Helium Atoms in Zeolite Cages: Novel Mott-Hubbard and Bose-Hubbard Systems

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Low-lying excitations of ^{4}He and ^{3}He atoms confined inside zeolite cages have been modeled by Bose-Hubbard and Mott-Hubbard rings with strong intrasite repulsion and finite intersite attraction. Differences between ^{4}He and ^{3}He arise due to mass and the statistics. Calculated temperature and concentration dependences of the heat capacity agree qualitatively with the experiment, but a quantitative comparison suggests that disorder may dominate at very low T.

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Properties of ^{4}He and ^{3}He atoms confined to move in restricted geometry have been of considerable interest during the last several decades. Examples of confining media are Vycor [1], aerogels [2], zeolites [3–6], fullerites [7], and the surface of graphite [8]. Some of the basic questions that have attracted both theoretical and experimental attention include the nature of Bose-Einstein condensation in porous media (singly and multiply connected pore structure) [9], quantum transport through microporous channels [10], and the ground and excited states of low-dimensional bosonic and fermionic quantum liquids [11,12].

In this Letter we address the last issue and discuss the results of our theoretical studies on the low-lying excitations of ^{4}He and ^{3}He atoms trapped near the inner wall of the cages of K-*L* zeolites, as shown schematically in Fig. 1. The cages are about 13 Å in diameter and 7.5 Å in length, and interconnected through apertures of diameter about 7.4 Å to form one-dimensional channels. The K^+ ions on the cage wall (large circles in Fig. 1) exert an attractive potential [13] on the He atoms. The potential produced by the zeolite cage gives rise to binding sites (in this case eight) for the He atoms arranged in a ring geometry near the cage wall shown as intermediate size circles in Fig. 1 where the medium circles indicate the binding sites occupied by He atoms.

It has been suggested [3] that at low temperatures ($T < 10$ K) and for sufficiently small concentration n, the number of He atoms per cage, He atoms are indeed bound near the wall of the cage with extremely small probability of going from one cage to another because the barrier for such intercage motion is estimated to be about 150 K from the isoelectric heat measurements [3]. These bound states will be referred to as cage states [13]. The dominant mode of thermal excitation at low T is therefore hopping (or tunneling) from one binding site to another inside a single cage. When n is increased beyond a critical value n_c, n_c He atoms fill up all the cage states, and the additional $n - n_c$ atoms move in the region near the cage axis and go from one cage to another. These states will be referred to as *channel* states. At higher temperatures, the atoms trapped in the cage states get thermally excited to the channel states.

Kato *et al.* [3] have made detailed measurements of the low-T heat capacity of He atoms adsorbed inside K-*L* zeolite. Their results in the concentration range $n \leq n_c$ can be briefly summarized as follows. (i) For fixed $T \leq 2$ K, the heat capacity/atom C vanishes at both $n = 0$ and $n = n_c$ and is a relatively flat function of n between these limits. (ii) For a given n, C is a monotonically increasing function of T. Furthermore, at the same T and n, C for ^{3}He is *larger* than that for ^{4}He by more than 25%. For $n \leq n_c$, the T dependence is complicated. Here we limit ourselves to $0 \leq n \leq n_c$ and low temperatures where the statistical mechanics of the cage states prevails over that of practically unoccupied channel states.

The excitations of the ^{4}He system in the manifold of cage states can be described by a Bose-Hubbard model [14] with binding sties localized on a ring. The

