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Separation by Diffusion of Hydrogen Clusters in a Metal Hydrogen System

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ABSTRACT

Dynamical problems facing hydrogen diffusion in metal hydrogen systems at low temperature are surveyed. A microscopic model is constructed based on the assumption that the functional units are clusters of Fermi or Bose particles, collectively referred to as spin clusters. Critical behavior of metal hydrogen systems provides a key approximation which makes our model soluble. The time-dependent autocorrelation functions are obtained by solving the Heisenberg equation of motion using a new mathematical technique called the recurrence relations. The dynamical solutions shed light on the reversed isotope effect in diffusion. The nature of interstitial spin clusters is examined and compared with atomic and nuclear spin clusters. The spin clusters show striking resemblance to the superfluid component in the two-fluid theory of liquid ^{4}He.

I. INTRODUCTION

The hydrogen isotopes absorbed in certain open metals are known to have some unusual transport characteristics.[1] If a particular transport property e.g. mass diffusion is properly understood, one might be able to utilize it to achieve a high degree of hydrogen separation.[2] Understanding hydrogen diffusion turns out to be no simple task, involving several areas of physics and chemistry. For example, the atomic ratio of hydrogen to the host

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metal is typically of order unity.[3] That is, the density of the interstitial hydrogen is rather high. Also, an interstitial hydrogen or deuterium atom loses much of its electron cloud.[4] Hence, we have a dense gas of the interstitial hydrogen or deuterium which must best be viewed as an ensemble of effectively fermions or bosons.

In addition, the interstitial hydrogen exhibits mean-field-like second order transition.[3] This kind of critical behavior indicates that there exist cooperative forces which are long-ranged but approximately constant. The diffusion process is likely to be governed by the same cooperative forces in some subtle way. Thus, the interaction of the interstitial hydrogen cannot be treated as a weak perturbation. To complicate the matter further, the diffusion of the interstitial hydrogen and deuterium shows a reversed isotope mass dependence.[1] A similar reversed isotope effect also exists in the superconducting temperatures of metals containing hydrogen and deuterium, which otherwise are nonsuperconductors in their pure metallic form.[5] Perhaps, most relevant is the existence of spinodals and relatively large regions of metastability in the phase space of density and temperature.[6,7] They strongly suggest that below the critical temperature T_c, the interstitial hydrogen exists in clusters.

These physical facts provide clues for constructing a microscopic model (which we shall denote by H). A microscopic model is a first item in developing a theory of interstitial-hydrogen diffusion. Such a model must be a dynamical one, incorporating spin statistics and cooperative forces. There are a few models in the literature. However, most of them ignore much of the physical realities. For example, some models can treat only the dilute density limit (i.e., single-atom hopping) or the ideal limit (i.e., no cooperative forces).[8,9] Others can treat only the high-temperature limit (classical region).[10] Virtually all existing models are non-dynamical or non-microscopic. One cannot use them to calculate the transport coefficients starting from first principles.

Diffusion in a homogeneous many-body system is characterized by the self-diffusion constant. This constant can be calculated from certain time-dependent autocorrelation functions e.g. the velocity autocorrelation function by a well-established relationship.[11] Given a model or H, the autocorrelation functions are obtained by solving the Heisenberg equation of motion. For $N \to \infty$ (where N is the number of particles or some other basic aggregates, i.e., functional units), solving the Heisenberg equation requires a special mathematical technique.[12] Thus studying diffusion from first principles requires a dynamical microscopic model H and the autocorrelation functions.

In Sec. II, we describe a dynamical model for the interstitial hydrogen and deuterium based on quantum statistical theory. There are two essential physical ideas characterizing our model: (1) For temperature below the transition temperature T_c, the functional units are clusters, not single particles. These clusters are composed of single particles and self-stabilized by spin statistics. The sizes and numbers of clusters also depend on temperature T and forces. For $T > T_c$, these clusters break down and there are only single particles. (2) Forces between clusters are long-ranged. Short-range forces are "integrated-out" in forming clusters. To prevent mutual penetration by these clusters, a hard-core-like property is built into the kinematics of the model.

