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QUANTUM THEOREM OF CORRESPONDING STATES AND SPIN-POLARIZED QUANTUM SYSTEMS"

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Résumé.- On donne une revue des propriétés thermodynamiques des systèmes quantiques macroscopiques du point de vue du Théorème Quantique des Etats Correspondants. Ces résultats sont utilisés pour prédire et discuter les propriétés thermodynamiques des systèmes quantiques spin-polarisés.

Abstract.- A review of the thermodynamic properties of macroscopic quantum systems is given from the unified point of view provided by the Quantum Theorem of Corresponding States. These results are used to predict and discuss the thermodynamic properties of spin-polarized quantum systems.

Introduction. One of the most exciting areas of investigation in this century has been and continues to be macroscopic quantum systems. Research in this area has uncovered an unexpectedly rich vein of unanticipated phenomena, the study of which has led to an ever deeper understanding of the laws of nature. New investigations have recently been undertaken on a new set of such macroscopic quantum systems; namely, spin-polarized quantum systems such as spinpolarized atomic hydrogen /01-06/ and spinpolarized helium-three /07, 08/. Recent experimental results /09, 10/ have been a major step forward and have brought an air of optimism to workers in this field that it will be possible to prepare these systems and keep them in stable form long enough to study their properties, even equilibrium properties, in detail.

The present review has as its goal a discussion of the possible thermodynamic properties of these systems. It turns out that it is possible to do this from a unified point of view because of the extension of the Quantum Theorem of Corresponding States recently developed by Nosanow and co-workers /11-13/. This theorem was originally proposed by de Boer /14/ and its initial applications carried out by the him and his co-workers /15/. The first discussion of spin-polarized atomic hydrogen using the quantum theorem of corresponding states was given by Hecht /01/. Thus, a general, over-all picture of the thermodynamics of macroscopic quantum systems will be presented and then corresponding

states arguments will be used to predict the thermodynamic properties of spin-polarized quantum systems.

This review is organized into the following Sections:

- o macroscopic quantum systems,
- o phenomenological potentials,
- o quantum theorem of corresponding states,
- o extended quantum theorem of corresponding states,
- thermodynamic properties of macroscopic quantum systems, and
- o spin-polarized quantum systems.

<u>Macroscopic Quantum Systems</u>. A macroscopic quantum system is a system of approximately 10^{23} particles which manifests quantum effects on a macroscopic scale. These systems exhibit phenomena, which are solely due to quantum effects and have no classical analog:

- o superconductivity in metals,
- o superfluidity of both helium isotopes, and
- o the existence of the liquid phase of both helium isotopes at zero temperature.

They also exhibit phenomena, which are due to quantum effects, but do have classical analogs:

o the liquid-to-crystal phase transition which occurs in both helium isotopes at zero temperature, and

- C7-2
- o the phase separation which occurs in both
 solid and liquid mixtures of the helium
 isotopes.

There are two aspects of quantum mechanics which give rise to these effects:

- o the quantum-mechanical zero-point kinetic energy (energetics), and
- o the symmetry of the wave function
 (statistics).

This review will emphasize those aspects of macroscopic quantum systems which depend more strongly on <u>energetics</u> than they do on <u>statistics</u>.

The most important aspect of the physics of macroscopic quantum systems is that the zeropoint kinetic energy per particle is comparable to the magnitude of the potential energy per particle. This fact has several consequences:

- the binding energy of the system is much less than the magnitude of the potential energy,
- o the density of the system is small compared to the density of a "classical" system, and
- o the ground state of the system can, as a consequence, be a <u>solid</u>, a <u>liquid</u>, or a <u>gas</u>!

There are also important aspects of the physics of macroscopic quantum systems that are due to <u>statistics</u>:

- o there is an "effective" interaction caused by the <u>statistics</u> -- it is repulsive for fermions and attractive for bosons and introduces strong correlations between the particles in both cases, and
- o there is a characteristic temperature at which the effects of statistics become important -- it is of the order of $\rho^{2/3}/k_Bm$ (p is the number density, k_B is Boltzman's constant, and m is the mass of a particle) -- for an ideal Fermi gas, this is the Fermi temperature, whereas, it is the Bose-Einstein condensation temperature for an ideal Bose gas.

