Effect of tunneling disorder on the low-temperature heat capacities of ^{3}He and ^{4}He in zeolite channels

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In an earlier work, interacting helium atoms confined inside *K-L* zeolite cages at low concentrations and low temperatures were assumed to tunnel between equivalent sites located near the cage wall. The corresponding Bose-Hubbard (for ^{4}He) and Mott-Hubbard (for ^{3}He) models yield heat capacities in reasonable agreement with experiments except at very low temperatures. Here we study the effect of disorder by extending the model by taking a random distribution of tunneling parameters, computing the energies and averaging the heat capacity using different probability distributions. This approach to a quantitative evaluation of the effects of disorder on the low-T heat-capacity yields results in much better agreement with experiment. [S0163-1829(96)03941-0]

I. INTRODUCTION

Experiments have been performed to study the thermal properties of helium atoms imbibed into *K-L* zeolite at low temperatures.[1] The microporous medium of *K-L* zeolite consists of open cylindrical aluminum-silicate cages arranged periodically and connected by smaller cylindrical tubes. The potassium ions close to the cage wall, together with the silicate framework, produce potentials which bind helium atoms at sites located near the wall. These binding sites are arranged in a ring geometry inside the cage. In a typical heat-capacity measurement, one determines the average number $\langle n \rangle$ of helium atoms per zeolite cage and measures the heat capacities of ^{3}He and ^{4}He as a function of temperature T for different values of $\langle n \rangle$. When the number (n) of He atoms per cage is less than a critical number, say n_c, the He atoms remain mostly confined within a particular cage at low temperatures with an extremely small probability of moving from one cage to another.[1,2] However, such atoms can tunnel from one binding site to another on the ring sites inside a particular cage and are said to exist in the ''cage states.'' [3] When n exceeds n_c, or for sufficiently high temperatures (even when $n<n_c$), some of the He atoms can overcome the barrier for intercage motion and move between cages. Such states of motion are called the ''channel states.'' [2,3] The present investigation is concerned with the heat capacity of the He atoms occupying the cage states.

In our earlier work,[3] we had argued that the excitation of He system within the manifold of the ''cage states'' (for $n<n_c$) can be described by Bose-Hubbard (for ^{4}He) or Mott-Hubbard (for ^{3}He) model with binding sites localized on a ring. Physically, the K^+ ions located close to the cage walls and the silicate network provide the potential in which the He atoms are bound. But the K^+ ions are not necessarily situated symmetrically around the ring. As a matter of fact, there are six equivalent sites available for the K^+ ions and a maximum of only four K^+ ions are available per cage to occupy these sites randomly. In addition there is disorder in the silicate framework because some of the silicon ions are randomly replaced by aluminum ions and K^+ ions not located near the cage wall are also randomly distributed inside the silicate framework. This random distribution of the ions can give rise to disorder in the physical parameters of the Hubbard-type models describing the excitations of the He system, namely the single-site binding energy, intersite tunneling matrix elements (also called hopping parameters), etc. Consequently the low-temperature heat capacity will be affected by the disorder. In this paper, we extend the earlier model[3] by introducing the effects of disorder, treating the hopping parameters as random variables and computing the average heat capacity of the He system using different probability distributions.

The presence of disorder, as noted in the previous work,[3] is expected to improve agreement of the computed results with experiment. This is so because the system without disorder has low-lying energy levels which are discrete (due to the small size) and separated from one another. Suppose the lowest energy gap is Δ. Then, the heat capacity of the system must exhibit a Schottky-type anomaly,[4] leading to an exponentially decreasing heat capacity at temperatures $T \ll \Delta/k_B$. In the present case, the discrete energy levels of the system calculated in the earlier work[3] lead to Δ/k_B greater than 5 K. Hence one gets vanishingly small heat capacity at temperatures below 0.5 K. In the presence of disorder the low-lying excitation spectrum is drastically modified and there is an increase in the density of low-energy excitations arising primarily from the region of smaller hopping parameters. This results in an enhancement of the heat capacity at low temperatures when a proper averaging over the various disorder states is performed.

