

## Kirkwood-Monroe approximation for quantum solids

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The energy of a Boltzmann quantum solid is calculated using the Kirkwood-Monroe liquid ansatz for the solid pair correlation function. Approximate liquid pair correlation functions generated from the Born-Bogoliubov-Green-Kirkwood-Yvon, Kirkwood-superposition-approximation (BBGKY-KSA) equation and from the hypernetted-chain (HNC) equation are used to calculate the energy of solids with  $\hbar^2/m\epsilon\sigma^2 = \eta$  of 0.1815 ( $^4\text{He}$ ) and 0.200. The calculations are done over the physical density range ( $0.024 \leq \rho \leq 0.035$  part./ $\text{\AA}^3$ ). The energy of the liquid is also calculated. Results are obtained for solid and liquid energies which depend critically on the choice of liquid correlation function and on  $\eta$ . For  $\eta = 0.1815$  and the BBGKY-KSA pair correlation function the system has a liquid  $\rightarrow$  solid  $\rightarrow$  liquid phase transition, whereas for  $\eta = 0.1815$  and the HNC pair correlation function the system can exist as a zero-pressure solid.

### I. INTRODUCTION

The solids formed by the helium isotopes,<sup>1</sup> molecular hydrogen,<sup>2</sup> and perhaps spin-aligned atomic hydrogen<sup>3</sup> are known as *quantum* solids because their small mass and weak attraction allows large zero-point excursions about the lattice sites. Nosanow and co-workers<sup>4</sup> pointed out that because of this motion one must take care to treat properly the short-range correlations which appear because of the strong interparticle repulsion in order to achieve reasonable agreement between calculated and measured energies. Two basic approaches to the liquid-solid phase transition have emerged. First is the variational method which utilizes products of one- and two-body trial wave functions (usually) explicitly parametrized and determined by minimizing the expectation value of the Hamiltonian. The application of Monte Carlo methods<sup>5</sup> to this technique is the most consistent calculational scheme available since the same *approximation* is used in both the liquid and solid phases. The second approach is perturbation-theoretic,<sup>6</sup> wherein one solves an appropriate Bethe-Goldstone equation for the correlated wave function. In this paper we shall study an approach to the quantum solid ground state which uses ideas based on the variational technique.

In their work on the liquid-to-solid phase transition in a classical system Kirkwood and Monroe<sup>7</sup> introduced the idea that one might be able to approximate the short-range correlations in a solid by those in a (metastable or fictitious) liquid having the number density of the solid. Such an assumption may be justified by noting that since the basic Hamiltonian is invariant under translations and rotations one only needs an *angle-averaged* two-particle distribution

function in order to calculate the energy. This object closely resembles, in form, the *liquid* radial-distribution function for which numerous calculational techniques are available. Thus Kirkwood and Monroe suggested that one try to take advantage of the extensive knowledge of the liquid problem in the treatment of the solid problem. In a series of papers Lowy and Woo<sup>8</sup> (LW) have generalized the Kirkwood-Monroe approach, by choosing the liquid radial-distribution function which minimizes the energy rather than that function corresponding to the "liquid" at that particular density, and applied their method to various quantum solids. They have studied the liquid-solid phase transition and find reasonable agreement between their results and those of Monte Carlo calculations. In addition to the generalized Kirkwood-Monroe procedure, LW also introduced a properly symmetrized *Bose* trial wave function for their solid. The use of this trial wave function, although correct in principle, yields a set of equations which tend to obscure somewhat the physical content of the Kirkwood-Monroe approximation. That is, the energy due to accounting properly for the statistics, the "exchange" energy<sup>9</sup> and the energies due to multiply occupied sites are typically much smaller than the "direct" energies and thus can hardly play a significant role in a variational calculation.

In this paper we investigate the Kirkwood-Monroe approximation for an unsymmetrized ("Boltzmann") solid. We show that the energy can be written in a simple form consisting of one-fold *configuration* space integrals summed over "shells." The advantage of this procedure is the simplicity of the expression for the energy since it allows for a very accurate numerical evaluation. In Sec. II we derive the equations for the Boltzmann-solid energy and show explicitly that

they contain a liquidlike solution. In Sec. III we compare our results in detail with LW. Our basic result is that the Kirkwood-Monroe ansatz for the solid correlation function can, depending on the details, give any of a variety of results, a liquid-solid transition, a liquid-solid-liquid transition, a zero-pressure solid, . . . and is therefore an unreliable approach to the *ab initio* determination of a liquid-to-solid phase transition.

