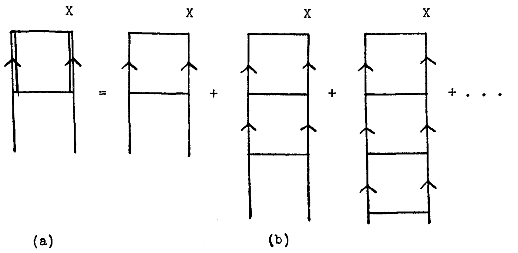

FIG. 1. Graphs for the Boltzmann equation. The double lines refer to the exact propagator $\zeta^*(iH)$ while the single line refers to propagator of the corresponding ideal gas, $\zeta^*(iK)$.

the graphs are the same as for weak coupling except for the argument of the propagator ζ^* which is now iH rather than iK. Note that the generalization given in this paper with regard to initial distributions applies to the weak-coupling expansion as well.

The product of operators acting on Φ^0 of Eq. (C1) is governed by the simple rules [where $n(A)$ means the number of A's that appear]

$$n(I)=1,\ n(L)=\mu,\ n(\zeta^*(iH))=\mu+1. \qquad \text{(C2)}$$

The "ordering" rule still holds: every interaction (I or L) is followed by a single propagator, reading from right to left. The particle numbers are given, as for weak coupling by

$$n(\text{out})=s,\quad n(\text{in})=s+n(L). \qquad \text{(C3)}$$

Similar rules are readily constructed for the dilute weak coupling as well as for the double expansion.

A simple example of the graph is one corresponding to the Boltzmann collision integral, Fig. 1(a). The expansion of the Green's function $\zeta^*(iH)$ given in Eq. (63) is shown in Fig. 1(b). This expansion yields in lowest order the Landau Fokker-Planck equation.

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Quantum Hard-Sphere Gas in the Limit of High Densities with Application to Solidified Light Gases*

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The properties of a quantum hard-sphere gas in the limit of high densities are investigated, with particular emphasis on the ground-state energy per particle. This has the asymptotic form

$$\frac{E_0}{N}\underset{\rho\to\rho_0}{\sim}\frac{\hbar^2}{2m}A\,(\rho^{-1/3}-\rho_0^{-1/3})^{-2},$$

as deduced from the Heisenberg principle, and is independent of particle statistics. A model of hard spheres arranged in a simple cubic lattice is solved by reduction to the known one-dimensional case, and gives $A_{\text{sc}}=\pi^2$. For more realistic close-packed systems we estimate $A_{\text{cp}}\approx 10$ to 15. This form connects smoothly to the well-known low-density gas-parameter expansions. Phonon properties in the Debye approximation are derived. The model is applied to the zero-point kinetic energies of hexagonal-centered-cubic (hcp) ^{3}He, ^{4}He, H_2, and D_2, as determined from pressure data. The helium data give $A\approx 15.7$, the hydrogen data $A\approx 15.9$. The fitted hard-core diameters, 1.73 Å and 1.90 Å, respectively, are smaller than expected from accepted potentials; this is discussed. Thermodynamics of the simple cubic system give $c_v\propto T$ for both bosons and fermions, which may explain the anomalous (non-Debye) heat capacities of solid ^{3}He and ^{4}He at low temperatures.

I. INTRODUCTION

THE properties of a quantum-mechanical hard-sphere gas are of great theoretical interest since such a gas is a simple approximate model for many systems of interacting particles. This problem has been solved for low densities by regrouping terms in a conventional perturbation series or by introduction of a "pseudopotential": Results appear as expansions in (fractional) powers of the dimensionless "gas parameter" ρa^3, where ρ is the number density and a is the sphere diameter. For densities greater than a few percent of the ultimate (close-packed) density, the last known terms dominate in both the Bose and Fermi expansions, and convergence of the partial sums is presumably poor. We need all orders in the gas parameter for convergence at the highest densities.

It would be useful to have a solution of this problem valid in the high-density limit. Such a solution could have direct applications to physical systems by providing a reasonable starting point for perturbation theory in the residual potentials. Examples might be nuclear

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matter,[1] liquid and solid light gases,[2] and the interior of stars in astrophysics.[3] It would also provide the opposite limit from the gas-parameter expansions, making possible an interpolation to intermediate densities as has been done with the electron gas.

The problem is greatly complicated by the importance of correlations between particles—each particle is strongly affected by all of its near neighbors and their relative positions. We may, however, argue naively that in the close-packed limit each particle of diameter a is confined to move in a space with characteristic dimension R, the mean-particle spacing. By the Heisenberg principle, each has a momentum $\propto \hbar(R-a)^{-1}$, and a kinetic energy $\propto (\hbar^2/2m)(R-a)^{-2}$.[4] There is no potential energy; the hard-sphere "potential" is simply a boundary condition on the wave function. Expressed in terms of densities, the ground-state energy per particle has the form

$$\frac{E_0}{N} \underset{\rho\to\rho_0}{\sim} A\frac{\hbar^2}{2m}(\rho^{-1/3}-\rho_0^{-1/3})^{-2},$$

where ρ_0 is the ultimate density. This result is independent of particle statistics (Bose or Fermi) since the particles are (in the limit) localized in a lattice and therefore distinguishable.