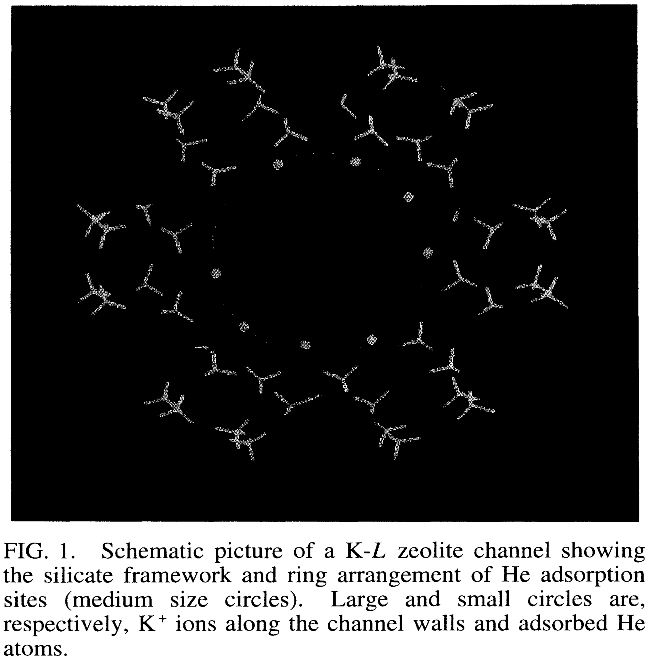

FIG. 1. Schematic picture of a K-*L* zeolite channel showing the silicate framework and ring arrangement of He adsorption sites (medium size circles). Large and small circles are, respectively, K^+ ions along the channel walls and adsorbed He atoms.

Hamiltonian is given by

$$H = -t\sum_{i=1}^{N_m}(b_i^\dagger b_{i+1} + \text{H.c.}) + \frac{U}{2}\sum_{i=1}^{N_m} n_i(n_i - 1) + V\sum_{i=1}^{N_m} n_i n_{i+1}\,, \tag{1}$$

where N_m is the number of binding (localized) sites and b_i ($b_i^\dagger$) destroy (create) a boson (B) at the ith localized site. In Eq. (1), t is the hopping energy, U is the repulsive energy between two He atoms occupying the same site, and V is the attractive energy between atoms occupying neighboring sites. The boson operators satisfy the usual commutation rules, and the number operator n_i has eigenvalues 0, 1, 2, etc. The actual physical system is complex, however, due to disorder in the positions of framework cations. This will result in random values of t, V, and U. Therefore a comparison of the results for our theoretical calculations without disorder with experiment will give us insight into the role of disorder on the low-lying excitations in these systems.

The ^{3}He system is similarly described by a Mott-Hubbard model [15] Hamiltonian

$$H = -t\sum_{i,\sigma}^{N_m}(f_{i\sigma}^\dagger f_{i+1\sigma} + \text{H.c.}) + U\sum_{i}^{N_m} n_{i\uparrow}n_{i\downarrow} + V\sum_{i}^{N_m} n_i n_{i+1}\,. \tag{2}$$

Here the fermion destruction ($f_{i\sigma}$) and creation ($f_{i\sigma}^\dagger$) operators associated with state i and spin σ satisfy the usual anticommutation rules, and $n_{i\sigma}$ has eigenvalues 0 or 1. The total number of fermions at site i is $n_i = n_{i\uparrow} + n_{i\downarrow}$. We first ignore the spin degrees of freedom of the ^{3}He atoms and treat them as spinless fermions (SF's) and later discuss the effects of including spin. Since He-He repulsion is quite strong when two atoms occupy the same binding site we let $U \to \infty$. Then n_i can have eigenvalues 0 or 1 for both bosons and fermions. In this limit both B and SF systems can be described by a single Hamiltonian.

$$H_{B(\text{SF})} = -t\sum_{i=1}^{N_m}(c_i^\dagger c_{i+1} + \text{h.c.}) + V\sum_{i=1}^{N_m}(n_i n_{i+1})\,, \tag{3}$$

where $c_i = b_i$ (f_i) and $n_i = c_i^\dagger c_i = 0$ and 1. The differences between B and SF lie in the commutation properties of the operators and different transfer energies t for ^{3}He and ^{4}He due to their mass difference. For the same t and V, the spectra of B and SF are identical for an open chain [16]. As discussed below, the same is true for periodic chains (the ring geometry in our case) when n ($= \sum n_i$) is *odd*. However, for *even* n, the corresponding spectra are different. Thus, in addition to the mass difference, the different statistics will give rise to differences in the heat capacities of the ^{3}He and ^{4}He systems in this ring geometry. In fact, we will argue that the difference in the statistics can explain the observed [3] trend in C, whereas the mass difference goes the other way.

