frac{\hbar ck}{2k_BT}\right)\right]\right\} \tag{22}$$

represents $\nu_T-\nu_0-(\nu_T^{\text{ph}}-\nu_0^{\text{ph}})$. $S(k)$ at low temperature has not been measured at this density and for $S_0(k)$ we use our Jastrow result for the ground state. $S(k)$ has been measured[25] at temperature 2.05 K and we have performed the computation at this temperature. For ϵ_k we have used the model energy spectrum of Ref. 26 with the experimental value[27] for the parameters of the roton region.

$\Delta_T(r)$ is an oscillatory function of r, being negative in the region of the first maximum of $g(r)$ and positive in the region of the first minimum.[23] Thus it induces an increase in the short-range order of the liquid as can be verified in Fig. 7 where our result for $g_T(r)$ is shown. This corresponds to a sharpening of $S(k)$ as can be seen in Fig. 8. This result is in agreement with the previous result at equilibrium density.[23] [Feenberg's formula[22] for $S_T(k)$, obtained with the approximation of separability, does not agree with the Monte Carlo result, as it can be seen in Fig. 8.]

To the problem we have applied the perturbation theory of liquids in the exponential approximation.[24] $\Delta_T(r)$ represents the perturbing term and $u(r)$ the reference system. $g_T(r)$ is given by

$$g_T(r)=g(r)\exp C_T(r)\ , \tag{23}$$

where $g(r)$ is the radial distribution function at $T=0$ K and C_T reads

$$C_T(r)=-(2\pi)^{-3}\rho\int d^3k e^{i\vec{k}\cdot\vec{r}}\frac{S_0^2(k)\Delta_T^*(k)}{1-\rho S_0(k)\Delta_T(k)}\ , \tag{24}$$

where S_0 is the structure factor corresponding to $g(r)$ and $\Delta_T(k)$ is the Fourier component of the "optimized" perturbation $\Delta_T^*(r)$. $\Delta_T^*(r)$ is a function which

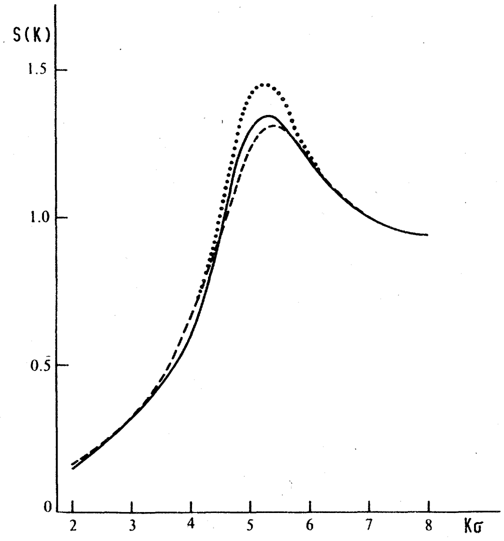

FIG. 8. $S(k)$ at $T=0$ K (dashed line) and at $T=2.05$ K: Monte Carlo result (solid line) and result with Feenberg's formula (Ref. 22) $S_T(k)=S_0(k)\coth[\epsilon(k)/2k_BT]$ (dotted line).

coincides with $\Delta_T(r)$ in the physically relevant region $r>d$ and it is such that $C_T(r)=0$ for $r<d$. d represents the diameter of the equivalent hard-sphere system,[2] $d=0.81\sigma$. We have verified that varying d between 0.80σ and 0.83σ makes a negligible difference on $C_T(r)$. The perturbation result for $g_T(r)$ is shown in Fig. 7 and one can see the good agreement with the Monte Carlo result.

We cannot make a direct comparison of our result with experiment because no measurement has been performed at low temperatures and, on the other hand, we cannot compare directly our $S_T(k)$ with experiment because our $S_T(K)$ reflects also the deficiencies of the Jastrow wave function for the ground state, deficiencies that increase when we consider densities above the equilibrium value as discussed in Sec. III.

V. DISCUSSION

We have found parametrizations of the pseudopotential of the Jastrow wave function of the Lennard-Jones Bose fluid that, compared with the smooth pseudopotentials like McMillan's, improve the energy, give an equilibrium density closer to the exact value, and in particular give an excellent description of the short-range order present in the fluid. The parametrization suggested by De Michelis and Reatto is found especially successful. The pseudopotential is characterized by having a correlation structure at intermediate distances that is strictly related to the oscillations of the radial distribution function. Such structure is similar to the one found in other systems, i.e., in the hard-sphere[5] and in the Yukawa[6] Bose system, even if its detailed shape is somewhat different. This suggests that this correlation structure of the pseudopotential $u(r)$ is a common occurrence in all high-density Bose fluids.