We may view this asymptotic form as the most divergent term in a Laurent series expansion in $\rho^{-1/3}$ about $\rho_0^{-1/3}$ and conclude that $(E_0/N)(\rho^{-1/3})$ has a second-order pole at $\rho_0^{-1/3}$ with no stronger singularities. Our aim in this paper is to test this form and to evaluate A, which is just $2m/\hbar^2$ times the leading Laurent coefficient.

II. THEORY OF THE IDEAL HARD-SPHERE GAS

The ground-state configuration of a hard-sphere system in the high-density limit is clearly either a face-centered cubic (fcc) or hexagonal close-packed (hcp) lattice. The many-particle wave function satisfies the Schrödinger equation $H_0\Psi(\mathbf{x}_1\cdots\mathbf{x}_N)=E_0\Psi$ where $H_0=-(\hbar^2/2m)\sum_i \nabla_i^2$, and the hard-sphere potential supplies the boundary condition $\Psi=0$ for any $|\mathbf{x}_i-\mathbf{x}_j|\leqslant a$, the hard-sphere diameter. We cannot solve this problem exactly.

We can, however, solve a somewhat unrealistic model of hard spheres arranged in a simple cubic lattice in the high-density limit of a finite volume where the spheres are "trapped" and cannot change their relative positions in the lattice. Labeling each particle by the triple of integers (ijk) which gives its position in the lattice, and letting

$$\mathbf{x}_{ijk}=x_{ijk}\hat{e}_1+y_{ijk}\hat{e}_2+z_{ijk}\hat{e}_3,$$

the Hamiltonian may be written as

$$H_0=-\frac{\hbar^2}{2m}\sum_{ijk}\nabla^2{}_{ijk}=\sum_{ij}H_{ij}+\sum_{jk}H_{jk}+\sum_{ki}H_{ki}.$$

Here

$$H_{ij}\equiv-\frac{\hbar^2}{2m}\sum_k\frac{\partial^2}{\partial z_{ijk}{}^2}$$

refers only to the z component of position of particles in the ijth row parallel to $\hat{e}_3$, and the other terms are similarly defined. The exact boundary condition $\Psi=0$ for any $|\mathbf{x}_{ijk}-\mathbf{x}_{lmn}|\leqslant a$ may be replaced in the high-density limit by $\Psi=0$ for any

$$|x_{i+1jk}-x_{ijk}|\leqslant a,\quad |y_{ij+1k}-y_{ijk}|\leqslant a,$$

or

$$|z_{ijk+1}-z_{ijk}|\leqslant a,$$

because in this limit the particles are localized and, e.g., $\mathbf{x}_{i+1jk}-\mathbf{x}_{ijk}$ is restricted to a domian which becomes parallel to $\hat{e}_1$. The difference from the exact boundary condition arises from the difference between

$$|\cos(\mathbf{x}_{i+1jk}-\mathbf{x}_{ijk},\hat{e}_1)|$$

and 1. This is of order $(\rho^{-1/3}-\rho_0^{-1/3})^2\rho^{2/3}$ because the maximum particle displacement goes as $(\rho^{-1/3}-\rho_0^{-1/3})$ and the mean separation as $\rho^{-1/3}$, and tends to zero as $\rho\to\rho_0$.

The problem then separates, and we write Ψ as a product of functions ϕ for the parallel coordinates of each row. Each ϕ satisfies the one-dimensional hard-sphere Schrödinger equation and boundary conditions, and we observe that the three-dimensional system is thus resolved into $3N^{2/3}$ independent one-dimensional systems, each with $N^{1/3}$ particles in a length $V^{1/3}$.

The exact solution for a one-dimensional system of N hard spheres in a length L is well known[5,6] and is based on the formal similarity to a free Fermi gas of point particles in the reduced length $l=L-Na$. The wave function is defined for $0\leqslant x_1-\frac{1}{2}a\leqslant x_2-\frac{3}{2}a\leqslant\cdots\leqslant x_N-(N-\frac{1}{2})a\leqslant L-Na\equiv l$, and is zero on all boundaries of this N-dimensional domain. It may be seen that the (unnormalized) solutions of the Schrödinger equation $H\phi=E\phi$ are

$$\phi_{\{i_k\}}(x_1\cdots x_N)=\mathcal{A}\{\prod_k \sin[i_k\pi(x_k-(k-\tfrac{1}{2})a)/l]\},$$

with energy

$$E_{\{i_k\}}=\frac{\hbar^2}{2ml^2}\sum_{k=1}^{N}i_k{}^2.$$

$\mathcal{A}$ is the operator which antisymmetrizes in the set of positive integers i_k which must therefore be distinct for ϕ to be nonzero. ϕ is essentially a Slater determinant, but the antisymmetrization has been performed to

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satisfy the boundary condition rather than Fermi statistics. The particles are distinguishable (by their order in the line), so that ϕ is the same for bosons and fermions: The boundary condition, physical exclusion of overlapping particles, is formally equivalent to a Pauli principle in coordinate space.

Spin wave functions may be trivially introduced since the Hamiltonian is spin-independent and the particles are distinguishable. If it is desired to treat them as indistinguishable, we must extend the domain of definition of ϕ to include other orderings of the particles in the line. Because the domains corresponding to distinct orderings are disjoint, separated by domains where some $|x_i-x_j|<a$ and ϕ is therefore zero, this extension is also trivial. We simply *define* ϕ for other orderings to be even or odd (including the spin part) under particle interchange as we choose.