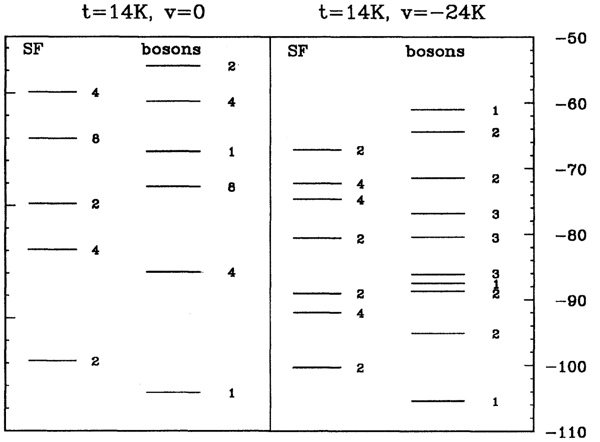

FIG. 2. Lowest 20 (out of 70) energy states of SF and B for four particles in an eight-site ring. The energy values are in K. The hopping parameter $t = 14$ K and the two values of intersite attractive interaction V are 0 and –24 K [see Eq. (3)].

The statistics-induced differences between B and SF systems can be seen by writing down the Hamiltonian matrix in localized (on the ring sites) representation. We denote the system of N_m sites and n particles as (N_m, n). For the same t and V, one gets identical matrices for the two systems when n is odd [16]. Therefore the corresponding energy spectra and C are also identical. When n is even, they differ considerably. An example is shown in Fig. 2 for the system (8,4). It has $8!/(4! \times 4!) = 70$ states. For finite t and $V = 0$, the SF states can be obtained simply by singly occupying the one-particle states $k_i = (\pi/4)(0, \pm1, \pm2, \pm3, 4)$ with energy $-2t\cos k_i$. But if $V \neq 0$ one must diagonalize the 70×70 matirx. The lowest 20 states for both $V = 0$ and

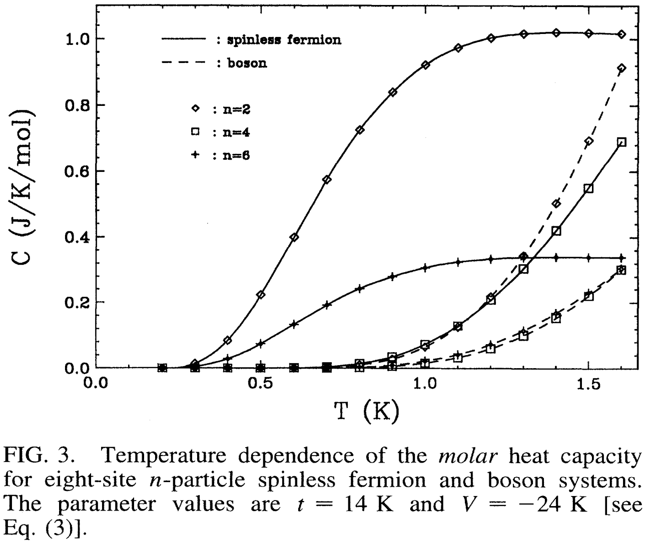

FIG. 3. Temperature dependence of the *molar* heat capacity for eight-site n-particle spinless fermion and boson systems. The parameter values are $t = 14$ K and $V = -24$ K [see Eq. (3)].

$V \neq 0$ are shown in Fig. 2. The energy spectrum depends sensitively on the statistics and intersite attraction. One characteristic feature of these results is that for SF each energy level is always $2n$-fold degenerate, whereas for B the levels can be either $2n$ or $(2n + 1)$-fold degenerate.

In Fig. 3, we show the T dependence of the molar heat capacity $N_A C(n,T)/n$ for the (8,4) system for difference even values of n. Here, N_A is Avogadro's number. Bosons are found to have much smaller heat capacity than spinless fermions. The reason for this is that for the same t and V the lowest energy gap for the bosons is found to be larger than that for the spinless fermions. Since for odd n, B and SF systems have identical spectra (for same t and V) and therefore the same heat capacity, one can use the odd-n results to extract the effect of mass difference (through t). The observed results for the even-n case would, in principle, disentangle the effects of mass and statistics on the heat capacity. In practice it may not be easy since one usually measures C as a function of $\langle n \rangle$, the mean occupation number of atoms/cage.