These are only a few of the most important aspects of the physics of macroscopic quantum systems.

<u>Phenomenological Interactions</u>. This work will focus on a class of systems of which the following are the known examples:

- o the isotopes of helium $({}^{3}\text{He}, {}^{4}\text{He})$,
- o the isotopes of molecular hydrogen (H $_{\rm 2},$ $\rm D_{\rm 2}),$
- o the heavy rare gases (Ne, Ar, Xe, Kr), and
- o the isotopes of spin-polarized atomic hydrogen (H+,D+).

Although it is possible, in principle, to calculate the pair interaction for these systems, this has been achieved only for H+ and D+ /16/. Many phenomenological interactions have been constructed for these systems. The more recent of these appear to be quite accurate /17,18/. For all calculations reported in this work, the well-known Lennard-Jones potential was used; i.e.,

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

where ϵ is the depth of the well and σ is the so-called collision diameter. Values of these parameters and the quantum parameter $n = M^2/m\epsilon\sigma^2$ are given in Table 1 for the class of systems under consideration.

Substance	ε	σ	
	deg	o A	η
H+	6 16	2 60	5.47 x 10^{-1}
D+	0.40	3.09	2.74×10^{-1}
³ He			2.41 $\times 10^{-1}$
4 _{He}	10.22	2.56	1.82×10^{-1}
H ₂			7.63 $\times 10^{-2}$
D ₂	3/.0	2.92	3.82×10^{-2}
Ne	35.6	2.74	9.00 $\times 10^{-3}$
Ar	120.0	3.41	8.70×10^{-4}
Kr	163.	3.65	2.67×10^{-4}
Xe	232.	3.98	1.01×10^{-4}

Table 1: Values of the Lennard-Jones parameters for the rare gases, molecular hydrogen, and spin-polarized atomic hydrogen. The latter are obtained by fitting the potentials /03/ calculated by Kolos and Wolniewicz /16/. A few comments on these recently developed, more accurate phenomenological potentials are in order. The parameters for the "best" of these as judged by the authors are shown in Table 2. Several observations are apparent:

- o the well depth is larger in each case,
- o the "core diameter" is smaller, except for He and Ne, and
- o the values of n are roughly 15% lower, except for those for H⁺ and D⁺, which are unchanged.

These results will have an importannt bearing on the assessment of the validity of conclusions to be drawn in later sections of this work.

Substance	ε	σ		
	deg	o A	η	
H↓	6 16	2 60	5.47 x 10^{-1}	
D+	0.40	3.09	2.74×10^{-1}	
³ He	10.05	2 642	2.122×10^{-1}	
⁴ He	10.85	2.043	1.599×10^{-1}	
Ne	42.0	2.764	7.498 x 10^{-3}	
Ar	142.1	3.351	7.613 x 10^{-4}	
Kr	201.9	3.569	2.251×10^{-4}	
Xe	281.0	3.885	8.714 x 10^{-5}	

Values of constants for recently Table 2. developed phenomenological potentials. Those for the heavy rare gases are taken from Barker /17/, those for helium from Aziz, et al. /18/, and those for spin-polarized atomic hydrogen are unchanged because the calculations /16/ are regarded as accurate to one percent. Results for the isotopes of molecular hydrogen /19/ are not included because they are not consistent with the rest of the results. It is important to note that the analytic form of the phenomenological potential varies slightly from substance to substance.

Quantum Theorem of Corresponding States. The quantum theorem of corresponding states was originally proposed by de Boer /14/ and discussed by him and his coworkers /15/. The fundamental physics underlying this theorem is that there is a class of systems such that the potential energy of the system is proportional to a coupling constant ε with the dimensions of energy, that <u>all</u> lengths in the potential energy scale with <u>one</u> length parameter σ , and that all other constants in the potential are the same for this class of systems when expressed dimensionlessly. Thus the potential energy $W(\{r_{i\alpha}\})$, where $r_{i\alpha}$ is the α th component of the position of the i th particle, may be written

$$W(\{r_{i\alpha}\}) = \varepsilon W^{*}(\{r_{i\alpha}/\sigma\}, \{c_{n}^{*}\}), \qquad (1)$$

where W* is a dimensionless function of its arguments and $\{c_n^*\}$ stands for the set of other dimensionless constants. It is important to note that Eq. (1) does <u>not</u> require that W be expressible as a sum of pair potentials. In his review article, Barker /17/ discusses the importance of three-body interactions and compares the values of the $\{c_n^*\}$ for a number of systems.