The ground state corresponds to $\{i_k\}=\{1,2,\ldots,N\}$, for which

$$E_0=\hbar^2\pi^2N^3/(6ml^2)$$

plus terms of relative order N^{-1}. This may be rewritten as

$$E_0/N=A(\hbar^2/2m)(\rho^{-1}-\rho_0^{-1})^{-2},$$

where $\rho=N/L$ is now the density in one dimension, $\rho_0=a^{-1}$, and $A=\frac{1}{3}\pi^2\approx 3.29$. This has the predicted form. For a state with a completely uncorrelated wave function, with each particle moving freely and independently in a box of length L/N, the energy has the same form with $A=\pi^2$. This shows that correlations reduce the energy by a factor of 3. The range of these correlations may be estimated by observing that for a line of length M,

$$\frac{E_0}{M}=\frac{1}{3}\pi^2\frac{\hbar^2}{2m}(\rho^{-1}-\rho_0^{-1})^{-2}\left(1+\frac{3}{2M}+\frac{1}{2M^2}\right).$$

To reduce the term $3/2M+1/2M^2$ to 10% of its value for $M=1$ (no correlation), M must be at least 8.

The thermodynamics of this system may be easily computed either directly or using the parallel to the free Fermi gas. The "Fermi energy" is just

$$\Delta\equiv kT^*=\frac{\hbar^2}{2m}\frac{\pi^2}{l^2}N^2=\frac{\hbar^2}{2m}\pi^2(\rho^{-1}-\rho_0^{-1})^{-2},$$

and at low temperatures the pressure and heat capacity are

$$p=\tfrac{2}{3}kT^*(\rho^{-1}-\rho_0^{-1})^{-1}[1+\tfrac{1}{4}\pi^2(T/T^*)^2+\cdots]$$

$$c_v/L=\tfrac{1}{6}\pi^2\rho k(T/T^*)[1+\cdots].$$

These results are exact, independent of density, and involve only neglect of terms of order N^{-1}.

Knowing this exact solution to the one-dimensional problem, we have a complete knowledge of the simple cubic system in the high-density limit of a finite volume. Results of interest are

$$E_0/N\underset{\rho\to\rho_0}{\sim}A(\hbar^2/2m)(\rho^{-1/3}-\rho_0^{-1/3})^{-2},$$

where $\rho=N/V$ and $\rho_0=a^{-3}$, with $A=\pi^2\approx 9.87$. With a Fermi energy

$$\Delta\equiv kT^*=(\hbar^2/2m)\pi^2(\rho^{-1/3}-\rho_0^{-1/3})^{-2},$$

we have

$$p\underset{\rho\to\rho_0}{\sim}\tfrac{2}{3}kT^*\rho^{2/3}(\rho^{-1/3}-\rho_0^{-1/3})^{-1}[1+\tfrac{1}{4}\pi^2(T/T^*)^2+\cdots]$$

$$\frac{c_v}{V}\underset{\rho\to\rho_0}{\sim}\frac{\pi^2}{2}\rho k\left(\frac{T}{T^*}\right)[1+\cdots].$$

Of particular interest is the Fermi-like $c_v\propto T$, which we emphasize is the same for bosons and fermions and arises from the physical exclusion of interpenetration rather than statistics.

While this model is not realistic, it may have some of the same qualitative properties as the actual close-packed system. For the true fcc or hcp lattice the analogy to a free Fermi gas does not hold, and we have only the variational limit of zero correlation with each sphere moving freely and independently in an individual cell. For either lattice the cell may be replaced by an inscribed sphere of radius $2^{-5/6}\rho^{-1/3}$ and each particle, of diameter $2^{1/6}\rho_0^{-1/3}$, then has an energy

$$\epsilon=\bar{E}/N=A(\hbar^2/2m)(\rho^{-1/3}-\rho_0^{-1/3})^{-2},$$

with $A=2^{5/3}\pi^2\approx 31.3$. The exact ground-state energy must be smaller, and may be different for the two lattices. On comparison with one dimension, we would guess an energy of this form in the limit $\rho\to\rho_0$ with A about 10 to 15.

	1-*D*	sc	hcp/fcc
$A_{\text{(no corr)}}$	π^2	$3\pi^2$	$2^{5/3}\pi^2\approx 31.3$
$A_{\text{(full corr)}}$	$\frac{1}{3}\pi^2$	π^2	$\sim$10 to 15 (estimate)
ρ_0	a^{-1}	a^{-3}	$2^{1/2}a^{-3}$

Although we know nothing of the excitation spectrum, we might expect that long-range correlations in one dimension would again give a T term in c_v and a T^2 term in p. For the simple cubic lattice, these came from the free energy

$$F/N=A(\hbar^2/2m)(\rho^{-1/3}-\rho_0^{-1/3})^{-2}-B(2m/\hbar^2)(\rho^{-1/3}-\rho_0^{-1/3})^2(kT)^2+\cdots,$$

with $A=\pi^2$ and $B=\frac{1}{4}$. If this form is general (with A and B determined by the lattice), it follows that

$$c_v/NkT=3(\rho^{-1/3}-\rho_0^{-1/3})\rho^{-2/3}(p(T)-p(0))/kT^2$$

independent of A and B.