We obtain the theoretical results for $C(\langle n \rangle, T)$ as follows. Using the computed spectra for different n, we compute the partition function $C(n,T)$ and the distribution function $P(n,T)$ that a given cage has n atoms at T. In the experiments, Kato *et al.* heated and quenched the system at T_0 ($\cong$20 K) and measured C at $T < 2$ K $\ll T_0$. Hence we use $P(n, T_0)$ in the expression for $C(\langle n \rangle, T)$ and write

$$C(\langle n \rangle, T) = \sum_{n=0}^{8} C(n,T) P(n,T_0), \tag{4}$$

where

$$\langle n \rangle = \sum_{n=0}^{8} n P(n,T_0).$$

The $C(\langle n \rangle, T)$ vs $\langle n \rangle$ or T so obtained are compared with the experiment. We calculate $P(n, T_0)$ by using the grand canonical ensemble.

As regards the parameter values, we have estimated [17] V to be about -20 K $- -25$ K. A large component of this attraction comes from the three-body He-K$^+$-He interaction. The hopping parameter t was chosen such that the heat capacity for both the systems is of the same order as the experiment ($\approx$0.6 J/K mol at $T \approx 1.5$ K). With the same parameter values we calculate C for both ^{3}He (using the SF model) and ^{4}He to see the effects of statistics. We then consider the effect of mass difference by changing t.

Figure 4 gives the theoretical values of $C(\langle n \rangle, T)$ for ^{3}He (treated as a SF) as a function of $\langle n \rangle$ and T for three different T values. As expected, $C = 0$ when $\langle n \rangle = 0$ and 8 when the sites are either all empty or all full. The rapid increase in C as one moves away from these two limits and a relatively flat structure of C for $2 < \langle n \rangle < 6$ is reproduced nicely in our calculations. The theoretical values agree qualitatively with experiment near 1.5 K but the agreement gets worse at lower temperatures. For ^{4}He, we also see a similar n-dependence, but with the choice of the same parameter values the theoretical values of C are too small compared to the experiment, particularly at low T.

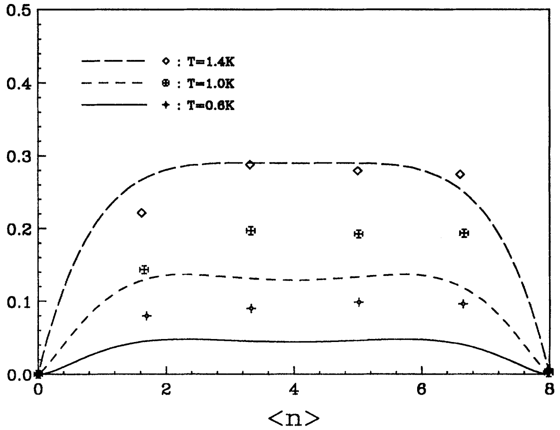

FIG. 4. Heat capacity for spinless fermions as a function of $\langle n \rangle$, average number of particles per cage, at three different temperatures. The symbols are experimental values for ^{3}He (Ref. [3]). Theoretical values have been obtained using $t =$ 14 K and $V = -24$ K [see Eq. (3)].

In Fig. 5, we show, for the SF system, the T dependence of C for three different values of $\langle n \rangle$. The qualitative T dependence and the order of magnitude agreement between theory and experiment (shown as inset) looks reasonable. For the bosons, our calculated C drops much faster with T compared to experiment. A plausible reason for this may be that t is too large. Since ^{4}He is heavier than ^{3}He, we expect the value of t to be smaller for ^{4}He. This will

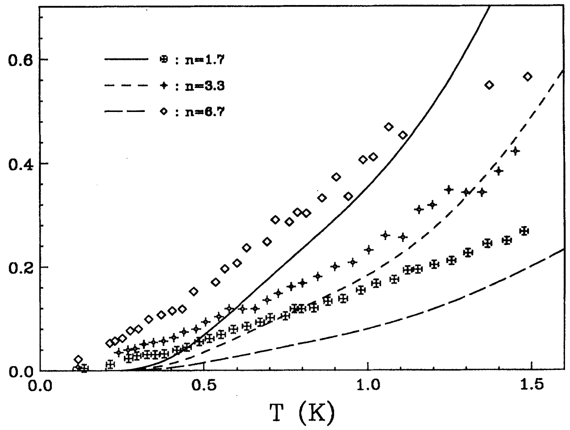

FIG. 5. Temperature dependence for heat capacity of the spinless fermions for three different values of $\langle n \rangle$, average number of particles per cage. The lines refer to the theoretical results and the symbols refer to the experimental results of Kato *et al.* (Ref. [3]) for ^{3}He.