To derive the theorem, consider the Hamiltonian

$$H = (-\aleph^2/2m) \sum_{i,\alpha} (\vartheta^2/\vartheta r^2_{i\alpha}) + W(\{r_{i\alpha}\}). \quad (2)$$

With the use of Eq. (1), the introduction of the dimensionless variables $x_{i\alpha} = r_{i\alpha}/\sigma$, and the definitions

$$t = (-1/2) \sum_{i,\alpha} (\vartheta^2/\vartheta x^2_{ia})$$

i,
w = W*({x_{ia}}, {c_n^})

$$= \aleph^2/\mathrm{me}\sigma^2 = (\Lambda^*/2\pi)^2,$$

where $\Lambda^* = h/\sigma(m_{\epsilon})^{1/2}$ is the de Boer parameter, the Hamiltonian may now be written in the form

$$H = \epsilon (nt + w). \tag{3}$$

The use of Eq. (3) in the partition function leads straightforwardly to the usual statement of the theorem; i.e.,

$$F^* = F^* (T^*, V^*, \eta),$$
 (4)

where the following dimensionless or "reduced" variables have been introduced:

$$T^* = k_B^T/\epsilon$$
, $V^* = V/N\sigma^3 = 1/\rho^*$,

 $P^* = P\sigma^3/\epsilon$, $F^* = F/N\epsilon$,

and T is the temperature, V is the volume, P is the pressure, and F is the Helmholtz free energy. The form of the reduced Helmholtz free energy depends only on two things:

- o the form of $W^{*}(\{x_{ia}\}, \{c_{n}^{*}\})$, and
- whether the system obeys Bose-Einstein or Fermi-Dirac statistics.

Thus, for this class of systems, <u>all</u> thermodynamic properties can be plotted on just two graphs -- one for Bose-Einstein statistics and one for Fermi-Dirac statistics. Values of the quantum parameter n are given in Table 1 for Lennard-Jones potential parameters. It is important to remember that n depends on four constants in the form $n = \frac{1}{2}/m\varepsilon\sigma^2$, which is the only possible dimensionless combination of these constants.

Let us now discuss the physical significance of the quantum parameter n. For this intuitive discussion, it is sufficient to approximate the system with a "cell" model, in which each particle is viewed as moving in a "cell" formed by its nearest neighbors. Let us introduce Δ , the average distance between particles. The following crude estimates of the kinetic energy per particle R and the potential energy per particle \overline{W} can be made:

$$R \cong \mu^2 / 2m(\Delta - \sigma)^2$$
$$|\overline{w}| \cong 6 v(\Delta),$$

where v(r) is the pair potential and the number of nearest neighbors is taken to be 12. It follows that

$$\bar{K}/|\bar{W}| \cong n fn(V^*),$$
 (5)

where fn(x) is some function of x. In this case n is proportional to the ratio $\bar{K}/|\bar{W}|$; in general, it is intuitively clear that n is a measure of this ratio and that this is the physical significance of n. This result is most significant, because it is just the value of $\bar{K}/|\bar{W}|$; i.e., of n, which determines the extent to which

macroscopic quantum systems manifest quantum
effects.

Extended Quantum Theorem of Corresponding States. The very form of the theorem, Eq. (4), and the physical significance of n, Eq. (5), suggest that it would be most useful to consider n as an independently variable continuous parameter and to treat it as a "conceptual" thermodynamic variable. To do this, it is necessary to extend the usual thermodynamic space to include the additional variable n, so that one may now consider, for example, P*-T*-n space instead of the usual P*-T* space. In this vein, it is straightforward to construct the thermodynamic variable conjugate to n and thence to derive the analogs of the usual thermodynamic relationships (Gibbs-Duhem, Clausius-Clapeyron, This structure then constitutes the etc.). extended quantum theorem of corresponding states.