For actual physical systems, and attainable temperatures and pressures, these could be totally obscured by the phonon contributions. We may estimate these properties in Debye approximation in terms of the parameter A, since the pressure at low temperatures is

$$p=-\partial E_0/\partial V|_T\underset{\rho\to\rho_0}{\sim}\tfrac{2}{3}A(\hbar^2/2m)\times(\rho^{-1/3}-\rho_0^{-1/3})^{-3}\rho^{2/3}+O(T^2).$$

If we again define

$$kT^* = (\hbar^2/2m)\pi^2(\rho^{-1/3} - \rho_0^{-1/3})^{-2}$$

for the close-packed lattice, although it no longer has the interpretation of a Fermi energy, the long-wavelength sound speed u is given by[7]

$$u^2 \approx -\frac{V}{m\rho}\frac{dp}{dV}\bigg|_{T=0} \underset{\rho\to\rho_0}{\sim} \frac{4A}{9\pi^4\hbar^2}\rho^{-1/3} \times (5\rho^{-1/3} - 2\rho_0^{-1/3})(kT^*)^2.$$

This gives a Debye temperature of

$$\Theta \approx \frac{\hbar u}{k}(6\pi^2\rho)^{1/3} \underset{\rho\to\rho_0}{\sim} \frac{2A^{1/2}}{3\pi}\left(\frac{6}{\pi}\right)^{1/3}\left[5 - 2\left(\frac{\rho}{\rho_0}\right)^{1/3}\right]^{1/2} T^*,$$

assuming equality of compressional and shear sound speeds. Further, the Grünesien constant is[8]

$$\gamma \equiv -\frac{d\ln\Theta}{d\ln V} \underset{\rho\to\rho_0}{\sim} \frac{2}{3}\left[1 - \left(\frac{\rho}{\rho_0}\right)^{1/3}\right]^{-1} + \frac{1}{6}\left[\frac{5}{2}\left(\frac{\rho_0}{\rho}\right)^{1/3} - 1\right]^{-1}.$$

At low temperatures ($T \ll \Theta$) where only the long-wavelength phonons are excited, Debye theory is valid and gives phonon contributions to the pressure and heat capacity of

$$p_D \approx \tfrac{3}{5}\pi^4(\gamma\rho kT^4/\Theta^3) \quad \text{and} \quad c_{v,D} \approx (12\pi^4 Nk/5)(T/\Theta)^3.$$

III. COMPARISON WITH LOW-DENSITY EXPANSIONS

It is interesting to compare our high-density asymptotic form with the conventional expansions in a gas parameter.[9] These are[10-12]

$$\frac{E_0}{N}\bigg|_{\text{Bose}} = \frac{2\pi\hbar^2 a\rho}{m}\left[1 + \frac{128}{15\sqrt{\pi}}(\rho a^3)^{1/2} + 8\left(\frac{4\pi}{3} - \sqrt{3}\right)\rho a^3 \ln(12\pi\rho a^3) + \cdots\right],$$

$$\frac{E_0}{N}\bigg|_{\text{Fermi}} = \frac{\hbar^2 k_F^2}{2m}\left[\frac{3}{5} + \frac{2}{3\pi}(ak_F) + \frac{4}{35\pi^2}(11 - 2\ln 2)(ak_F)^2 + 0.23(ak_F)^3 + \cdots\right],$$

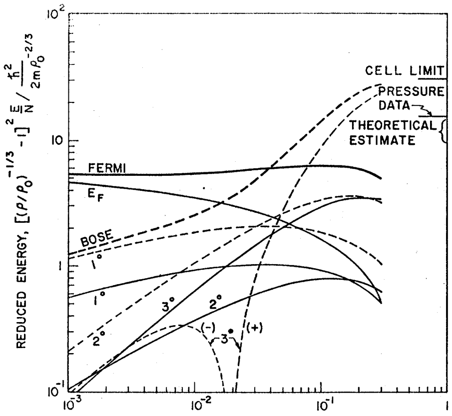

FIG. 1. Reduced kinetic energy of hard-sphere gases as functions of reduced density, showing terms in gas-parameter expansion for spin-zero bosons and spin-$\frac{1}{2}$ fermions. High-pressure limit is indicated at $\rho/\rho_0 = 1$. Here ρ_0 is the ultimate close-packed density.

for spin-zero bosons and spin-$\frac{1}{2}$ fermions. Here $a = 2^{1/6} \times \rho_0^{-1/3}$ is the particle diameter and $k_F^3 = 3\pi^2\rho$. We expect the energy to have a pole at $\rho = \rho_0$, so we consider the reduced quantity

$$\left[\left(\frac{\rho}{\rho_0}\right)^{-1/3} - 1\right]^2 \frac{2m\rho_0^{-2/3}}{\hbar^2}\frac{E_0}{N}.$$

Figure 1 shows the individual terms in the expansions and the sums as plotted against ρ/ρ_0. Both expansions clearly break down by $\rho/\rho_0 \approx 3 \times 10^{-2}$, where the last term becomes dominant in each case, but below this density they are remarkably constant. Both could be very smoothly extrapolated to match the asymptotic form with A in the range of 10 to 15.

It is suggestive that the Fermi expansion appears to converge better (the Bose expansion is probably an asymptotic series). We have noted in several places the strong similarity between a hard-sphere system and a free Fermi system: it is not surprising that this should appear yet again.

Using either our theoretical estimate or an experimentally derived value for A, we could interpolate in Fig. 1 to get E_0/N for the entire range of densities, accurate to perhaps a factor of 2.