## II. THEORY

Consider a system of  $N$  particles in a box of volume  $\Omega$  which are described by a trial wave function  $\psi$  of the form

$$\psi = \prod_{i=1}^N \phi_i(\vec{r}_i) \prod_{i<j} f(r_{ij}) , \quad (1)$$

$$E = \int \psi^2 \left[ -\frac{\hbar^2}{8m} \sum_i \nabla_i^2 t_i(\vec{r}_i) + \sum_{i<j} \left[ v(r_{ij}) - \frac{\hbar^2}{4m} \nabla_i^2 u(r_{ij}) \right] \right] d\vec{r}^N (I_N)^{-1} \\ - \frac{\hbar^2}{4m} \sum_{i=1}^N \int \bar{\nabla}_i \left[ \psi^2 \left( \frac{1}{2} \bar{\nabla}_i t_i(\vec{r}_i) + \frac{1}{2} \sum_j' \bar{\nabla}_i u(r_{ij}) \right) \right] d\vec{r}^N (I_N)^{-1} , \quad (4)$$

where we have introduced the notation

$$\phi_i(r_i) = e^{t_i(r_i)/2} , \quad (5)$$

$$f(r_{ij}) = e^{u(r_{ij})/2} , \quad (6)$$

$$I_N = \int |\psi|^2 d\vec{r}^N , \quad (7)$$

and the prime on the summation in Eq. (4) indicates that the  $i=j$  term is to be excluded. Now let us define  $m$ -particle distribution functions for a system of  $m$  distinguishable particles

$$n_{1,2,\dots,m}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_m) \\ = \int \psi^2 d\vec{r}_{m+1} \dots d\vec{r}_N (I_N)^{-1} . \quad (8)$$

Thus, using (8) in (4), we find

$$E = -\frac{\hbar^2}{8m} \sum_{i=1}^N \int n_i(\vec{r}_i) \nabla_i^2 t_i(\vec{r}_i) d\vec{r}_i \\ + \sum_{i<j} \int n_{ij}(\vec{r}_i, \vec{r}_j) \\ \times \bar{v}(\vec{r}_{ij}) d\vec{r}_i d\vec{r}_j + E_s , \quad (9)$$

where we have defined

$$\bar{v}(r) = v(r) - (\hbar^2/4m) \nabla^2 u(r) , \quad (10)$$

and  $E_s$  is a surface integral

where the  $i$  subscript on the single-particle functions denotes the lattice site for particle  $i$ . We assume that the two-particle functions  $f$  depend only on the scalar distance between those two particles and so in the liquid state  $\phi_i(\vec{r}_i) \rightarrow \text{const}$  and we have the usual product pair functions description of a Bose liquid. The Hamiltonian  $H$  for the  $N$  particles is given by

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i<j} v(r_{ij}) , \quad (2)$$

where  $v(r)$  is the two-particle potential which for the numerical work shall be chosen to be in Lennard-Jones form

$$v(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] . \quad (3)$$

Then calculating the expectation values of  $H$  we have

$$E_s = -\frac{\hbar^2}{8m} \sum_{i=1}^N \oint n_i(\vec{r}_i) \bar{\nabla}_i t_i(\vec{r}_i) \cdot d\vec{s}_i \\ + \sum_{i,j} \int \oint n_{ij}(\vec{r}_i, \vec{r}_j) \\ \times \bar{\nabla}_i u(r_{ij}) \cdot d\vec{s}_i d\vec{r}_j . \quad (11)$$

The  $m$ -particle and  $(m+1)$ -particle distribution functions are related by a set of identities known as the Born-Bogoliubov-Green-Kirkwood-Yvon (BBGKY) relations. They are generated by applying the gradient operator to Eq. (8) and for the case of  $m=1$ , the first BBGKY equation, we find

$$\bar{\nabla}_1 n_1(\vec{r}_1) = \bar{\nabla}_1 t_1(\vec{r}_1) n_1(\vec{r}_1) \\ + \sum_{j \neq 1} \int \bar{\nabla}_1 u(r_{1j}) \\ \times n_{1j}(\vec{r}_1, \vec{r}_j) d\vec{r}_j . \quad (12)$$

Thus, using the first BBGKY equation in Eq. (11), we find

$$E_s = \frac{\hbar^2}{8m} \sum_{i=1}^N \oint \bar{\nabla}_i n_i(\vec{r}_i) \cdot d\vec{s}_i . \quad (13)$$

Since  $n_i(\vec{r}_i)$  is a short-ranged function (about lattice site  $\vec{R}_i$ ) this integral clearly vanishes on a surface at infinity. The integral in fact vanishes identically if  $n_i(\vec{r}_i) = n(\vec{r}_i - \vec{R}_i)$ .