On intuitive physical grounds, it is clear that, although the free energy is a continuous function of η , its derivatives with respect to η are not necessarily continuous. After all, as n is increased from the value for Ar to the value for He, the ground state changes from solid to liquid. Thus, it is to be expected that there will be values of n at which "phase" transitions occur. This view suggests that it would be useful to construct phase diagrams in P*-T*-n space and that these would give a general view of the phases of macroscopic quantum systems. Such an approach has the utility that it is often possible to calculate accurately the values of n at which transitions occur; then it is possible to predict the phase behavior of real systems simply by comparing the value of n for the real system with the calculated values of n at which phase transitions occur.

Let us now introduce the "thermodynamic" variable conjugate to n. The usual equation for the Helmholtz free energy is

$$dF^* = -S^* dT^* - P^* dV^* + \phi^* d\eta, \qquad (6)$$

where

$$\phi^* \equiv (\partial F^* / \partial n)_{T^*, V^*}$$
(7)

If Eq. (3) is used in the partition function, then Eq. (7) with the use of the finite temperature Feynman-Hellman theorem /11/ yields

$$\phi^* = \langle t \rangle / N, \qquad (8)$$

where the average in Eq. (8) is the standard statistical mechanical average. This result is easily understood from the form of Eq. (3) by analogy with the form of the Hamiltonian for a system in a magnetic field, $H = -\underline{B} \cdot \underline{M}$, where <u>B</u> is the magnetic field, <u>M</u> is the magnetic moment operator, and the thermodynamic variable conjugate to <u>B</u> is $\langle \underline{M} \rangle$. Thus, the quantum parameter n can also be viewed as an "external field" which can change the kinetic energy of the system independently of the potential energy.

Once the conjugate variable is defined, the full formalism of statistical mechanics and thermodynamics can be utilized. Several interesting results /13/ are as follows:

- a new statistical mechanical ensemble can be constructed in which \$*\$ is the independent variable and only average values of n are meaningful,
- the Gibbs phase rule in this extended thermodynamic space becomes

$$D = C - P + 3,$$
 (9)

where D is the number of degrees of freedom, C is the number of components, and P is the number of phases -- thus in this "conceptual" space there can be a quadruple point for a <u>one</u> component system! -- there is no conflict with ordinary thermodynamics, which applies only in a physical subspace in which n is fixed, and

o the analog of the Clausius-Clapeyron equation at zero temperature is

$$(dP*/dn)_{c} = -(\phi_{I}^{*} - \phi_{II}^{*})/(V_{I}^{*} - V_{II}^{*}),$$
 (10)

where the derivative is taken along the coexistence curve, and the subscripts I and II refer to the two coexisting phases.

This completes the discussion of the extended quantum theorem of corresponding states.

<u>Thermodynamic Properties of Macroscopic Quantum</u> <u>Systems</u>. In this section, the thermodynamic properties of macroscopic quantum systems will be treated from a unified point of view utilizing the extended quantum theorem of corresponding states. The presentation is organized into three parts:

- o ground-state results,
- o triple-point and critical-point data, and
- o generalized "phase" diagrams.

This point of view has been used to treat other aspects of macroscopic quantum systems, such as itinerant ferromagnetism /20/, quantum solutions /21/, and two-dimensional systems /22/. These aspects will not be discussed in this review.

The ground-state results which we will discuss were obtained from variational calculations of the ground-state energies of fluid and solid Bose and Fermi systems /11-13/ as a function of the quantum parameter n. They are summarized in Table 3 and Figure 1. The main factor responsible for the general features of these results is the <u>energetics</u> of these systems. Since the quantum parameter $n \ \kappa R/|\bar{W}|$, there are three regimes:

- o "small" n -- the ground state is crystalline,
- o "intermediate" n -- the ground state is liquid, and
- o "large" n -- the kinetic energy is dominant and the ground state is a gas; i.e., an <u>unbound</u>, many-body quantum system.