IV. APPLICATION TO PHYSICAL SYSTEMS

In constructing a theory for application to physical systems at high densities, we should pass to the infinite system limit *before* the high-density limit. This is because the high-density limit (in the required sense) is totally unattainable for any finite macroscopic system. We cannot pack the spheres so tightly that they are confined to a lattice and diffusion is impossible. Although both the model considered above and the more general arguments from the Heisenberg principle are explicitly valid only for the high-density limit of a finite volume,

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[7] In the expressions for u^2, Θ, and γ, we should strictly replace the terms $5\rho^{-1/3} - 2\rho_0^{-1/3}$ by $3\rho_0^{-1/3}$ since terms of the same order arising from the next term in the Laurent series expansion for E_0/N have been neglected.

[8] It is interesting to note that for $(\rho/\rho_0)^{-1/3} = 0.55$, corresponding to solid helium at 13 to 15 cm³/mole, this equation gives $\gamma \approx 1.9$. This compares favorably with the measured $\gamma \approx 2.4$, despite the neglect of potential energy.

[9] The discussion at the beginning of Sec. IV is pertinent to the justification of this comparison with regard to the order of limits involved.

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[11] T. T. Wu, Phys. Rev. **115**, 1390 (1959).

[12] V. F. Efimov and M. Ya. Amus'ya, Zh. Eksperim. i Teor. Fiz. **47**, 581 (1964) [English transl.: Soviet Phys.—JETP **20**, 388 (1965)].

a rough argument may be given which suggests that the order of the limits may be interchanged. The infinite system at high densities will be made up of regions packed into a lattice separated by regions of disorder. As $\rho \rightarrow \rho_0$ the fraction of the volume which is disordered must vanish, and all but a vanishing fraction of the packed regions must tend to infinite size in this limit. These packed regions are "stable" for long times [compared with $\hbar(E_0/N)^{-1}$] because of the restrictions on particle motion, so that they are well described by wave functions of exactly the type we have considered. Then E_0/N differs for the two orders of the limits only in the contribution from a vanishing fraction of the system; this difference should therefore vanish.

For most physical systems we must also consider a nonsingular residual potential V' in addition to the hard-sphere potential. If, as in solidified gases, this potential is attractive and binds the system into a lattice, the difficulty with the order of limits does not arise. It is reasonable to treat such systems in a perturbation expansion in V', using as unperturbed states the ideal hard-sphere states. We would expect good convergence since so much of the correlation is already included. In first order in V', states have an energy per particle of

$$E/N = E/N|_{\text{hard sphere}} + \langle\Psi|V'|\Psi\rangle,$$

where $|\Psi\rangle$ is the hard-sphere state. This looks much more useful than it is. We know $|\Psi\rangle$ only very approximately and are seldom much surer of V'; in fact, all we know is the form of $E/N|_{\text{hs}}$ for the ground state.

If we have two systems with the same V' and ρ_0 but different particle masses, M_1m_u and M_2m_u (m_u is the atomic-mass unit) and V' is sufficiently small that first-order perturbation theory is a good approximation, then E_0/N as a function of ρ differs for the two systems only through the $1/m$ in $E/N|_{\text{hs}}$, regardless of the form of V'. Explicitly,

$$\frac{E_2(\rho)}{N}-\frac{E_1(\rho)}{N}=\frac{M_1-M_2}{M_2M_1}E(\rho)/N\bigg|_{\text{hs},\, m=m_u}.$$

The volume derivative of this equation is a relation between pressures and may be written as

$$\rho^{-1/3}=\rho_0^{-1/3}+\tfrac{2}{3}A(\hbar^2/2m_u)^{1/3}\rho^{2/9}p_0^{-1/3},$$

where

$$p_0=[M_1M_2/(M_1-M_2)][p_2(\rho)-p_1(\rho)]_{T=0}$$

for the ground state. Therefore, a plot of $\rho^{2/9}p_0^{-1/3}$ against $\rho^{-1/3}$ should be a straight line whose slope gives A and $\rho^{-1/3}$ intercept gives ρ_0.

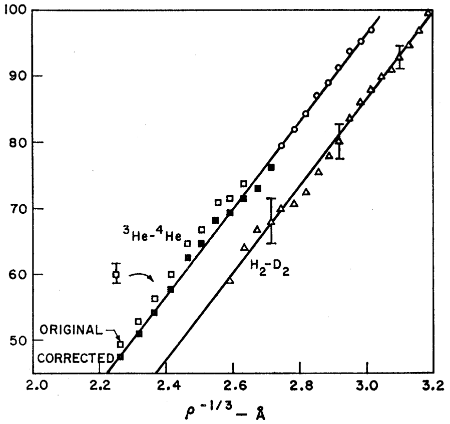

FIG. 3. The pressure parameter $y=\rho^{2/9}p_0^{-1/3}$ as a function of $\rho^{-1/3}$ for He and H. Lines fitted by least squares. ⊙: Dugdale and Franck (Ref. 13); ⊡: Stewart (Ref. 14). For explanation of correction see text. △: Stewart (Ref. 15). Error bars give round-off and interpolation error.

