TABLE II. $R(r)$ data for ^{3}He.

Volume (cm³/mole)	Particle displacement from equilibrium $r(\sigma)$										
	0	0.05	0.10	0.15	0.20	0.30	0.40	0.50	0.60	0.70	0.80
10.25	1.00	0.928	0.717	0.466	0.254	0.042	0.0035				
11.82	1.00	0.935	0.757	0.559	0.363	0.107	0.019	0.0018			
14.00	1.00	0.957	0.824		0.480	0.206	0.060	0.012	0.0015		
16.16	1.00	0.961	0.859		0.567	0.293	0.117	0.036	0.0078		
20.8	1.00	0.975	0.905		0.688	0.445	0.246	0.116	0.046	0.0148	0.0039
24.5	1.00		0.922		0.738	0.515	0.317	0.173	0.083	0.034	0.012

work at $V = 11.17$ cm³/mole gives $E = 32.06$ and 30.15 K, respectively. Again, it is evident that there is close agreement between experiment, the MC calculation, and the dynamic-field results. As for ^{3}He, however, calculated results lie slightly below experiment at the higher pressures. Figure 9 shows the PV results and Figs. 3 and 10 give the single-particle distribution function for solid ^{4}He for various molar volumes. Note the considerable narrowing of $R(r)$ with decreasing molar volume. Figure 3 shows a comparison of results for $R(r)$ at $V = 21.6$ cm³/mole obtained from the static-field approximation and from the dynamic-field approximation. As expected, the static-field approximation yields a narrower $R(r)$ indicating that the particle is more localized about its equilibrium lattice site than is predicted by the dynamic-field approximation. This result, of course, confirms our speculation that the static molecular field confines λ and κ more than if the molecular-field atoms also are allowed to dynamically respond to a changing environment, as provided for in the dynamic-field approximation. Also shown in Fig. 3 is the MC solution[1] for $R(r)$. The close comparison with the dynamic-field approximation is evident. The data for $R(r)$ is tabulated in Table IV.

3. Molecular-hydrogen results

In Fig. 11 the energy of molecular hydrogen is presented over the volume range $10 \leqslant V \leqslant 22.65$
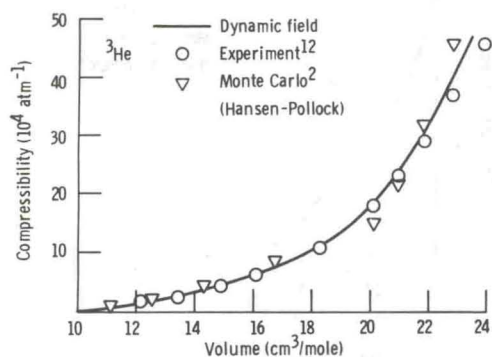
FIG. 7. Compressibility vs volume for solid ^{3}He.

cm³/mole. All calculations on H_2 are based on an fcc lattice structure. The solid line represents the results of the dynamic-field approximation and the squares show the MC calculations of Bruce.[3] The triangles display the Heitler-London results of Etters, Raich, and Chand[15] and the inverted triangles represent a Domb-Salter[16] approximation scheme. At normal vapor pressure, $V = 22.65$ cm³/mole, the dynamic-field calculation gives a ground-state energy $E_0 = -85$ K, which is virtually identical to the MC result of Bruce. At $V = 11.39$ cm³/mole, a comparison of our work with Bruce's gives $E = 444.71$ and 445.34 K, respectively. Similarly, at $V = 8.34$ cm³/mole, the comparison is $E = 2296.51$ and 2300.83 K, respectively. The dynamic-field and the MC results agree closely over the entire volume range, but not with the Heitler-London[15] and Domb-Salter[16] calculation, especially at the lower densities. This is not surprising since the latter two calculations are inherently unreliable at low pressure. In Fig. 12, the energy is displayed for the volume range $5 \leqslant V \leqslant 11$ cm³/mole. The comparisons and format are identical to Fig. 11. It is apparent that, at these high pressures, the results of all four calculations displayed here are in fair agreement with one another. However, the MC data of Bruce extends only to $V = 9.34$ cm³/mole. The pressure-volume data is shown in Fig. 13 for the volume range $10 \leqslant V \leqslant 22.65$ cm³/mole. In addition to the format of Figs. 11 and 12, the experimental data of Stewart[17] are displayed as circles. It is apparent that, at low molar volumes, the different theoretical calculations all predict pressures considerably higher than experiment.[17] Until recently, it was considered possible that this discrepancy was due to experimental effects. However, recent measurements indicate that the original data was reasonably accurate.[18] It also appears certain that the theoretical calculations are fairly accurate at high densities.[15] Hence, the discrepancy between theory and experiment is almost certainly due to the poor representation of the pair interaction provided by the Lennard-Jones 6-12 potential. In Fig. 14 the pressure calculated over the volume range $5 \leqslant V \leqslant 11$ cm³/mole is

TABLE III. bcc ^{4}He results.