Property	Statistics	Critical n
Liquid-Solid Transition (P* = 0)	Bose Fermi	0.14 0.18
Liquid-Gas Transition (P* = 0)	Bose Fermi	0.29
Critical Point	Bose Fermi	0.46 0.33

Table 3. Critical values of the quantum parameter n for ground-state transitions. The values for the liquid-solid transition are also the values of n for which the triple-point temperature goes to zero; they have been adjusted to fit the experimental zero-temperature solidification pressures /13/ for ³He and ⁴He. The other values are taken from Miller, et al. /12/. The value for the Bose critical point was shown to be exact by Bruch /23/.



Figure 1. Ground state P^*-n phase diagram for Bose and Fermi macroscopic quantum systems. The left- and right-hand pressure scales are for the liquid-solid and the liquid-gas curves, respectively. The results are taken from Nosanow, et al. /11, 13/ and from Miller, et al. /12/.

In addition, there are also important effects due to statistics:

- o the solidification pressure for a given value of n is higher for a Bose system than for a Fermi system -- this result is due to the higher energy of a Fermi liquid because of the kinetic energy of the Fermi sea /11/, and
- o the liquid and gas phases can coexist for a Fermi system at zero temperature; whereas, these phases cannot coexist for a Bose system at zero temperature -again this result is due to the kinetic energy of the Fermi sea /12/.

Thus, an important result of these calculations is that the general features of the ground-state thermodynamic properties of these systems depend only on the "physics" of these systems and not on the details of the calculations. The precise numbers do, of course, depend on these details as well as on the phenomenological potential. We believe that the numerical results describe the real physical systems with an accuracy of approximately ten percent, because this is probably a good estimate of the accuracy of n itself as shown in Tables 1 and 2.

Let us now turn to a discussion of the critical points and triple points of the class of systems under consideration. Corresponding states plots of the reduced temperatures, pressures, and densities are given in Figures 2, 3, and 4, respectively. These thermodynamic quantities are "reduced" (i.e., brought into dimensionless form) using the Lennard-Jones potential parameters given in Table 1. In addition, the results of the ground-state calculations, summarized in Table 3, are included in these Figures. Several important points emerge from these graphs:



Figure 2. Plot of the reduced critical and triple-point temperatures versus the quantum parameter η . The data for the rare gases is taken from Crawford /24/ and that for the H₂ isotopes from Roder, et al. /25/. The solid curves are only a guide to the eye.

- the reduced values for the heavy rare gases are independent of n, thus confirming the applicability of corresponding states to these systems,
- o all of these reduced quantities eventually <u>decrease</u> with <u>increasing</u> n -this result is understandable intuitively in terms of the increase in the zeropoint kientic energy, so that the system requires less thermal energy or less



Figure 3. Plot of the reduced critical and triple-point pressures versus the quantum parameter n. The data are obtained as for Figure 2. The left- and right-hand scales are for the critical and triple-point pressures, respectively.



Figure 4. Plot of the reduced critical and triple-point densities versus the quantum parameter n. The data are obtained as for Figure 2.

pressure to effect the transition in question,

- o for sufficiently large values of n, the effects of statistics cause the curves to bifurcate -- again these results can be understood intuitively in terms of the effective repulsion between fermions and the effective attraction between bosons, so that the critical temperatures and pressures are lower for fermions than for bosons, and
- o in all cases, the curves vanish for a critical value of n -- thus, systems with sufficiently large values of n will behave like a fluid above its critical point at all temperatures including T = 0!

A close look at these graphs also reveals some nagging discrepancies:

- o the values for the reduced pressures and densities for Ne are not the same as those of the other heavy rare gases, and
- o the values for the isotopes of ${\rm H}_2$ and He appear to be a bit irregular.

In our opinion, these discrepancies are due to inadequacies in the phenomenological pair potential. If the parameters determined by Barker /17/ are used, the Ne discrepancies disappear because of the improved accuracy of the length parameters. The irregularities in the hydrogen and helium curves probably have the same source; however, an internally self-consisten°t set of phenomenological potentials has not yet been developed for these systems, so that the question still remains open for these two cases.