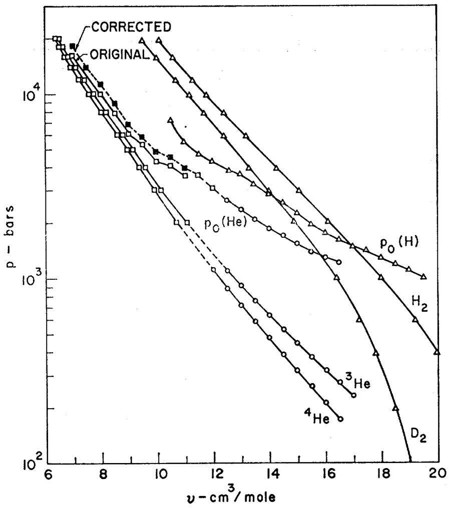

FIG. 2. Pressures and pressure differences of ³He–⁴He and H₂–D₂ as functions of molar volume. $p_0(\text{H})=2(p_{\text{H}_2}-p_{\text{D}_2})$, $p_0(\text{He})=12(p_{^3\text{He}}-p_{^4\text{He}})$. ⊙: Dugdale and Franck (Ref. 13); ⊡: Stewart (Ref. 14). For explanation of correction, see text. △: Stewart (Ref. 15).

V. SOLIDIFIED LIGHT GASES

Two systems for which this model might hold are the ³He–⁴He and H₂–D₂ pairs. Both are hcp at low temperatures and high pressures. The helium data of Dugdale and Franck[13] and of Stewart[14] and the hydrogen data of Stewart[15] (Table I) are plotted in Fig. 2, along with the derived values of p_0 for each system. Numerical values of p_0 are given in Table II, together with $\rho^{-1/3}$ and $\rho^{2/9}p_0^{-1/3}$; these are then plotted in Fig. 3. The last digit in the pressure is almost certainly not significant, but has been carried to avoid round-off errors: accuracy of the data will be considered in more detail later. Stewart's data are for 4.2°K rather than 0°K, but the difference is negligible. (A Debye-approximation estimate gives $\Delta V \lesssim 0.0005$ cm³/mole.)

For each set of data the variation of p_0 is reasonably smooth and the points in Fig. 3 are well fitted by a

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[14] J. W. Stewart, Phys. Rev. **129**, 1950 (1963).

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TABLE I. Pressure data.

v^a cm^3/mole	$p_{^4\text{He}}$ kg/cm^2	$p_{^3\text{He}}$ kg/cm^2	$p_{\text{He}}{}^b$ bars	$v_{4\text{He}}$ cm^3/mole	$v_{4\text{He}}$ cm^3/mole	$v_{3\text{He}}{}'^c$ cm^3/mole	p^d kg/cm^2	v_{H_2} cm^3/mole	v_{D_2} cm^3/mole
12.0	1134.6						0	22.65	19.56
12.5	904.7	1128.8	2×10^3	10.72	11.07	11.10	2×10^2	21.0	18.5
13.0	732.5	931.7	3	9.93	10.16	10.19	4	20.0	17.8
13.5	596.6	772.9	4	9.38	9.60	9.63	6	19.2	17.2
14.0	487.1	644.1	5	8.96	9.15	9.18	1×10^3	18.0	16.4
14.5	395.9	538.9	6	8.59	8.79	8.81	2.043	16.1	14.9
15.0	323.8	453.7	8	8.01	8.21	8.24	3	15.1	14.0
15.5	266.0	383.7	1×10^4	7.58	7.76	7.78	4	14.3	13.3
16.0	215.7	326.4	1.2	7.21	7.41	7.43	6	13.2	12.4
16.5	175.6	278.3	1.4	6.94	7.12	7.14	8	12.4	11.7
17.0		238.0	1.6	6.72	6.86	6.88	1×10^4	11.8	11.2
			1.8	6.53	6.66	6.68	1.2	11.3	10.7
			2.0	6.37	6.48	6.49	1.6	10.6	10.0
							2.0	10.1	9.5

[a] Reference 13.
[b] Reference 14.
[c] Prime denotes corrected values (see text).
[d] Reference 15.

straight line. However, Stewart's[14] high-pressure data for helium do not join smoothly onto Dugdale and Franck's[13] at lower pressures. This is felt to be largely due to the approximate tie-in point $v=11.07$ cm^3/mole for ^{3}He at 2000 bars and $T=0$, all other molar volumes being measured relative to this.

No direct measurements of this volume have been reported, but we may calculate it more accurately in two ways. At low temperatures, where the thermal contribution to the total pressure is extremely small,

$$\Delta v(T)\equiv v(T)-v(0)\approx p_{\text{th}}\partial v/\partial p|_{v(0),\,T\approx 0}.$$

The thermal pressure p_{th} may be approximated by the Debye pressure

$$p_D \propto \gamma p T^4 \Theta^{-3},$$

to give

$$\Delta v(T)\propto -\gamma\alpha T^4\Theta^{-3},$$

where $\alpha=-v^{-1}\partial v/\partial p|_T$ is the compressibility. We may use this relation to reduce Grilly and Mills'[16] melting point data to $T=0$ .The necessary data are

	^{4}He	^{3}He
p	2000 bars	2000 bars
T_m (Ref. 16)	21.60°K	20.88°K
v_m (Ref. 16)	10.84 cm^3/mole	11.19 cm^3/mole
Θ (Ref. 13)	127°K	118°K
α (Ref. 14)	9.72×10^{-6} bar^{-1}	10.18×10^{-6} bar^{-1}
$\Delta v(T_m)$ (Ref. 14)	0.12 cm^3/mole	$\cdots$

The data for Θ are extrapolated by the Grüneisen relation

$$\Theta\propto v^{-\gamma}.$$

This gives

$$\Delta v_3(T_{m3})/\Delta v_4(T_{m4})\approx 0.7$$

rather than 1.0 as assumed by Stewart.[14] Thus $\Delta v_3(T_{m3})$ ≈ 0.08 cm^3/ mole and $v_2\approx 11.11$ cm^3/mole at 2000 bars, $T=0$.