The static critical behavior is determined by the cluster-cluster interaction. Our model exhibits first and second order transitions. There is a tricritical point. It shows that the critical temperature, for example, hardly depends on the cluster sizes or masses, i.e. isotope independent. The dynamical behavior, however, arises from the motions of clusters. The sizes and masses should therefore enter into the structure of the transport coefficients. In atomic and nuclear physics one finds clusters which are stabilized by spin statistics. Available evidence on these clusters shows that the Bose clusters are stabilized by very few Bose particles, whereas the Fermi clusters by larger

numbers of Fermi particles. If our interstitial clusters have similar properties, our model has a basis for explaining the reversed isotope effect.[1] Our model actually makes a prediction on the relative diffusion coefficients.

In Sec. III, we describe a new mathematical technique of solving the Heisenberg equation of motion for many-body systems. The original idea was given by H. Mori in 1965 who showed that the Heisenberg equation is equivalent to a generalized version of the quantum Langevin equation.[12] The Langevin equation of course is well known for its connection to Brownian motion and is widely applied today for stochastic processes.[11] This unexpected formal connection provided Mori with an insight into the Heisenberg equation. But because of certain technical difficulties (stemming from continued fractions which have to do with the mathematical theory of the problem of moments), he was unable to obtain complete formal solutions for the Heisenberg equation.

Very recently the author was able to obtain complete mathematical solutions for the Heisenberg equation using Hilbert space theory.[13] It was made possible by the realization that Mori's approach is couched in the Gram-Schmidt orthogonalization process. Although valid, this process complicates, not simplifies, the Heisenberg equation. A new orthogonalization process (named the orthogonalization by recurrence relations) expresses the Heisenberg equation into a set of time-dependent functions. These functions are all linked by an exact recurrence relation.[14] This method was first applied to study the dynamics of electrons in normal metals in two and three dimensions, for which there are well established (and relatively simple) models.[15] This paper describes some of our initial work on the cluster model by the method of recurrence relations.

II. PHYSICAL MODEL

A. Physical Information

We will briefly summarize main experimental facts which are basic ingredients for our diffusion model. The experimental

evidence is obtained largely from the Pd-H system. (1) Neutron scattering. The scattering experiments show that the absorbed hydrogen atoms occupy the interstitial sites of the host lattice. These sites form an octahedral sublattice of the fcc structure.[16] (2) α-β transition. The absorbed hydrogen undergoes a gas-liquid-like phase transition. There is a critical point which is completely mean-field-like.[3] From these results, we infer that there are cooperative forces and that these forces are long-ranged and roughly constant. Such forces can only arise from the large compressibility of the lattice with respect to interstitial occupation. Consequently the sublattice of hydrogen must be a nonrigid one.[17] (3) Spinodals and metastability. Recent measurements of spinodals show that there are large areas of metastability bounded by the solubility and coherent spinodal curves.[6,7] The curves do not even meet at T_c and are separated at all temperature values. In these areas one knows that nucleation and growth take place via cluster formation. Hence there must be some types of atomic clusters. (4) Compton profiles.[18,20] Experimental profiles strongly suggest that the interstitial hydrogen is very nearly proton-like bereft of the electron cloud. Similarly the interstitial deuterium is deuteron-like. The interstitials carry at best a very small fraction of the electron charge and they are effectively bare nucleons, i.e., fermions or bosons. (5) Reversed isotope effect.[1,21,22] The existence of a reversed isotope effect indicates that the fundamental dynamical processes of hydrogen diffusion have quantum mechanical origin. Classical rate theories are not applicable in their usual form.

We assume that below T_c the functional units are clusters. These clusters are composed of protons (Fermi clusters) or deuterons (Bose clusters). Above T_c, the clusters break up into the constituent single particles. The mechanisms of cluster formation, the cluster sizes, stability and temperature dependence (referred to as single-cluster properties) will be discussed in Sec. VI. Single-cluster properties depend on spin statistics explicitly.