Now substituting (12) into (9) yields

$$E = \frac{\hbar^2}{8m} \sum_i \int \bar{\nabla}_i n_i(\bar{r}_i) \cdot \bar{\nabla}_i \ln n_i(\bar{r}_i) d\bar{r}_i + \sum_{i < j} \int n_{ij}(\bar{r}_i, \bar{r}_j) \left[ \bar{v}(r_{ij}) - \frac{\hbar^2}{4m} \bar{\nabla}_i \ln n_i(\bar{r}_i) \cdot \bar{\nabla}_i u(r_{ij}) \right] d\bar{r}_i d\bar{r}_j . \quad (14)$$

We see that, formally, we have eliminated the  $t$ 's and hence the single-particle functions  $\phi$ , from the energy. Next in an approach similar to that used in the study of the surface of liquid  $^4\text{He}$ ,<sup>10</sup> we shall introduce an explicit functional form for the one-particle distribution function. We choose a Gaussian form so that

$$n_1(\bar{r}_1) = (A/\pi)^{3/2} e^{-A(\bar{r}_1 - \bar{r}_1)^2} \quad (15)$$

Thus, for a given two-particle distribution function  $n_{ij}(\bar{r}_i, \bar{r}_j)$  and  $u(r)$ , Eq. (12) determines the  $t_i(r_i)$  necessary to generate the Gaussian one-particle distribution functions of Eq. (15). From the Monte Carlo studies<sup>5</sup> of solid He we expect that the approximation of Eq. (15) should be entirely reasonable. Now we define auxiliary functions  $g_{ij}(\bar{r}_{ij})$ ,

$$n_{ij}(\bar{r}_i, \bar{r}_j) \approx n_i(\bar{r}_i) n_j(\bar{r}_j) g_{ij}(\bar{r}_{ij}) , \quad (16)$$

where the  $g_{ij}$  are a measure of the short-range correlations between particles  $i$  and  $j$ , and here are assumed to depend only on the relative position vector. In general, the  $g_{ij}$  will also depend on the center-of-mass vector of  $i$  and  $j$ . Then using (15) and (16) in (14) and performing the center-of-mass integrations we find

$$E = \frac{3\hbar^2 A}{4m} N + \left( \frac{A}{2\pi} \right)^{3/2} \sum_{i < j} \int e^{-(A/2)(\bar{r} - \bar{\Delta}_{ij})^2} \times g_{ij}(\bar{r}) \omega_{ij}(\bar{r}) d\bar{r} , \quad (17)$$

where we have introduced an effective two-particle interaction  $\omega_{ij}$ :

$$\omega_{ij}(\bar{r}) = \bar{v}(r) - (\hbar^2/4m) A u'(r) (r - \hat{r} \cdot \bar{\Delta}_{ij}) , \quad (18)$$

where  $\bar{\Delta}_{ij}$  is a relative lattice vector,  $\hat{r}$  is a unit vector, and the prime in Eq. (18) stands for differentiation. To proceed further we now assume that the two-particle correlations depend only on the scalar distance between particles and  $d$ , the magnitude of the distance between lattice sites. Then additional integrations over angles can be performed to yield

$$\frac{E}{N} = \frac{3\hbar^2 A}{4m} + \frac{1}{2} \left( \frac{A}{2\pi} \right)^{1/2} \times \sum_d \frac{n_d}{d} \int_0^\infty g_d(r) [e^{-(A/2)(r-d)^2} \omega_d^-(r) - e^{-(A/2)(r+d)^2} \omega_d^+(r)] r dr , \quad (19)$$

where we have defined

$$\omega_d^\pm(r) = \bar{v}(r) + (\hbar^2/2m) [u'/r + A u'(r \mp d)] . \quad (20)$$

The  $d$ 's in Eq. (19) are distances to shells of lattice points from any given lattice point and  $n_d$  is the number of lattice points in that particular shell.

Next we derive the normalization, sequential relation and liquid ( $A \rightarrow 0$ ) limit for these results. We introduce one- and two-particle distribution functions corresponding to any single or pair of particles

$$n^{(1)}(\bar{r}_1) = \sum_i n_i(\bar{r}_1) , \quad (21)$$

$$n^{(2)}(\bar{r}_1, \bar{r}_2) = \sum_{i,j} n_{ij}(\bar{r}_1, \bar{r}_2) . \quad (22)$$

Then we immediately have

$$\int n^{(1)}(\bar{r}) d\bar{r} = N , \quad (23)$$

$$\int n^{(2)}(\bar{r}_1, \bar{r}_2) d\bar{r}_1 d\bar{r}_2 = N(N-1) . \quad (24)$$

Using (22) in (24) with the decomposition (16) for  $n_{ij}$  we find

$$\frac{1}{2} \left( \frac{A}{\pi} \right)^{1/2} \sum_d \frac{n_d}{d} \int_0^\infty [g_d(r) - 1] (e^{-(A/4)(r-d)^2} - e^{-(A/4)(r+d)^2}) r dr = 0 . \quad (25)$$