With these results, it is now straightforward to construct the $P^{*}-T^{*}-n$ phase diagrams for Bose

and Fermi systems /13/. These are given on Figures 5 and 6. Experimental data (Crawford /24/ and Roder, et al. /25/) are used for the P*-T* phase diagrams for A, H₂, ⁴He and ³He and the theoretical results given in Table 3 are used for T* = 0. Figures 2 and 3 are projections of these curves on to the T*-n and P*-n planes, respectively. Thus, the intuitive physical arguments given to gain an understanding of their behavior also obtain for Figures 5 and 6. Thus, we believe that these phase diagrams give a qualitatively correct and reasonably accurate quantitative picture of the solid, liquid and gas phases of Bose and Fermi macroscopic quantum systems.

It is of interest to examine the P*-T*-n phase diagram for Bose systems from the point of view of the Gibbs Phase Rule, Eq. (9). Clearly, there are four phases which need to be considered -- solid, liquid, gas and superfluid. In this "extended" thermodynamic space, there is already a line of triple points where the solid, liquid, and gas coexist. The reduced λ -point temperature for ⁴He at saturated vapor pressure can easily be determined and another line of triple points (liquid-gas-superfluid) constructed through it using the intuitive physical idea that the reduced λ -point temperature is proportional to the quantum parameter n. The point where these two lines cross is the quadruplepoint, and the third line of triple points (solid-liquid-superfluid) can be constructed to pass through this point. This construction does not prove that a quadruple point must exist; only that it can exist. There will, of course, be a Bose-Einstein condensation in the gas phase; however, this is not pictured in Figure 5.

The P*-T*-n phase diagram for Fermi systems is very much like that for Bose systems. The critical point occurs at a smaller value of n and there is a liquid-gas coexistence curve at zero temperature. Both of these results are due to the kinetic energy of the Fermi sea /12/. There is, of course, an extensive structure, which is not shown, due to the existence of superfluidity in ³He. In addition, there is another extensive structure, which is not shown, due to the possibility of itinerant ferromagnetism in Fermi



Figure 5. Phase diagram for Bose macroscopic quantum systems in P*-T*-n space. Experimental data are used for the A, H₂ and ⁴He curves. The value for the ⁴He λ -point is that at the saturated vapor pressure. The zero-temperature results are taken from Table 3. The figure is constructed so as to show how a quadruple point could exist. The curve for the Bose-Einstein condensation temperature for H^a is taken from Stwalley and Nosanow /03/.

systems. This subject is discussed by Guyer and Miller /20/.

This completes our discussion of the thermodynamic properties of macroscopic quantum systems. Use of the extended quantum theorem of corresponding states enables one to form a unified, over-all view of these properties. It is worth emphasizing that these results depend only on the "physics" of these systems and not on theoretical details. Thus, they are of general validity and certainly qualitatively correct. We believe that they quantitively describe real systems to an accuracy of approximately ten percent.

<u>Spin-Polarized Quantum Systems</u>. In this Section the formalism developed in the previous Sections will be used to predict some of the thermodynam-



Figure 6. Phase diagram for Fermi macroscopic quantum systems in P*-T*-n space. Experimental data are used for A, H_2 and ³He curves. Data for A and H_2 are used because Figures 2, 3 and 4 show that the effect of statistics is unimportant for small n. The results for D* are taken from Miller and Nosanow /26/. The spin-polarized scale is discussed in the Section on spin-polarized quantum systems.

ic properties of spin-polarized quantum systems. First, H_{+} and D_{+} are discussed in general. Then a corresponding states discussion of the properties of their fluid phases is given. After that a rather speculative discussion of the properties of solid H_{+} and D_{+} is presented. Finally, spin-polarized ³He is briefly discussed.

Let us first consider spin-polarized atomic hydrogen and deuterium in general. It is believed that H+ obeys Bose statistics because it is a tightly bound system of <u>two</u> fermion (one proton and one electron); whereas, D+ obeys Fermi statistics because it is a tightly bound system of <u>three</u> Fermions (one proton, one neutron and one electron). This problem is fundamentally the same as that of the statistics obeyed by 3 He and 4 He and has been extensively discussed by Girardeau /27/. A cursory look at Table 1, shows that H+ has the largest n of all of the systems and should therefore manifest quantum effects most strongly on a macroscopic scale. On the other hand, D+ has a value of n a little larger than that for 3 He and hence should behave very much like it.