For $T < T_c$ our system is an ensemble of interacting clusters of Fermi or Bose type. The forces between clusters are assumed to be long-range but constant and independent of spin statistics. Then the ensembles of both the Fermi and Bose clusters have the same many-body properties e.g. phase transition. Any subtle difference e.g. reversed isotope effect must ultimately arise from single-cluster properties.

B. Partition Function and Transformation

It is convenient and now customary to describe many-body systems like ours in the language of second quantization.[23] We use pseudospin-$\frac{1}{2}$ operators, s_i^+ and s_i^- defined as follows: $s_i^{\pm} = s_i^x \pm i\, s_i^y$ and $s_i^{\pm}\, s_i^{+} = \frac{1}{2} \pm s_i^z$, where s_i^μ, $\mu \equiv x,y,z$, are the three Pauli matrices at lattice site i. These operators act on clusters and they satisfy spin-$\frac{1}{2}$ algebra.[24] That is, at the same site these operators anticommute and at different sites they commute. The spin algebra prevents clusters from penetrating each other. Our Hamiltonian H, which defines our model, is given by[25]

$$H = -\sum_{\alpha}\sum_{i} E_{ij}(x_\alpha)\, s_i^{+} s_j^{-} + \tfrac{1}{2}\Lambda_\alpha (\Delta x_\alpha)^2,$$

$$E_{ij}(x_\alpha) = h^2/2Md^2 - U_{ij}(x_\alpha)$$

$$\Delta x_\alpha = x_\alpha - \bar{x}_\alpha \qquad (1)$$

where h is the Planck constant, M is the mass of a cluster, d the average cluster spacing, x_α and $\bar{x}_\alpha$ are the host metal's instantaneous and equilibrium coordinates, respectively; U_{ij} is the interstitial occupation energy due to transition between a pair of neighboring sites i and j; Λ is the lattice spring constant. The model contains only the pair-wise interaction and it limits the cluster transition to near-neighbor pairs only. As a many-body model, it has a relatively simple form of energy. One can obtain all the equilibrium properties form the partition function $Z = \mathrm{Tr}\, \exp(-H/kT)$, where k is the Boltzmann constant

and Tr means a diagonal sum. A direct evaluation of the partition function is difficult because of the nonrigidness of the sublattice. By applying a unitary transformation $\mathscr{T}$, under which Z is invariant, one can remove the nonrigidness at the expense of having a more complicated form of the interaction. The unitary-transformed model $\tilde{H} = \mathscr{T}H\mathscr{T}^{-1}$ may contain multi-body terms, but they may be more easily approximated. The transformation itself is rather technical and will not be given here.[25] Our unitary-transformed model has the following form

$$\tilde{H} = \mathscr{T}H\mathscr{T}^{-1} = -\sum_{\alpha}\sum_{ij} E_{ij}^{\alpha} s_i^{+} s_j^{-}$$

$$- \frac{1}{2\Lambda} \sum_{\alpha}\sum_{ij}\sum_{mn} U_{ij}^{\alpha} U_{mn}^{\alpha} (s_i^{+} s_j^{-})(s_m^{+} s_n^{-}),$$

$$E_{ij}^{\alpha} = E_{ij}(\bar{x}_{\alpha}), \quad U_{ij}^{\alpha} = d/dx_{\alpha} U_{ij}(\bar{x}_{\alpha}). \tag{2}$$

The unitary transformation has removed the rigidness but introduces a biquadratic coupling.