A model of disorder which was proposed to explain the enhanced heat capacities seen in disordered solids at low temperature is specially relevant to the present work. This rather simple model by Kaplan, Mahanti, and Hartmann (KMH)[5] within the context of standard Hubbard model has three characteristic parameters; single-site energy (ϵ), tunneling matrix element (t), and intrasite Coulomb interaction (U). In the KMH model, the single-site energies (ϵ_i) are assumed to be random, $t=0$, $U=$const. For a continuous

distribution of ϵ_i one obtains a heat capacity linear in T at low T. In the context of Hubbard-type models, our present model is an *extension* of the KMH model taking into account a finite but random t, constant ϵ_i, $U=\infty$, and a finite intersite Coulomb interaction V. In the most general case, all the parameters of the Hamiltonian can be random.

Although mathematically our present model is an extension of the KMH model,[5] physically it is much closer to the one proposed by Anderson, Halperin, and Varma (AHV)[6] and by Phillips.[7] This model was proposed to explain the observed low-temperature specific heat varying linearly with T in a variety of insulating glasses. The essence of the model is the hypothesis that in any glass system there should be a certain number of atoms (or group of atoms) which can occupy one of several equivalent equilibrium positions. The thermal excitation between the associated localized ''tunneling levels'' leads to a Schottky-type heat capacity with a characteristic energy Δ. A statistical distribution $P(\Delta)$ with finite $P(\Delta=0)$ of these localized tunneling levels (LTL's), also referred to as two-level systems, gives a linear heat capacity at low T. Although this model describes the correct physics of the observed large low-T heat capacity in insulating glasses, a microscopic picture of these LTL's in disordered systems is not easy to come by.[8] Our model of helium atoms trapped inside zeolitic cages with random tunneling matrix elements indeed gives a microscopic picture of these LTL's.

It is in general quite difficult to compute thermodynamic quantities by introducing disorder in the Hamiltonian and then averaging over the disorder. The ring geometry with a small number of sites in the present problem leads to some simplifications, but even then, the computations are quite involved. Therefore, only some calculations illustrating the important trends at low temperatures are presented below. Nevertheless, the numerical evaluation of the effect of disorder by introducing randomness and computation of the average heat capacities is an important feature of the present work. It must be emphasized that the goal of the present paper is to show the improvements in the computed low-temperature specific heat by including disorder rather than fitting the experimental results exactly.

The essential details of the model used in the previous work[3] are briefly described in the next section and the model Hamiltonian is generalized in the presence of disorder in Sec. III. Results for the computed heat capacities are presented in the last section followed by a brief discussion.

II. THE MODEL WITHOUT DISORDER

The Mott-Hubbard and Bose-Hubbard models developed for ^{3}He and ^{4}He, respectively, confined inside zeolite cages have been described in detail in the previous publication.[3] For reasons described earlier,[3] we ignore the spin states of ^{3}He and treat it as spinless fermions (SF). ^{4}He is of course a boson (B). The system is described by (N_m,n) where n is the number of He atoms and there are N_m sites ($\geqslant n$) on a ring where the He atoms can sit. In the Hubbard model with very strong intrasite repulsion (very strong repulsion when two atoms occupy the same binding site), $U=\infty$, and the Hamiltonian (for both B and SF) can be written as

$$H_{B(\mathrm{SF})}=-t\sum_{i=1}^{N_m}(c_i^{+}c_{i+1}+\mathrm{H.c.})+V\sum_{i=1}^{N_m}n_in_{i+1}, \qquad (1)$$

where t is the hopping parameter (energy), V is the attractive energy between atoms occupying neighboring sites, $c_i(c_i^{+})$ is particle destruction (creation) operator at the site i, and $n_i(=c_i^{+}c_i)$ is the number operator. In the case of bosons (B), one uses the commutation rules for c_i and c_i^{+} while anticommutation rules are imposed in the case of spinless fermions (SF). The single-site energies have been assumed to be the same and define the zero of the energy scale. Computing the energy spectrum for the Hamiltonian of Eq. (1), one can find the partition function and the heat capacity $C(n,T)$ for $n\leqslant N_m$, and $n\geqslant n_c$ atoms tunnelling on the ring at temperature T.