Volume (cm^3/mole)	$\langle V \rangle$ (K)	$\langle T \rangle$ (K)	E_0 (K)	Pressure (atm)	$\langle r^2 \rangle^{1/2}$ (A)	β (σ^{-2})	κ (σ^{-1})
21.60	−27.48	22.29	−5.19		1.03	4.5	1.13
17.50	−34.27	30.85	−3.42	93	0.83	5.7	1.13
15.50	−38.9	39	0.1	250	0.76	8.0	1.12
13.75	−40.46	49.07	8.61	500	0.64	11.5	1.11
11.82	−40.46	65.83	25.37	1035	0.56	15.0	1.10
10.25	−31.25	83.42	52.17	1790	0.48	20.0	1.10

presented. The close agreement of the dynamic-field results to those derived from the Heitler-London[15] and Domb-Salter[16] calculations indicates that the overlap of the wave function between neighboring sites is very small at these pressures. Otherwise, these latter two approximate methods would not yield satisfactory results. The results confirm the claim[15, 16] that solids become more and more classical in behavior as the pressure is increased. The data for H_2 are tabulated in Table V.

IV. CONCLUSIONS AND DISCUSSION OF APPROXIMATIONS

There are two features of the Monte Carlo calculations that make them suspect at high pressures. At high enough pressures, the number of atoms contained in a volume sufficiently large to simulate the bulk system becomes great, perhaps beyond available computer resources. Then any proposed solution requires a compromise which weakens the integrity of the results. In addition, the Monte Carlo program may not sample phase

space ergodically at high pressure because the close-packed repulsive potential cores give rise to walls of very low probability surrounding regions of high probability. This difficulty has been well documented for a collection of hard disks.[4] We have been concerned that the poor agreement at high pressures between the MC results for helium and experiment is from one of these effects. The close comparisons between the dynamic-field calculations and the MC work[1, 2] dispell that concern, however, because the dynamic-field approximation is in no way limited at high pressures. In addition, the unsatisfactory nature of the Lennard-Jones 6-12 potential at high pressure has also been demonstrated by others, using a simplified theoretical approach.[5]

The variational parameter κ, which minimizes the energy, remains essentially constant at all volumes for both helium and hydrogen. For molecular hydrogen this parameter remains very near $\kappa \approx 1.13$ over the entire volume range $5 \leq V \leq 22.65$ cm^3/mole. This general result agrees completely with the findings of Hansen and Pollock on helium[2] but not quite so well with those of Bruce on hydrogen.[3] The results of Bruce are admittedly not calculated to high accuracy and it is our opinion that κ is approximately density independent. We agree with Hansen and Pollock that
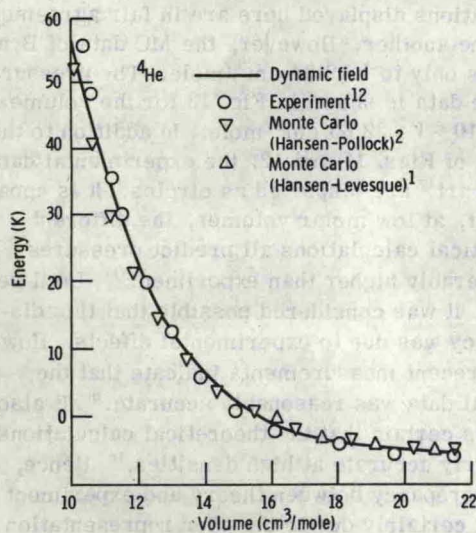
FIG. 8. Energy vs volume for solid ^{4}He over the volume range $10 \leq V \leq 21.65$ cm^3/mole. A comparison is made with other theoretical work and experiment.
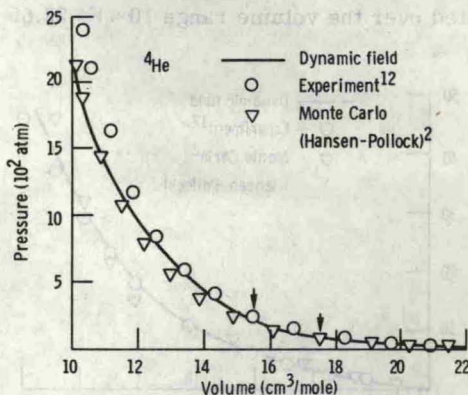
FIG. 9. Pressure vs volume for solid ^{4}He. A comparison is made with other theoretical work and experiment.