C. Constant-coupling Approximation

It is very well established that the critical behavior of PdH is mean-field-like.[3] Hence for (2) we make the following mean-field approximation:

$$E_{ij}^{\alpha} = E\delta_{\alpha o} \quad \text{and} \quad U_{ij}^{\alpha} = U\delta_{\alpha o},$$

where E and U are now constants and δ is the Kronecker delta. Then

$$\tilde{H} \to \tilde{H}^{MF} = - E\sum_{ij} s_i^{+} s_j^{-} - L \sum_{ij}\sum_{mn} (s_i^{+} s_j^{-})(s_m^{+} s_n^{-}) \tag{3}$$

where $L = U^2/2\Lambda$. The mean-field model consists of quadratic and biquadratic spin exchange terms and this model is soluble. From the recent work of Lee and Banerjee,[26] we see that this particular form is a special case of the biquadratic generalization of the spin van der Waals model of Dekeyser and Lee H_{DL},[27] given below:

$$H_{DL} = -(J S^2 - \lambda S_z^2) - (Q S^4 - 2Q S^2 S_z^2 + \eta S_z^4), \qquad (4)$$

where $\lambda = J - J_z$, $\eta = Q - Q_z$; J, J_z and Q, Q_z are, respectively, the quadratic and biquadratic exchange constants. The total pseudospin operator S_μ is given by

$$S_\mu = \sum_{i=1}^{N} s_i, \quad \mu = x, y, \text{ or } z$$

where N is the total number of pseudospins (i.e., the sublattice points). Dekeyser and Lee[27] studied this model when $Q = Q_z = 0$. Kim extended their work by studying the full model.[28] The mean-field model (3) represents the case in which $E = J$, $L = Q$, $J_z = Q_z = 0$. Hence we understand the static properties of (3) completely. For $Q < Q_o \equiv 2J/3$, the model has a second order transition defined by $T_c = J/2k$ independently of Q. There is dipolar ordering but no quadrupolar ordering below T_c. Above T_c there is no long-range order at all. At $Q = Q_o$, $T = T_c$, the second order ceases and the first order begins. The point, Q_o and T_c, is a tricritical point. The boundary of the first order region is described by $T_c(Q) = T_c(Q/Q_p)^{\frac{1}{2}}$, $Q \geq Q_o$. Hence for $Q < Q_o$, the system behaves essentially like the pure spin van der Waals with little or no influence by the biquadratic exchange. To obtain nonequilibrium properties, we use the method of recurrence relations described in Sec. III.

III. THE METHOD OF RECURRENCE RELATIONS

We shall briefly describe the method of recurrence relations (RRs),[13] mainly to introduce the notation of nonequilibrium statistical mechanics needed for calculating various time-dependent autocorrelation functions e.g. the velocity autocorrelation function. Consider a dynamical variable of interest, say A, which may be the velocity of a cluster or the cluster-density fluctuations. The time evolution is denoted by A(t), formally given by the Heisenberg representation

$$A(t) = \exp(iHt)\, A \exp(-iHt),$$

which satisfies the Heisenberg equation of motion

$$\dot{A}(t) = i[H, A(t)] = i\{HA(t) - A(t)H\}$$

where the dot denotes a derivative with respect to time. The physical information contained in A(t) is extracted by forming an autocorrelation function (A(t), A), where the inner product usually means the Kubo scalar product.[13] Sometimes it can be approximated by a cannonical ensemble average $\langle A(t)A \rangle = \mathrm{Tr}\{A(t)\, A \exp(-H/kT)\}/Z$. The method of RRs solves the Heisenberg equation formally. Given A(t), there is a second independent dynamical quantity called the random force F(t), responsible for the memory of an externally induced perturbation. The method of RRs gives the following solutions for A(t) and F(t):

$$A(t) = \sum_{n=0}^{\infty} a_n(t) f_n \quad \text{and} \quad F(t) = \sum_{n=1}^{\infty} b_n(t) f_n \tag{5}$$

where $\{f_n\}$ is a set of orthogonalized basis vectors which span the Hilbert space of A; $\{a_n\}$ and $\{b_n\}$ are sets of real time-dependent functions. In linear response theory, a_0 and b_1 are called the relaxation and memory functions, respectively.[23] The above RR (referred to as RR-I) represents an orthogonalization process; and it is superior to the usual Gram-Schmidt process, if Hilbert space is realized.[14]