In the  $A \rightarrow 0$  limit (25) becomes

$$4\pi\rho_0 \int_0^\infty [g(r) - 1] r^2 dr = -1 , \quad (26)$$

where

$$\rho_0 \equiv N/\Omega , \quad (27)$$

and the liquid radial-distribution function is obtained from

$$g(r) = \frac{1}{N} \sum_d g_d(r) . \quad (28)$$

In order to obtain (18) from (25) we let  $(A/2\pi)^{3/2} \rightarrow 1/\Omega$  when  $A \rightarrow 0$ , as determined by (23). Then using this limit and Eq. (28) we find

$$\lim_{A \rightarrow 0} \left( \frac{E}{N} \right) = 2\pi\rho \int_0^\infty g(r) \bar{v}(r) r^2 dr , \quad (29)$$

which is the energy of the liquid phase.

If we now take the  $g$ 's to be independent of  $d$

$[g_d(r) \rightarrow g(r)]$  then they can be considered to be generated by  $u(r)$  only (i.e., they are the solution of an associated liquid problem). We parametrize  $u(r)$  in the usual form<sup>5</sup>

$$u(r) = -(b\sigma/r)^5, \quad (30)$$

where  $b$  is determined by minimizing the energy. We use  $g(r)$ 's which are solutions of the BBGKY-Kirkwood-superposition-approximation (KSA) and hypernetted-chain (HNC) approximate integral equations. For a discussion of these integral equations and their application to liquid He see Ref. 11.

We have examined the possibility of permitting shell dependence in the  $g(r)$ 's [i.e.,  $g(r) \rightarrow g_d(r)$ ]. One can then determine the  $g_d(r)$  from an approximate self-consistent Euler-Lagrange equation. This results in a differential equation for the  $g_d(r)$  which is very similar in appearance to the  $T$ -matrix types of Bethe-Goldstone equation for the pair wave function. We have not attempted to solve this equation because we felt that, although it is pedagogically interesting that contact has been made between the  $T$  matrix and variational approaches, the various approximations necessitate the loss of the variational principle and thus if one prefers a differential equation approach the usual  $T$ -matrix method should be used.

We now introduce a set of reduced units,<sup>11</sup> denoted by an asterisk, where energies are measured in units of  $\epsilon$  and lengths in units of  $\sigma$ . Thus, Eqs. (19) and (20) become

$$\begin{aligned} \frac{E^*}{N} = & \frac{3}{4}\eta A^* + \frac{1}{2} \left( \frac{A^*}{2\pi} \right)^{1/2} \\ & \times \sum_{d^*} \frac{n_d}{d^*} \int_0^\infty g(r^*) [e^{-(A^*/2)(r^*-d^*)^2} \omega_{d^*}^-(r^*) \\ & - e^{-(A^*/2)(r^*+d^*)^2} \omega_{d^*}^+(r^*)] \\ & \times r^* dr^*, \quad (31) \end{aligned}$$

$$\begin{aligned} \omega_{d^*}^\mp(r^*) = & v^*(r) - \frac{1}{4}\eta[\nabla^2 u(r^*) \mp u'/r^* \\ & \mp A^* u'(r^* \mp d^*)] \quad (32) \end{aligned}$$

and we have defined

$$\eta = \hbar^2/m\epsilon\sigma^2; \quad (33)$$

for  ${}^4\text{He}$ ,  $\eta = 0.1815$  and  ${}^3\text{He}$ ,  $\eta = 0.2409$ .

Using the methods of Ref. 11 we calculate a set of  $g(r)$ 's corresponding to various values of  $b$ . We then minimize  $E^*$  with respect to  $b$  and  $A^*$  at a particular density  $\rho^*$  to obtain the equations of state.<sup>12</sup>

The solid energies in Eq. (31) were calculated by summing over thirty-five shells of an assumed face-centered cubic lattice which yields a maximum shell size  $d_{\text{max}}^* = 7.45$ . A cutoff correction is then applied