In I it has been suggested that the physical origin of this structure is the zero-point motion of rotonlike excitations. This suggestion was based on the fact that a similar structure is found in the pseudopotential of a model wave function obtained under the assumption that rotons, considered in the Feynman approximation, can be treated as harmonic oscillators. We find confirming evidence for this suggestion because when we also take into account the backflow, i.e., we start with the Feynman-Cohen wave function, the model ground state has a Jastrow term with a pseudopotential that has a pronounced structure at intermediate distances. While the basic structure of these $u(r)$, a minimum followed by a maximum, is the same as our variational $u(r)$, their detailed shape is rather different and this confirms that such model wave functions can be considered only on a qualitative basis. Backflow also introduces three-particle correlations in the wave function that have been considered in I.

Our variational results are in reasonable agreement with those obtained by Jastrow functional minimization.[8–11] Also in this approach it is found that $u(r)$ has some structure at intermediate distances but the effect is smaller and slightly displaced toward the core in comparison with our $u(r)$. This explains why we find an $S(k)$ in better agreement with the "exact" results and it indicates that the approximations introduced in the functional minimization approach are not accurate enough. The hypernetted-chain approximation[8,9] (HNC) is known to give a rather poor energy. Inclusion of some of the elementary diagrams[11] improves the situation but, from comparison with our results, it is clear that some relevant contribution is still missing. In this respect the computations of Rosenfeld and Ashcroft[28] suggest that more accurate results should be obtained by performing the functional minimization with the HNC equation modified by inclusion of the contribution of *all* elementary diagrams of a suitable *classical* hard-sphere system.

Another functional minimization computation[10] uses the Monte Carlo method with the approximation of separability of effects of different wave vectors. It is possible that this is responsible for the discrepancies that we find with our results for $S(k)$. The energy is in good agreement with our value. In this respect it is relevant to recall the discrepancy that we find[15,23] between the Monte Carlo computation of the temperature dependence of $S(k)$ and the result found under the same approximation of separability starting from the same density matrix.

Our variational results are not so good at high density near solidification, even if they improve previous results. However on the basis of our limited investigation of this case we cannot decide if this deficiency is intrinsic to Jastrow wave functions because of the presence of important three-particle correlations. In any case these correlations must also be important at the equilibrium density because only in this way can one explain the remaining difference between the Jastrow value (~ -6.10 K) of the ground-state energy and the "exact" value (-6.85 K) and approximate calculations[8, 17] support this view.

Our best pseudopotential (the one labeled α' in Table II) becomes slightly negative, but this is not enough to give a self-bound state. However, we find that pseudopotentials exist that describe a self-bound state and give an energy that, if it is not minimum, is quite acceptable and, in fact, of the order of that obtained with McMillan's $u(r)$. Such pseudopotentials, for example, the one labeled β' in Table II, should be used in those computations in which the use of a wave function that describes a self-bound state is expected to be important. Moreover $\beta' - u_3$ gives an $S(k)$ almost coincident with the "exact" one so that this pseudopotential is close to the one that gives maximum overlap between ψ_J and the "exact" ψ_0.

It has been shown already[23] how the structure factor $S(k,T)$ can also be approximately computed with the Monte Carlo method at finite temperature. We have performed some other similar computations that confirm that the main temperature dependence of $S(k,T)$ at fixed density consists of an increase and of a sharpening of the main peak of $S(k,T)$ as the temperature increases. We have also studied this temperature dependence on the basis of a perturbation approach inspired by perturbation theories of classical liquids. We have used the optimized "exponential" approximation and we find good agreement with the Monte Carlo results. We conclude that in the study of $S(k,T)$ this perturbation approach is more convenient to use than the Monte Carlo one because no statistical errors are present, and in this way one can also extend the study of temperature effect to smaller temperatures where the effect is rather small.

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APPENDIX

The form[2] KLV of the pseudopotential $u_0(r)$ modeled on the solution of the two-body problem and on the pseudopotential of the hard-sphere system is defined by

$$f(r) = e^{-u_0(r)/2} = \frac{1}{x-1} \tanh\left(\frac{x^m - 1}{b^m}\right) w_0(x), \quad x = r/a \ ,$$

$$w_0(x) = \begin{cases} [c_0 + c_1(x-1)]e^{-w(x^{-5}-1)}, & x \leqslant 1 \\ x - 1 + c_0[1 + c_2(x-1)^2]e^{-k(x-1)}, & x > 1 \ , \end{cases}$$

where

$$w = 8\pi/10\Lambda^* a^5, \quad \Lambda^* = (\hbar^2/m\sigma^2\epsilon)^{1/2} = 2.67 \ ,$$

$$c_0 = 0.04118, \quad c_1 = 0.0515, \quad c_2 = -30.18, \quad k = 11.56 \ .$$

a is the unique variational parameter of u_0; m and b have the value determined in the hard-sphere problem,[29] $m = 2$ and $b = 1.2$.

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