There is a second RR (referred to as RR-II) which is satisfied by $\{a_n\}$

$$\Delta_{n+1}\, a_{n+1}(t) = -\dot{a}_n(t) + a_{n-1}(t), \quad n \geq 0 \tag{6}$$

where $a_{-1} = 0$ and $\dot{a}_n = da_n/dt$. Also $\{b_n\}$ satisfies the same RR starting with n = 1. The RR-II is characterized by Δ's, which are functions of static properties only. If Δ's are known

(exactly calculable for our mean-field model $\tilde{H}^{MF}$), one may be able to obtain $a_n(t)$ and $b_n(t)$ and hence $A(t)$ and $F(t)$.

For detail, we refer to the original papers.[13,14] This method has been successfully applied to electron transport processes in normal metals.[15]

IV. AUTOCORRELATION FUNCTIONS

Following the method of RRs we shall calculate Δ's for H_{DL} confining ourselves to $Q<Q_o$ and $T<T_c$. Recall that $\tilde{H}^{MF}$ is a special case of the biquadratic spin van der Waals. Our calculations show that 's follow a very simple form:

$$\Delta_n = n\Delta$$

where $\Delta = 2\lambda kT/N$. For this set of Δ's, the RR-II is uniquely satisfied by

$$a_n(t) = (\Delta^{\frac{1}{2}n} t^n/n!) \exp(-\tfrac{1}{2}\Delta t^2) \tag{7}$$

for all $n \geq 0$. We do not have a closed expression for $b_n(t)$ but only a series form in powers of $\Delta^{\frac{1}{2}}t$ (for simplicity Δ is suppressed in the following):

$$b_1(t) = 1 - 2t^2/2! + 10t^4/4! - 74t^6/6! + 706t^8/8! - 8162t^{10}/10! + \ldots$$

$$b_2(t) = t - 5t^3/3! + 37t^5/5! - 353t^7/7! + 4081t^9/9! - \ldots$$

$$b_3(t) = t^2/2! - 9t^4/4! + 93t^6/6! - 1125t^8/8! + \ldots$$

$$b_4(t) = t^3/3! - 14t^5/5! + 193t^7/7! - \ldots \tag{8}$$

and so on. Now a_n and b_n are exactly related by convolution

$$a_n(t) = \int_o^t dt'\, a_o(t')\, b_n(t-t'). \tag{9}$$

Hence anyone of $\{b_n\}$ is effectively known to any order of a series expansion, e.g.

$$t \exp(-\tfrac{1}{2}t^2) = \int_0^t dt' \exp(-\tfrac{1}{2}t'^2)\, b_1(t-t'). \tag{10}$$

Observe that $b_1(t) \neq \dot{a}_1(t) \equiv (1 - t^2) \exp(-\frac{1}{2}t^2) = 1 - 3t^2/2! + 15t^4/4! - 105t^6/6! + 945t^8/8! - \ldots$. For t small, clearly $b_1(t) > \dot{a}_1(t)$. Now the cluster mobility μ is given by $\mu = \int_0^\infty dt\, b_1(t)$. Since $\int_0^\infty dt\, \dot{a}_1(t) = 0$, we conclude that $\mu > 0$. The memory function $b_1(t)$ thus directly yields a finite value for the mobility as a function of temperature contained in Δ.

The self-diffusion constant D_s can be deduced from the relaxation function $a_o(t)$ as $D_s = \alpha\Delta^{\frac{1}{2}}$, where α is a constant depending only a kinematical factors.[29] The diffusion constant contains the cluster mass M in Δ through E (see our original expression for the model). For the region $Q \ll Q_o$, $E \approx h^2/2Md^2$ and the self-diffusion is expected to decrease with the growth of the cluster mass. To evaluate D_s absolutely, we need to know the kinematical factors, most of which are still unavailable from experiment. We can however use our result to obtain an expression which gives the relative size of proton and deuteron clusters in terms of some measurable quantities.