by approximating the contribution of the omitted shells as an integral and interchanging this integration with the integration over  $r^*$  (this procedure is described in detail in Appendix A). The numerical error introduced in truncating the sum over shells is complementary to that introduced by approximating the remainder by an integral in the sense that the sum converges quickly in the  $A^* \rightarrow \infty$  limit while the integral is exact in the  $A^* \rightarrow 0$  (liquid) limit. There is a region of  $A^*$  where the combined inaccuracy is worst and this is approximately given by  $A^* \sim 1/d_{\text{max}}^{*2} = O(10^{-1})$  which is an unimportant region for this calculation. Our calculation should thus yield very accurate energies over a large range of  $A^*$  values. There are two obvious tests. First, in the  $A^* \rightarrow 0$  limit we compare the present results [which we emphasize are obtained solely from the cutoff correction, the lattice sum being  $O(1/N)$  in this limit], with previous results for the liquid<sup>11</sup> and we find agreement to within small numerical errors. Second, we calculate the energy and pressure for solid Ne ( $\eta = 0.008842$ ) at  $\rho^* = 0.9579$  and obtain  $E^* = -5.986$ ,  $P^* = -0.03$  in excellent agreement with Mullin<sup>13</sup> and Nosanow.<sup>14</sup> These tests give us confidence in our cutoff corrections and lattice sums (since the Ne result is basically a single-particle Hartree calculation).

### III. RESULTS AND DISCUSSION

In Tables I and II and Figs. 1 and 2 we show the results of calculations of the liquid and solid energies using the BBGKY-KSA and HNC  $g(r)$ 's, respectively.

We first consider the BBGKY-KSA results shown in Fig. 1. For  ${}^4\text{He}$  ( $\eta = 0.1815$ ) the solid-energy curve crosses the liquid curve twice affording the opportunity for two Maxwell constructions and a liquid  $\rightarrow$  solid  $\rightarrow$  liquid phase diagram (see Fig. 3). On the other hand, at  $\eta = 0.20$  the solid energy is always greater than that of the liquid and no liquid-solid equilibrium is possible. This latter result is in conflict with experiment (a liquid-solid transition of course occurs in  ${}^3\text{He}$ ,  $\eta = 0.2409$  at 30 atm) and with the Monte Carlo results of Nosanow, Parish, and Pinski.<sup>12</sup> (In fact, since one does not expect a pressure- $\eta$  space critical point there should be liquid-solid transitions for all  $\eta$ .) Our calculations at  $\eta = 0.1815$  should be compared directly with those of Lowy and Woo<sup>8</sup> who found liquid-solid coexistence between  $V^* = 1.93$  and  $V^* = 2.07$ . We see that their liquid-solid transition seems to correspond to neither of the Maxwell constructions on Fig. 1.

The HNC results are shown in Fig. 2. For  ${}^4\text{He}$  ( $\eta = 0.1815$ ) the solid is at higher energy than the liquid at large  $V^*$  and vice versa at small  $V^*$ . A Maxwell construction at below zero pressure is possi-

TABLE I. Energy  $E^*$  as a function of volume  $V^*$  at  $\eta=0.1815$  ( ${}^4\text{He}$ ) for the BBGKY-KSA data. For energies in K multiply by  $\epsilon$  and for volumes in  $\text{\AA}^3$  multiply by  $\sigma^3$ . Solid energies are in the top half of the table; liquid energies in the bottom half.

$\rho^*$	$V^*$	$E^*$	$A^*$	$b$
0.400	2.50	-0.580	7	1.112
0.425	2.35	-0.606	8	1.122
0.450	2.22	-0.629	10	1.101
0.475	2.11	-0.645	11	1.110
0.500	2.00	-0.652	12	1.105
0.525	1.91	-0.649	14	1.101
0.550	1.82	-0.634	15	1.109
0.585	1.71	-0.589	18	1.098
0.400	2.50	-0.682	0	1.176
0.425	2.35	-0.685	0	1.181
0.450	2.22	-0.682	0	1.186
0.475	2.11	-0.674	0	1.190
0.500	2.00	-0.662	0	1.194
0.525	1.91	-0.647	0	1.197
0.550	1.82	-0.629	0	1.200
0.585	1.71	-0.607 <sup>a</sup>	0	1.215

<sup>a</sup>This energy is lower than that of LW by more than 1 K. We are unable to explain this discrepancy.

TABLE II. Energy  $E^*$  as a function of volume  $V^*$  at  $\eta=0.1815$  ( ${}^4\text{He}$ ) for the HNC data. For energies in K multiply by  $\epsilon$  and for volumes in  $\text{\AA}^3$  multiply by  $\sigma^3$ . Solid energies are in the top half of the table; liquid energies in the bottom half.