It is practically impossible to introduce exactly the same number n of He atoms in all the zeolite cages. In fact, the sample is heated as the He atoms are introduced and then quenched at a temperature T_0 which is of the order of 20 K in the experiments of Kato *et al.*[1] The heat-capacity measurements are however done at a much lower temperature denoted by T, in the range of 0–2 K. At the quenching temperature there is a fluctuation in the number of atoms from one cage to another. Due to the lack of intercage thermal equilibration at lower temperatures where the heat capacity is measured, we assume that the distribution of n is determined by the quench temperature T_0. We define the distribution function $P(n,T_0,\mu)$ for a cage to have n atoms at a temperature T_0 and a given chemical potential μ. If the system is heated and then *quenched at temperature* T_0, then the average number of particles per cage is

$$\langle n\rangle=\sum_{n=1}^{N_m}nP(n,T_0,\mu). \qquad (2)$$

Thus, $\langle n\rangle$ is independent of the temperature T at which the heat capacity is measured. The heat capacity at temperature T corresponding to the number distribution $P(n,T_0,\mu)$ is given by

$$C(\mu,T)=\sum_{n=1}^{N_m}C(n,T)P(n,T_0,\mu). \qquad (3)$$

Eliminating μ (which is just a parameter now) between Eqs. (2) and (3), one obtains $C(\langle n\rangle,T)$. Note that we have used $P(n,T_0,\mu)$, not $P(n,T,\mu)$, in calculating the heat capacity at temperature T. This takes into account the fact that the number fluctuations from cage to cage and the average number of He atoms per cage is determined by the quench temperature T_0. The above equations were used to obtain the results given in the earlier work.[3] Comparison with experiment showed fair agreement at temperatures above 1 K. But at low temperatures, the computed heat capacities were considerably smaller than the experimental results. Also, the computed heat capacity vanished around $T=0.25$ K whereas the experimental results were nonzero down to about $T=0.1$ K. Since the computed results reflected the Schottky-type anomaly, it was clear that important contributions at low temperatures would come from the effects of disorder following the ideas of AHV.[6]