Our formal result applies equally to proton and deuteron clusters. The essential difference between the two types of clusters is assumed to arise from single-cluster properties. For example, the proton and deuteron clusters should not have the same size at the same temperature since the physical mechanisms of their formation depend on statistics explicitly. That is, at a given temperature, the proton and deuteron clusters differ considerably in size and hence in mass. Now the experimental diffusion data are usually fitted to the Arrhenius form[1]

$$D_s = D_o \exp(-W/kt) \tag{11}$$

where D_o is a constant proportional to $m_o^{-\frac{1}{2}}$ (m_o the mass of the diffusing unit which may be a single particle or cluster) and W is the activation energy. For 200K < T < 500k, Völkl et al[21] have fitted the data from the diffusion of the hydrogen isotopes p and d in Pd by

$$D_s(p)/D_s(d) = \sqrt{2} \exp(-W_{Pd}/kT) \quad (12)$$

where $W_{Pd} = W_p - W_d$ and $W_{Pd}/W_p \approx 0.1$. Note that $T_c = 566k$ for PdH.

We introduce a mass number z, which is the average number of single particles in a cluster defined by $z \equiv M/m$, where m is the single-particle mass and M the cluster mass. Then using our results for D_s and combining it with the Arrhenius form, we get

$$\theta \equiv z_d/z_p = \exp(-W_{pd}/kT). \quad (13)$$

For high temperature, $M \to m$ and $z \to 1$. Hence $\theta \to 1$, i.e., there are no clusters, only single particles. For low temperature, $\theta < 1$, i.e., the proton clusters are on the average larger than the deuteron clusters. This can account for the reversed isotope effect in diffusion. The exponential factor approximately indicates the degree of involvement by clusters in the diffusion process. The above result may be regarded as a semi-phenomenological rate-theory expression for clusters.

V. SINGLE-CLUSTER AUTOCORRELATION FUNCTION

It is possible to obtain the autocorrelation function for a single cluster initially localized at site o. There are three diagonal elements $G_{\mu\mu}(t) = \langle s_o^\mu(t)\, s_o^\mu \rangle$, $\mu = x, y, z$. The six non-diagonal elements vanish for our mean-field model. The rotational symmetry of our model also makes $G_{xx} = G_{yy}$. Hence there are only two non-zero elements of the autocorrelation function. G_{xx} is more interesting than G_{zz}. Hence we discuss the former only.

We are principally concerned with the long-time behavior ($t \to \infty$), which can be most readily compared with experiment. To solve this problem we first divide our system into two subsystems, one small and one large. The small subsystem contains only the tagged cluster and the large subsystem contains the rest. A

great deal of simplification arises if we can regard the large subsystem as a thermal bath or reservoir for the tagged cluster. Using our previous results, we find that[30]

$$G_{xx}(t) \equiv \langle s_o^x(t)\, s_o^x \rangle$$

$$= \tfrac{1}{2} \int_0^1 du\, e^{-Bu^2} (1 - 2Bu^2)(1 - u^2)/(1 - \alpha u^2) \qquad (14)$$

$$+ \tfrac{1}{4} \int_{-1}^1 du\, e^{-Br^2} (1 - 2Br^2) [1 + bu(1 - \alpha u^2)^{-\frac{1}{2}}]^2,$$

where $B = (abJt/N)^2$, $a^2 = N/(2-J/kT)$, $b^2 = \frac{1}{2}(2-J/kT)$, $\alpha = 1-b^2$, $r = u - (1 - \alpha u^2)^{\frac{1}{2}}/b$. The above integrals can be evaluated analytically for $t \to \infty$

$$G_{xx}(t) \equiv \tfrac{1}{4}\sqrt{\pi}\, b^2 B^{-3/2} + \tfrac{1}{2} b^4 B^{-1} \equiv \text{const.}\ t^{-2}, \qquad (15)$$