$\rho^*$	$V^*$	$E^*$	$A^*$	$b$
0.31	3.23	-0.407	4.5	1.132
0.33	3.03	-0.429	5.5	1.129
0.35	2.86	-0.450	6.0	1.126
0.37	2.70	-0.469	7.0	1.124
0.39	2.56	-0.485	8.5	1.121
0.41	2.44	-0.498	9.5	1.124
0.43	2.33	-0.508	10.5	1.117
0.45	2.22	-0.509	12.0	1.101
0.47	2.13	-0.510	13.0	1.114
0.49	2.04	-0.501	14.0	1.126
0.25	4.00	-0.484	0	1.155
0.27	3.70	-0.495	0	1.159
0.29	3.45	-0.499	0	1.163
0.31	3.23	-0.494	0	1.166
0.33	3.03	-0.480	0	1.170
0.35	2.86	-0.455	0	1.173
0.37	2.70	-0.420	0	1.176
0.39	2.56	-0.371	0	1.179
0.41	2.44	-0.309	0	1.182

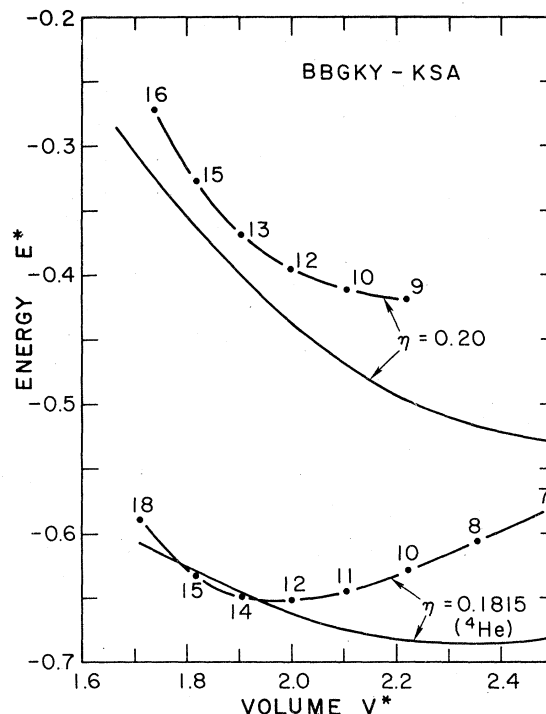


FIG. 1. Reduced energy  $E^*$  as a function of the reduced volume  $V^*$  for  $\eta=0.1815$  ( ${}^4\text{He}$ ) and  $\eta=0.20$ , calculated with the BBGKY-KSA  $g(r)$ 's. The solid lines are the liquid ( $A^*=0.0$ ) energies and the dashed lines are the solid energies (where the associated numbers give the values of  $A^*$ ). This figure shows a liquid-solid-liquid transition at  $\eta=0.1815$  and no transition at  $\eta=0.20$ . For energies in K multiply by  $\epsilon$  and for volumes in  $\text{\AA}^3$  multiply by  $\sigma^3$ .

ble. Thus  ${}^4\text{He}$  would be predicted to form a zero-pressure solid. At  $\eta=0.20$  we obtain quite plausible results.

The very different results obtained in the BBGKY-KSA and HNC calculations show the extreme sensitivity of the liquid and solid energies to the treatment of short-range correlations. The importance of the short-range correlations for the solid can be gleaned from Tables I and II where  $b \sim 1.11$  (similar to the liquid value) and only slowly decreases with increasing density. Different choices of the  $g(r)$  to be employed with the Kirkwood-Monroe ansatz for the two-particle distribution function  $n_{ij}(\bar{r}_1, \bar{r}_2)$ , lead to very different energies for the liquid and solid. Therefore the situation for this ansatz is really no different than from that of the truncated cluster expansion where one introduces the notion of a "restricted" variation: meaning that one should use only those wavefunctions which yield the "correct" answer. Here one must use only that set of  $\{g(r)\}$ 's which yields the "correct" answer. Thus calculations with the Kirkwood-Monroe ansatz may be capable of