We shall now consider the fluid phases of H+. Because $\eta(H_{+}) = 0.55$ and the value of the zero temperature critical point for Bose systems is n(Bose critical point) = 0.46, the corresponding states analysis predicts that H+ will be a gas at zero temperature and will behave like a fluid above its critical point for all temperatures including zero temperature! This means that H+ is predicted not to have a liquid phase; i.e., there can not be coexisting liquid and gas phases for H+ under any conditions. This prediction is strengthened by the fact that the exact values of n are expected to be roughly 15% lower than the Lennard-Jones values for all systems other than H⁺ and D⁺ (see Tables 1 and 2). It is, of course, expected that this quantum gas will exhibit a Bose-Einstein condensation to become a superfluid gas /01-03/. Results of recent calculations by Lantto and Nieminen /28/ are shown on Table 4.

Since H+ is a weakly interacting Bose gas, the usual theory should apply /29/. In addition, it should be possible to make a clear cut observation of the Bose condensate.

We shall now consider the fluid phases of D+. Because n(D+) is very close to $n({}^{3}He)$, its properties may be very like those of ³He. However, it may be that use of accurate phenomenological pair potentials would reduce the critical values of n for Fermi systems given on Table 3 by roughly 15%, in which case n (liquidgas) \approx 0.25 and n (critical point) \approx 0.28. If this were true, the η for D+ would fall in between, and D+ would have a gaseous ground state and the possibility of liquid-gas coexistence at zero temperature! In this event it might be possible to observe quantum effects on the singularities of thermodynamic functions in the neighborhood of the critical point /13/. It is, of course, expected that D+ will exhibit

р 10 ²¹ /ст ³	۷ m cm ³	T _{BE} deg	n _c	^B min kG
0.2	3027	0.55	0.95	6
0.5	1209	1.01	0.89	17
1.0	605	1.60	0.81	38

Table 4. Properties of H+ calculated by Lantto and Nieminen /28/. Here ρ is the number density, V_m is the molar volume, T_{BE} is the Bose-Einstein condensation temperature, and n_c is the zero temperature condensate fraction (note that $T_{BE} \propto \rho^{2/3}$). The quantity B_{min} is the magnetic field necessary to stabilize H+ against decay due to collective excitations first studied by Berlinsky, et al. /06/.

a phase transition to a superfluid state at temperatures of the order of 1 mK. This behavior should be completely analogous to that of ³He; e.g., there should be both A and B phases. This behavior would still be expected even if D⁺ were to be gaseous.

Let us now try to predict the properties of solid H+ and D+ using corresponding states arguments. This is necessarily a rather speculative endeavor. In the first place, Berlinsky, et al. /06/ have shown that very large magnetic fields are necessary to stabilize the solid against decay due to collective ex

citations. In addition, the only existing data /11, 13/ refer to the liquid-solid transition; not to the liquid-gas transition. Nevertheless, the properties of the solid at the liquid-solid transition appear to be dominated by the properties of a hard-sphere system with the size of the sphere renormalized by the effects of energetics. Thus, we believe that the results will certainly be qualitatively correct, and the numbers may serve as a guide to experiments. It is possible to make estimates of the zero temperature solidification pressure P_c, the volume V_s of the solid at this pressure, and the zerotemperature Debye Theta Θ_0 . The former can be estimated from Figure 1. One finds that for both Bose and Fermi systems

 $\Delta P_{s}^{\star} \propto 7.5 (\Delta n).$

In addition, Nosanow, et al. /11/ found that V_s^* rapidly approached an asymptotic value as a function of n, so that it is approximately constant for He and H. Finally, a crude estimate of Θ_0 can be obtained from the approximate result that

which follows from Greywall's results /30/,

where $\Theta_0^* \equiv k_B \Theta_0/\epsilon$ and the proportionality only holds at constant V*. The results are given in Table 5 along with those for ³He and ⁴He for comparison. Several points emerge from Table 5:

- o the conversion factors ε/σ^3 and $N_{0}\sigma^3$ differ significantly for He and H because the value of σ is much larger for H than for He,
- o thus, the molar volumes at solidification of solid H+ and D+ are predicted to be very large, with the consequence that the nearest-neighbor distances are quite large -- these solids would be quite open structures,
- o similarly, the solidification pressures are relatively low, in the case of D+ only 12 atm, and
- o the θ_0 for D+ is also quite low, which is to be expected due to the large zeropoint kinetic energy; the θ_0 for H+ may be quite large, but the extrapolation is probably unreliable.
- A few other comments are in order:
 - o the coefficient of thermal expansion should be quite low because these systems exist at temperatures such that the thermal kinetic energy is small compared to the zero-point kinetic energy,
 - o the sound velocities and phonon spectra should look pretty much like those for either bcc 3 He or 4 He -- the magnitudes should scale roughly with the 9 o's, and
 - o exchange effects due to the symmetry of the wave function should be larger than for ³He; however, this exchange interaction is small compared to the electronic singlet-triplet exchange -- there would be a large coefficient of self diffusion which might be detectable by a resonance technique in a weakly inhomogeneous magnetic field.

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Property	H+	4 _{He}	D†	³ Не
n	0.547	0.182	0.274	0.241
ε/σ ³ (atm)	17.5	83.89	17.5	83.89
N _o σ ³ (cm ³ /mole	30.2 e)	10.06	30.2	10.06
P*(T*=0)	≃ 3.1	0.298	≃ 0.7	0.405
P _s (T=O) (atm)	≃ 54 .	24.97	≃ 12.	33.95
V*(T*=0) s	≈ 2.1	2.091	≃ 2.4	2.409
V _s (T≈O) (cm ³ /mole	≃ 63. :)	21.04	≃ 73.	24.23
∆(bcc) (Â)	≃ 5.1	3.57	≃ 5.4	3.74
e★(T*=0)	≃ 5.3	1.78	≈ 2.1	1.84
ə _o (T=0) (deg)	≃ 34 .	19.0	≃ 14.	18.5

Table 5. Corresponding states estimates of properties of solid H+ and D+. The properties of solid 3 He and 4 He are included for comparison. Here N_o is Avogadaro's number, P_s and V_s are, respectively the pressure and volume of the solid at solidification, and \vartriangle is the nearest-neighbor distance. The helium volume and pressure data are taken from Crawford /24/. The Debye \varTheta_{o} data are taken from Greywall /30/.

Finally, it is of interest to speculate further on the possibility of observing "supersolid" behavior in solid H+ and D+. One might think that this would be possible because of the low density and high zero-point kinetic energy of these systems. However, as commented earlier V_s^* rapidly approaches an asymptotic value as a function of n as n increases. Since it may be the reduced quantity which determines supersolid behavior, this fact may mitigate against the occurance of this behavior in H+ and D+.

In conclusion, let us turn to a brief discussion of spin-polarized 3 He. The essential physics of this system is that in the presence of a sufficiently large external magnetic field only one

half of the spin states of the Fermi sea will be populated. Although the actual calculations are quite complicated, the general features are easy If one considers only the ideal to obtain. ground state energy, then we find that only the ratio $n/g^{2/3}$ appears, where g is the spin degeneracy. Thus, to a first approximation, a calculation for all n for g = 1 can be deduced from a calculation for all n for g = 2 by simply stretching the scale of the quantum parameter n. Miller and Nosanow /26/ found that the change from g = 2 to g = 1 did not affect things too much. Thus, this effect is pictured on Figure 6 by a modest stretching of the n scale. It is clear that the qualitative features of the P*-T*-n phase diagram are unchanged. Possible effects on the melting curve and other properties have been discussed by Lhuillier and Laloe /07/.

<u>A Last Remark</u>. Whenever a new macroscopic quantum system is found, it is worth examining its possible utility as a refrigerant. In this respect H may very well be unique, because it may be the only substance that remains gaseous at all temperatures, even absolute zero. Thus, if it were once cooled below its Bose-Einstein condenstaion temperature, its use as a refrigerant would, in principle, permit the attainment of temperatures arbitrarily close to absolute zero.

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