where the first term can be dropped compared with the second for $t \to \infty$. The autocorrelation function shows a long-time tail, rather than an exponential decay (Ornstein-Zernicke). The existence of long time-tails, first suggested by computer simulations using Brownian-like systems, has been a source of controversy recently.[40] Long-time tails indicate that the time correlations persist for a long period of time and the dispersal of particles or clusters (i.e. diffusion) takes place very slowly. We can show that the long-time tails do not always exist in H_{DL}. Defining $R = J_z/J$, we find for $R \geq 2$, $G_{xx}(t) = \exp(-gt^2)$ for some $g>0$. But for $0<R<2$ (but $R \neq 1$), $G_{xx}(t) \equiv \text{const.}\ t^{-3}$. For $R \equiv 1$, $G_{xx}(t)$ is also Gaussian. Our first result corresponds to $R = 0$. This rather remarkable behavior indicates that the motion of a cluster depends sensitively on the symmetry of competing interactions. Since the transport coefficients are obtained by integrating the autocorrelation function over all times, the presence of long-time tails can influence the magnitude of these coefficients

enormously. Some of these numerical details will be published elsewhere.[30]

VI. NATURE OF SPIN CLUSTERS

Our work is premised on the following two basic assumptions: (1) For low temperature, the functional units are Fermi or Bose clusters (hence referred to as spin clusters collectively). Nucleation and growth of spin clusters are determined principally by spin statistics and short-range forces. (2) Given the spin clusters, their numbers and multiplication are determined principally by temperature and long-range forces. The applicability of our work to hydrogen metal systems rests on the validity of these assumptions. We shall see whether these assumptions and their implications are physically reasonable. We shall also see whether there are some physical evidence for them.

Low-temperature measurements of the diffusion of the hydrogen isotopes p and d in Pd show reversed isotope behavior. It was our conclusion that transport behavior can appear anomalous because the functional units are clusters and not single particles. Furthermore, the deuteron clusters are "hard and small" containing few deuterons, whereas the proton clusters are "soft and large" containing many protons. This conclusion may be compared with the behavior of spin clusters found in atoms and nuclei.

Atomic spin clusters are found in liquids ^{3}He and ^{4}He at very low temperatures. The electron wave functions for ^{3}He and ^{4}He are almost identical.[31] The pronounced difference in the low-temperature behavior between the two liquids is generally attributed to the difference in spin statistics obeyed by ^{3}He and ^{4}He. When mixed, the two liquids show some very remarkable miscibility properties such as phase separation and tricritical point.[32] Inside the miscibility gap, one finds metastable and spinodal regions.[33] In these regions there are indeed two types of clusters, one metastabilized by Fermi particles ^{3}He and the other by Bose particles ^{4}He. Hence they are spin clusters. The nucleation and growth rates of these spin clusters are found

to be very different. Hoffer et al[34] found that when the mixtures are quenched, ^{3}He-rich clusters show growth, whereas ^{4}He-rich clusters do not appear to grow. The behavior of these atomic spin clusters seem to be consistent with our first assumption and its implications.

It is generally held that the nuclei are made up of certain discrete functional units resulting in some definite structure.[35] Clusters and spin statistics play an important role in understanding the formation and stability of nuclear matter. Nuclear clusters most frequently discussed are Bose clusters of the α-particle model and Fermi clusters of the independent-pair model. Hence these nuclear clusters are also spin clusters. The α-particle model can account for certain light nuclides e.g. C^{12} and O^{16}, but not heavier ones.[36] The independent-pair model, however, can describe much of the physics of nuclear matter very adequately. That is, heavier nuclides are <u>not</u> composed of Bose clusters, but composed of Fermi clusters. Apparently even the nuclear Bose clusters do not enjoy growth and they do not therefore contribute much to building of heavier nuclei. The behavior of nuclear spin clusters to be consistent with our first assumption.