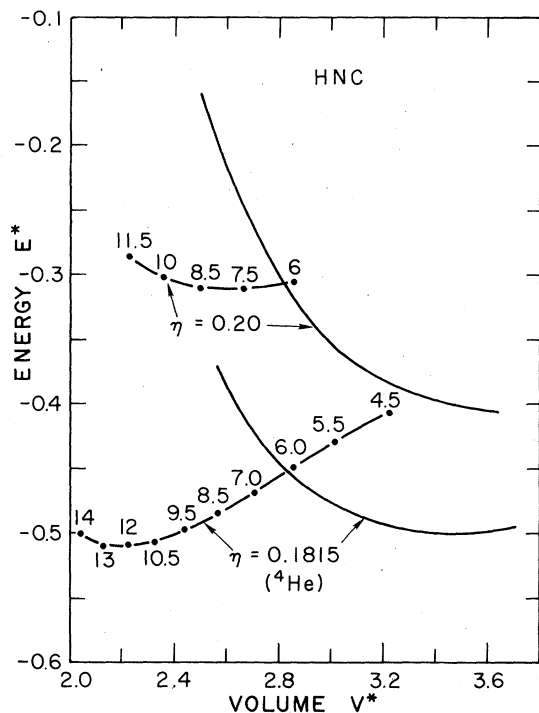


FIG. 2. Reduced energy  $E^*$  as a function of the reduced volume  $V^*$  for  $\eta = 0.1815$  ( $^4\text{He}$ ) and  $\eta = 0.20$ , calculated with the HNC  $g(r)$ 's. The solid lines are the liquid ( $A^* = 0.0$ ) energies and the dashed lines are the solid energies (where the associated numbers give the values of  $A^*$ ). This figure shows that  $\eta = 0.1815$  is a zero-pressure solid. For energies in K multiply by  $\epsilon$  and for volumes in  $\text{\AA}^3$  multiply by  $\sigma^3$ .

confirming what is known by other means (e.g., experiment, Monte Carlo calculations, etc.) but they cannot stand by themselves. The basic physical point is that liquid correlations are not the same as solid correlations (there is ample evidence in the literature<sup>6</sup> for this) and approximating one by the other does not make much sense. In addition, although lots of nice equations for liquid correlation functions exist, the liquid correlations are themselves poorly understood by any reasonable standard (cf. the energy of the liquid in Figs. 1 and 2). One is hard pressed to find an argument for choosing one among several liquid  $g(r)$ 's with which to approximate the solid  $g(r)$ .

Let us try to compare our results and conclusions with those of Lowy-Woo. We note first that their and our single-particle wave functions are in principle different. LW chose a set of single-particle functions which are both symmetric and *delocalized*

$$\prod_{i=1}^N \psi(\vec{r}_i) = \prod \exp \left[ \sum_{\vec{G}} t_{\vec{G}} e^{i\vec{G} \cdot \vec{r}_i} \right], \quad (34)$$

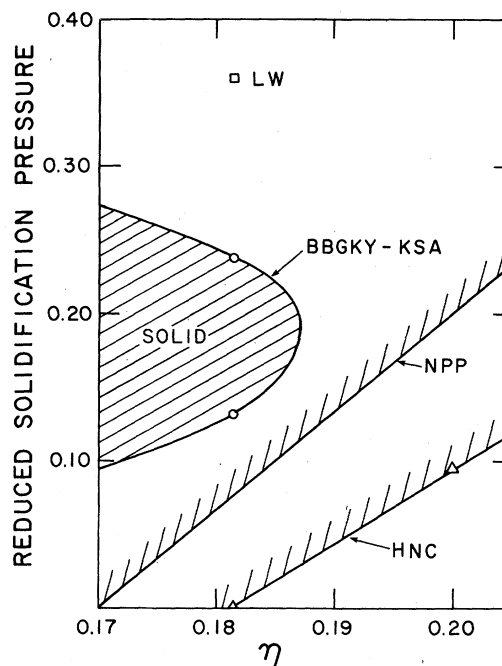


FIG. 3. Reduced solidification pressure as a function of  $\eta$  from this calculation (circles and triangles) compared with the Kirkwood-Monroe result of Lowy and Woo (Ref. 8) and the Monte Carlo results of Nosanow, Parish, and Pinski (Ref. 12).

where the  $\{\vec{G}\}$  are reciprocal-lattice vectors and  $t_{\vec{G}}$  are variational parameters. One can also construct LW-like trial functions using the localized wave functions of Eq. (5), viz,

$$\prod_{j=1}^N \tilde{\phi}(\vec{r}_j) = \prod_{j=1}^N \sum_{i=1}^N \phi_i(r_j). \quad (35)$$

The complexity of the wave functions in Eqs. (34) and (35) is evident. They contain *every* possible way of arranging  $N$  sites among the  $N$  particles. This includes all configurations with  $N$  particles on  $N$  sites,  $N$  particles on  $N-1$  sites (double occupation), ..., and the  $N$  possibilities for all  $N$  particles on one site. Instead of the symmetrized wave function of LW we have used the Boltzmann wave function of Eq. (5). We expect the results of our calculation at  $\eta = 0.1815$ , using the BBGKY-KSA  $g(r)$ , to be the same as those of LW except for differences that arise because of the two choices of single-particle wave functions.

Our wave function can be properly symmetrized by taking a permanent of wave functions based on Eq. (5). Then, our wave function would be the appropriate *valence-band* wave function for the  $N$ -particle system, whereas the LW wave function is the appropriate *molecular-orbital* wave function for the  $N$ -particle

system. We know from experimental investigations<sup>1</sup> of solid <sup>3</sup>He and from theoretical calculations of double-occupation effects<sup>15</sup> that a valence-band wave function is good, for purposes of calculating the energy, to one part in 10<sup>3</sup> or 10<sup>4</sup>. the wave function of Lowy-Woo admits double (multiple) occupation of lattice sites and at least part of the work their  $g(\bar{r})$  will have to do is to correlate pairs of particles that are sitting on top of one another. Our valence-band wave function does not permit double occupation of a lattice site so that our  $g(r)$  only needs to correlate pairs of particles that are held by the crystal at nonzero average distance from one another.