Alternatively, we may extrapolate the low pressure p_0 along a least-squares fitted straight line ($A=14.18$, $\rho_0{}^{-1/3}=1.55$ Å) and combine this with ^{4}He pressures to to get $v_3=11.10$ cm^3/mole. This value agrees well with the Debye-theory estimate, and is probably accurate to ±0.01 cm^3/mole (±0.006 from the extrapolated p_0 and ±0.005 from interpolation of the ^{4}He total pressure). The high-pressure helium data have therefore been revised, using a value of 11.10 cm^3/mole for the ^{3}He tie-in point.[17]

By fitting a line to the revised helium data and one to the hydrogen data in Fig. 3, we find

	He	H
A	15.7 ± 0.6	15.9 ± 1.0
$\rho_0{}^{-1/3}$	1.54 ± 0.05 Å	1.69 ± 0.10 Å
$a=2^{1/6}\rho_0{}^{-1/3}$	1.73 ± 0.06 Å	1.90 ± 0.11 Å
$\sigma_y(y=p^{2/9}p_0{}^{-1/3})$	0.8 (cm/erg)$^{1/3}$	1.1 (cm/erg)$^{1/3}$

where the limits are one standard deviation. σ_y is the standard deviation of the data points from the fitted line. The two values of A are in remarkably good agreement, and near our estimated value. The hard-core diameters seem reasonable though smaller than one might expect from commonly used intermolecular potentials. For a scale comparison, the internuclear distance for H$_2$ and D$_2$ is about 0.75 Å.

The question of accuracy is quite difficult to answer. Each y involves a small difference in large total pressures, but much of the error in each pressure is systematic and will tend to cancel in pressure differences. If we assumed the errors to be uncorrelated and used Stewart's[14] estimate of 2 to 3% in v–v(2000 bars) for helium, we would conclude that the high-pressure y's

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[16] E. R. Grilly and R. L. Mills, Ann. Phys. (N. Y.) 8, 1 (1959).

[17] J. W. Stewart (private communication) says that such a correction is "within error" and not unreasonable.

TABLE II. Pressure-difference data.

v cm^3/mole	$\rho^{-1/3}$ Å	p_0(H) erg/cm^3	p_0(He) erg/cm^3	p_0'(He)[a] erg/cm^3	y(H)[b] (cm/erg)$^{1/3}$	y(He) (cm/erg)$^{1/3}$	y'(He)[a] (cm/erg)$^{1/3}$
7.0	2.265		16.2	18.3		49.4	47.4
7.5	2.318		12.6	14.0		52.9	51.0
8.0	2.368		10.0	11.3		56.3	54.0
8.5	2.417		7.94	8.92		60.0	57.7
9.0	2.463		6.05	6.81		64.8	62.3
9.5	2.508		5.37	5.85		66.6	64.8
10.0	2.551		4.32	4.85		70.8	68.2
10.5	2.593	7.26×10^9	4.06	4.53	59.0	71.6	69.0
11.0	2.634	5.53	3.60	3.97	63.9	73.7	71.3
11.5	2.673	4.73		3.62	66.6		72.9
12.0	2.711	4.33		3.08	68.0		76.2
12.5	2.748	3.88	2.64		69.9	79.4	
13.0	2.784	3.66	2.35		70.6	81.8	
13.5	2.820	3.32	2.08		72.4	84.4	
14.0	2.854	2.88	1.85		75.3	87.1	
14.5	2.888	2.55	1.69		77.8	89.0	
15.0	2.920	2.28	1.53		80.1	91.3	
15.5	2.952	1.96	1.39		83.6	93.8	
16.0	2.984	1.76	1.30		86.1	95.2	
16.5	3.015	1.61	1.21		88.1	96.9	
17.0	3.045	1.49			89.8		
17.5	3.074	1.41			90.9		
18.0	3.103	1.30			92.8		
18.5	3.132	1.20			94.7		
19.0	3.160	1.10			96.9		
19.5	3.187	1.00			99.5		

[a] Prime denotes corrected values (see text).
[b] $y=\rho^{2/9}p_0^{-1/3}$.

were good only to ±20 or 30%, which is clearly much too large. At the other extreme, if we assume that the errors are completely systematic we are left with the round-off, tie-in, and interpolation errors in v. These are about ±0.01 and ±0.05 cm^3/mole for Stewart's helium and hydrogen data, respectively. The resulting errors in y are shown in Fig. 3, being roughly $\pm1.6(\text{cm/erg})^{1/3}$ for helium and $\pm2.5(\text{cm/erg})^{1/3}$ for hydrogen. These are within a factor of 2 of the standard deviation of y from the fitted line, thus supporting our contention that most of the error in total pressure is systematic. The limits on A and a given above, representing one standard deviation from the least-squares fitted values, should probably be at least doubled to allow for the additional uncertainties in the data.

Such close agreement is, in a way, surprising. It is not at all obvious that the perturbation assumption is justified, since the kinetic energy contributes only about half of the total pressure. It is also not clear that ρ_0 should be a constant—at high pressures a change in electronic configuration may be energetically favorable, thus changing the size of the hard core. This effect should be small since, for the pressures considered, the average kinetic energy per particle is at most a few times 10^{-2} eV. The energy of relative motion between neighbors is presumably somewhat reduced by correlations and is therefore small compared to electronic excitation energies. Finally, hydrogen is a molecular crystal, and the molecules might better be modeled as "hard eggs" than as hard spheres. However, at least at low pressures, the anisotropic part of the intermolecular potential is so small that each molecule rotates freely and is in a spherically symmetric Σ state.[18] Then the averaged interaction might again be considered as having a hard-sphere core. (Anisotropy in V' is significant only if it differs for H_2 and D_2.)