The different clustering behavior between Fermi and Bose particles is not unreasonable. Because of the Pauli exclusion principle, the Fermi particles are prevented from close approach, but the Bose particles are not. As a result, a small number of Bose particles may readily form a droplet-like structure and quickly saturate e.g. the α-particle. Owing to the exclusion Fermi particles enjoy greater correlation and find more difficult to saturate. Hence Fermi clusters involve larger numbers and they are more elastic. That is, the Fermi clusters are generally bigger and have greater degrees of freedom than the Bose clusters.

Now turning to the second assumption, we note that it does not involve spin statistics. It really need not be an assumption. It could be proved within the framework of our mean-field model. In our work we have simply taken it as an assumption as it appears

to be well justified by the behavior of ordinary clusters. The BCS theory of superconductivity, for example, assumes that Cooper pairs multiply as the temperature is lowered below the superconducting transition temperature.[37] The modern theory of liquid ^{4}He assumes that below the lambda temperature, a fraction of the liquid is in the superfluid state whose density increases with lowering of the temperature.[38] The population growth rates of these quasiparticles are difficult to calculate from first principles. (Hence they have never been exactly calculated.) For our model this calculation appears feasible because the mean-field approximation is applicable ab initio.

Our calculation of the cluster density as a function of the temperature is based on the following idea: Below the transition temperature T_c, spin clusters are assumed to be randomly distributed in a sea of single particles. The total number-density ρ, which is a constant, is a sum

$$\rho = \rho_{cl} + \rho_{sp} \tag{16}$$

where ρ_{cl} is the cluster density and ρ_{sp} the single-particle density. As $T \to 0$, more and more clusters appear reducing the single-particle population. The ground state contains clusters only. As $T \to T_c$, more and more clusters break down, increasing the population of single particles. Above T_c there are no spin clusters. This picture is very similar to the two-fluid concept of liquid ^{4}He due to Tisza,[38] according to which the helium liquid below the lambda temperature T_λ is composed of 2 components, superfluid and normal fluid. The two fluids interpenetrate, one serving as the reservoir for the other. The superfluid has no entropy. At $T = 0$, the liquid contains only the superfluid component and above T_λ, only the normal fluid component. The superfluid density ρ_s just below the T_λ has been calculated by a scaling argument,[39]

$$\rho_s \sim (1 - T/T_\lambda)^{2/3}. \tag{17}$$

Using this idea we obtain the cluster density near T_c

$$\rho_{cl}/\rho \sim (1 - T/T_c) \qquad T \lesssim T_c$$

$$= 0 \qquad T > T_c \tag{18}$$

The cluster density has an exponent 1 because our model is a mean-field system. Our calculation appears to be extendable to T = 0 by a method due to Dekeyser and Lee.[27] This work is in progress.

Finally the analogy between liquid ^{4}He and our model is strengthened by the following fact: The lambda transition in liquid ^{4}He is second order. The transition temperature T_λ shows a very weak dependence on pressure P, so that it can be effectively represented as[38]

$$T_\lambda(P) = T_\lambda \qquad \text{for } P < P_o \tag{19}$$

where $T_\lambda \approx 2.2$ k $\quad P_o \approx 25$ atm.

For $P > P_o$, the transition is first order and the transition temperature becomes noticeably pressure-dependent. This behavior of T_λ is strikingly similar to the behavior of the transition temperature T_c of our model [see sec. II].

$$T_c(Q) = T_c \qquad \text{for } Q < Q_0$$

$$= T_c(Q/Q_0)^{\frac{1}{2}} \qquad Q \gtrsim Q_0. \tag{20}$$

For $Q < Q_p$, the transition is second order; for $Q \gtrsim Q_o$ it is first order. The main difference between the two systems is in the nature of second order. Our model has mean-field critical exponents, whereas liquid ^{4}He has non-mean-field critical exponents. We observe that the correspondence between the two systems is made by the pressure P and the biquadratic interaction Q.

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