reduce the excitation energy and hence increase the low-T heat capacity. For example, for the system (8,4), if we choose $t = 12$ K instead of 14 K, the lowest energy gap Δ changes from 10.3 K to 7 K. This reduction in Δ increases the heat capacity at 1 K from 0.015 to 0.189 J/K mol, an increase by nearly a factor of 10. We find that for $\langle n \rangle = 1.67$, our theoretical value is 0.344 J/K mol compared to the experimental value of 0.4 J/K mol. However, the theoretical values are still too small at temperatures less than 0.5 K. From the above discussions, we see that (i) the difference in statistics leads to a larger heat capacity for the spinless fermions, whereas the mass difference, through a smaller excitation energy gap, leads to a larger heat capacity for the bosons, and (ii) theoretical values are smaller than experiment at very low T.

Inclusion of spin for ^{3}He dramatically increases the dimension of the Hilbert space. For example, if we include spin in the system (8,4), the manifold of states we have to consider is 1120 instead of 70 for the spinless fermions. But, if the spin and translational degrees of freedom had decoupled [18], as in the case of an open chain geometry or an infinite system (both with $U = \infty$), then the T dependence of C would have been identical for the SF's and fermions except for a delta function at $T = 0$ for the latter; the total number of states associated with this peak being 2^4. On the other hand, for the ring geometry, the spectra of SF and fermions differ from each other, and, in principle, the heat capacities will be different. Furthermore, for fermions, one has to take into consideration the lack of thermal equilibration between states differing in total spin quantum number as in the classic ortho and para hydrogen (H_2) problem [19].

In (8,2) and (8,3) systems, assuming thermal equilibrium takes place between states with the same total spin quantum, number, we find that $C(2,T)$ is smaller and $C(3,T)$ is larger compared to the corresponding SF values. Thus we believe that inclusion of spin and averaging over n will not change $C(\langle n \rangle, T)$ very much when we include spin for ^{3}He. However, a detailed calculation with proper consideration of equilibration between states of different total spin can confirm this conclusion.

In summary, we have shown that the low-T thermodynamic properties of ^{3}He and ^{4}He atoms trapped inside the cages of K-L zeolite can be modeled by Mott- (Bose-)Hubbard rings. The *ring* geometry brings out nicely the differences between bosons, spinless fermions, and fermions. Our work also suggests that at very low T, effects of disorder are important. In fact, the He-zeolite system that we have discussed here provides a microscopic model of tunneling states in disordered systems such as glasses, which are known to exhibit a linear T heat capacity at low temperatures.

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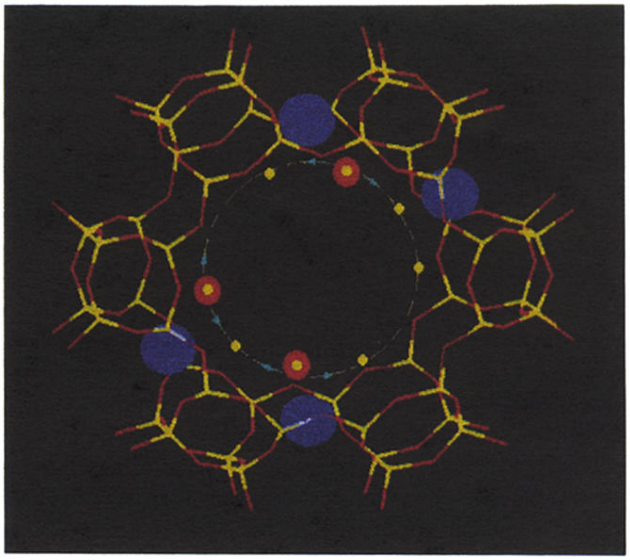

FIG. 1. Schematic picture of a K-*L* zeolite channel showing the silicate framework and ring arrangement of He adsorption sites (medium size circles). Large and small circles are, respectively, K^+ ions along the channel walls and adsorbed He atoms.