Another difference with the LW calculation is, as mentioned above, our use of a Gaussian  $n_1(r_1)$  [Eq. (15)], whereas LW use Eq. (34) with the nearest and next-nearest neighbor  $t_{\bar{G}}$ 's as variational parameters. Finally, we note that there is an unexplained discrepancy in liquid energy values at high density between the LW calculation and ours (see Table I).

Thus our calculation is in principle not exactly equivalent to that of Lowy-Woo. However, we believe our results and conclusions should apply equally well to similar calculations undertaken using the LW molecular-orbital (MO) wave function. That is, we feel that the use of the Kirkwood-Monroe ansatz by LW would, if investigated more thoroughly, exhibit the same problems as we have encountered in our examination of the Boltzmann-solid ground state.

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#### APPENDIX A: CUTOFF CORRECTION TO THE SUM OVER SHELLS

The expression for the energy, Eq. (19) or (31), is written as a sum over shells of neighboring particles. As this energy is evaluated numerically the sum is truncated after some finite number of shells (35 for this work)<sup>16</sup> and the remainder must be estimated in

some manner. The importance of this cutoff correction depends on the size of  $A$  relative to  $d_{\max}$  (the distance out to the farthest shell). In the limit as  $Ad_{\max}^2 \gg 1$  the sum over shells converges very quickly and the cut-off correction is unimportant (thus it does not matter that in this limit it is also least accurate). In the limit  $A \rightarrow 0$  only the cut-off correction makes appreciable contribution to the energy [since the contribution of the sum over shells is  $O(1/N)$ ].

We shall thus estimate the cut-off correction by assuming that for  $d > d_{\max}$  the summation can be replaced by an integration

$$\sum_{d \geq d_{\max}} n_d \rightarrow 4\pi\rho \int_0^{\infty} x^2 dx \quad (A1)$$

There are two types of sum which need to be evaluated

$$I_1^{\pm}(r) = \sum_{d \geq d_{\max}} \frac{n_d}{d} e^{-(A/2)(r \pm d)^2} \quad (A2)$$

$$I_2^{\pm}(r) = \sum_{d \geq d_{\max}} \frac{n_d}{d} (1 + Ar^2 \pm Ard) \times e^{-(A/2)(r \pm d)^2} \quad (A3)$$

Then using Eq. (A1) we find

$$I_1^+(r) = 4\pi\rho \{e^{-y^+}/A - [r/(2A)^{-1/2}]\Gamma(\frac{1}{2}, y^+)\} \quad (A4)$$

$$I_{1<}^-(r) = 4\pi\rho \{e^{y^-}/A - [r/(2A)^{1/2}]\Gamma(\frac{1}{2}, y^-)\} \quad (A5)$$

$$I_{1>}^-(r) = 4\pi\rho \{e^{-y^-}/A + [r/(2A)^{1/2}] \times 2\pi^{1/2} - \Gamma(\frac{1}{2}, y^-)\} \quad (A6)$$

$$I_2^{\pm}(r) = 4\pi\rho (1/A \pm rd_{\max}) e^{-y^{\pm}} \quad (A7)$$

where we have defined

$$y^{\pm} = \frac{1}{2} A (d_{\max} \pm r)^2 \quad (A8)$$

the  $\Gamma$ 's are incomplete gamma functions<sup>17</sup> and  $I_{1<}^-$  ( $I_{1>}^-$ ) is to be used for  $r < d_{\max}$  ( $r > d_{\max}$ ).

Upon use of Eqs. (A4)–(A7) the cutoff correction to the energy  $E_{co}$  can be written

$$\begin{aligned} \frac{E_{co}}{N} = \frac{1}{2} \left( \frac{A}{2} \right)^{1/2} & \left[ \int_0^{d_{\max}} g(r) \left\{ \bar{v}(r) [I_{1<}^-(r) - I_1^+(r)] - \frac{\eta}{4} \frac{u'}{r} [I_2^-(r) - I_2^+(r)] \right\} r dr \right. \\ & \left. + \int_{d_{\max}}^{\infty} g(r) \left\{ \bar{v}(r) [I_{1>}^-(r) - I_1^+(r)] - \frac{\eta}{4} \frac{u'}{r} [I_2^-(r) - I_2^+(r)] \right\} r dr \right] \quad (A9) \end{aligned}$$

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