There is a possible experimental confirmation of the suggestion that both the Bose and Fermi systems should have a heat capacity $\propto T$ at high pressures and low temperatures. Several workers[19,20] have observed an anomalous (non-Debye) contribution to the heat capacities of solid ^{3}He and ^{4}He of perhaps (10^{-3} cal/mole °K^2)T, although there is also contrary evidence. (At somewhat lower densities, $v>16.90$ cm^3/mole, the T term is at most 5% this great.)[21] Blind application of the simple cubic expression for c_v at 12 cm^3/mole gives a value about 100 times larger. However, this term, which arises from long-range correlations in one dimension, could easily be much different for different lattices. In particular, the motion of atoms in an hcp lattice is restrained in every direction by several neighbors simultaneously as opposed to the simple cubic case where motion along a crystal axis is restricted by only one nearest neighbor.

It has been noted that the observed T term in c_v is reduced by annelaing the sample,[19,21] suggesting a defect

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[18] J. VanKranendonk and V. F. Sears, Can. J. Phys. **44**, 313 (1966).

[19] J. P. Franck, Phys. Letters **11**, 208 (1964).

[20] E. C. Heltemes and C. A. Swenson, Phys. Rev. **128**, 1512 (1962).

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mechanism and that, for example, pinned dislocations give a $c_v \propto T$.[19,22] In the absence of compelling evidence, we feel that the question is still open.

VI. COMMENTS ON POTENTIALS

It is common to represent the helium-helium interaction and the isotropic part of the hydrogen-hydrogen interaction by a Lennard-Jones 6-12 potential,

$$V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^{6}],$$

with[18,23]

$$\epsilon_{\mathrm{He}} \approx 9\times10^{-4}\ \mathrm{eV}, \quad \epsilon_{\mathrm{H}} \approx 3.2\times10^{-2}\ \mathrm{eV}, \quad \sigma_{\mathrm{He}} \approx 2.56\ \text{Å}, \quad \sigma_{\mathrm{H}} \approx 2.93\ \text{Å}.$$

Other potentials are used which are very similar.

Both theoretical calculations[24,25] and fits to experimental data (virial coefficients, transport properties, and scattering cross sections)[26–29] for helium are in reasonable good agreement with the 6-12 potential, though both are somewhat less repulsive at short distances. All give $V \approx 0.2$ to 0.4 eV at our hard-core distance of 1.73 Å, far larger than the average kinetic energy. All give a classical turning point at about 2.1 Å for an energy of 2×10^{-2} eV. The discrepancy seems real. Part of the difficulty is that the hard core is an "effective" potential, and replaces much of the repulsive potential; we must be careful not to count this repulsion twice.

Further, the idea of a simple additive two-body force within the lattice must be used with care because there are real many-body forces. The presence of several atoms simultaneously within a few angstroms puts further constraints on the electron clouds over the simple scattering case, and must change the interaction energy. At the very least, we should define an effective two-body potential by averaging over the coordinates of all other particles, and consider the possibility that it may be density-dependent.

The small size of the effective hard-core diameter for helium is supported by two recent calculations. Burkhardt[30] has fitted a potential of hard core plus attractive square well to reproduce the deBoer phase shifts and finds $9_{\mathrm{He}} = 1.71 \pm 0.06$ Å. Brueckner[31] has used the effective hard-core diameter as a single adjustable parameter to fit transport properties of the liquid. His value is $9_{\mathrm{He}} = 1.77 \pm 0.07$ Å. Both values are in excellent agreement with our value of 1.73 ± 0.06 Å.

Since our theory fits quite well, we conclude that the effective potential is not so repulsive as the conventional Lennard-Jones potential. From the nonkinetic part of the pressure, we know $\langle V' \rangle$ as a function of ρ within an additive constant. Given the two-particle correlation function, perhaps from experimental measurement of the structure factor in diffraction experiments, we could fit a simple effective two-body potential to this. At present, however, this seems impossible because there are not sufficient data.

VII. CONCLUSION

The asymptotic form in s dimensions,

$$\frac{E_0}{N} \underset{\rho\to\rho_0}{\sim} \frac{\hbar^2}{2m} A_s(\rho^{-1/s} - \rho_0^{-1/s})^{-2}$$

is exact in one dimension with $A = \frac{1}{3}\pi^2$ and also holds for an artificial simple cubic lattice with $A = \pi^2$. We predict an energy of this form for a close packed lattice, with A in the range of 10 to 15 or so. An experimental value of $A \approx 15.8$, found by consideration of the zero-point kinetic energies of solid hcp helium and hydrogen, is near this range. An energy of this form with any of these values of A can be matched smoothly onto the low-density gas-parameter expansions for both Bose and Fermi systems.

For the simple cubic lattice, the excitation spectrum may also be found and the thermodynamics derived. Of particular interest is the heat capacity which has a term $\propto T$, arising from long-range correlations in one dimension. If this effect is general and applies to other lattices (which is pure speculation) it may explain the anomalous heat capacities observed at low temperatures in solid ^{3}He and ^{4}He.

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