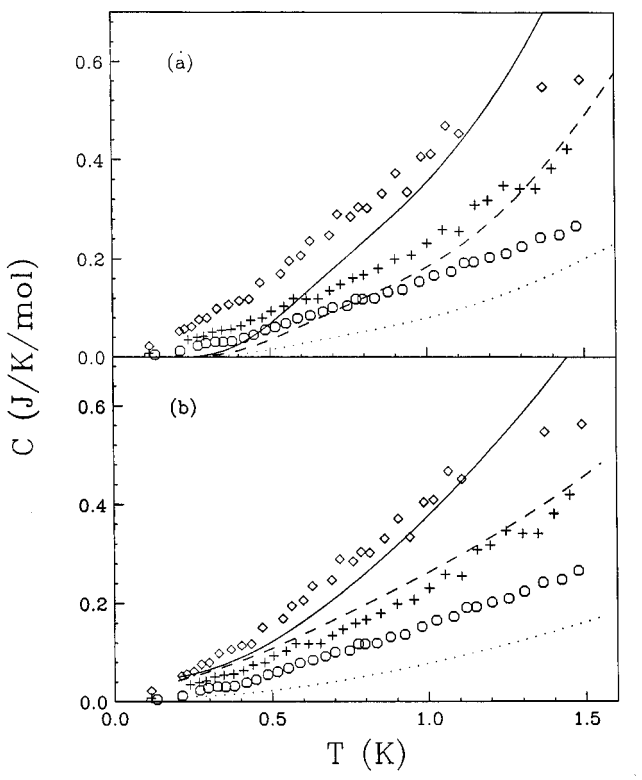

FIG. 1. Heat capacity vs temperature for different $\langle n\rangle$, the average concentration of ^{3}He atoms, treated as spinless fermions. The solid, broken, and dotted lines are the results of our calculations for $\langle n\rangle=6.7$, 3.3, 1.7, respectively, and the corresponding experimental results are shown as open circles, crosses, and diamonds. (a) is without disorder and the parameter values are $t=-14$ K, $V=-24$ K. (b) is with disorder, and the parameter values are $t_0=-17$ K, $V=-24$ K, and $\sigma=7$ K.

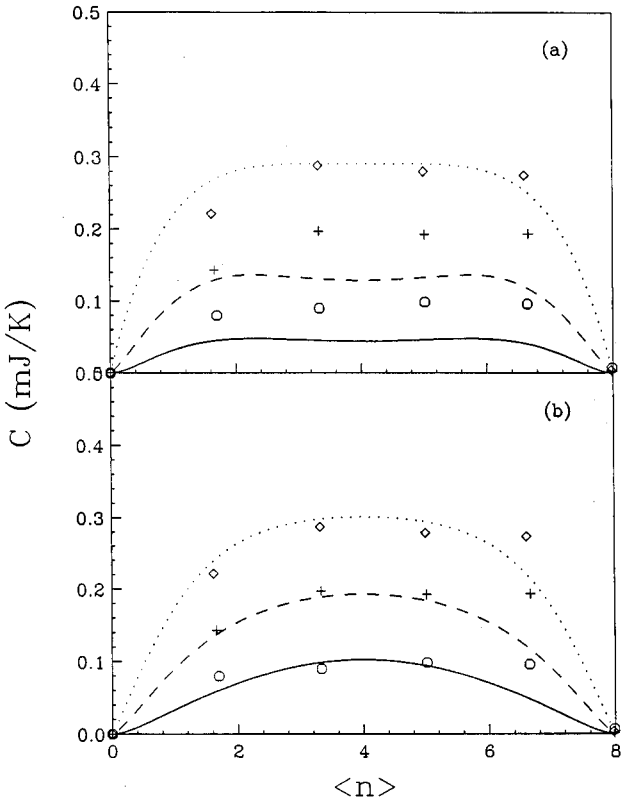

FIG. 2. Heat capacity vs average helium atom concentration $\langle n\rangle$ for fixed temperatures for ^{3}He (treated as spinless fermions). The solid, broken, and dotted lines are the results of our calculations for $T=0.6$, 1.0, and 1.4 K, respectively, and the corresponding experimental results are shown as open circles, crosses, and open diamonds. (a) corresponds to no disorder with parameter values $t=-14$ K, $V=-24$ K. (b) includes disorder with parameter values $t_0=-17$ K, $V=-24$ K, and $\sigma=7$ K.

III. THE MODEL WITH DISORDER

Disorder in the system can arise due to various reasons. One reason could be the random occupation of K^+ ion sites by the ions. Distortions, imperfections, etc. would give rise to additional disorder. In terms of the Hamiltonian, there can be randomness in the single-site energies [which were assumed to be zero in Eq. (1)], tunneling parameter t, and the attractive potentials V. For simplicity, we consider only the disorder in the tunneling parameters in the present paper. Then, the Hubbard Hamiltonian may be written as

$$H_{B(\mathrm{SF})}=-\sum_{i=1}^{N_m} t_i(c_i^+ c_{i+1}+\mathrm{H.c.})+V\sum_{i=1}^{N_m} n_i n_{i+1}, \qquad (4)$$

where the tunneling parameters are random numbers which may follow some distribution function $f(t_i,\sigma)$, with σ defining some kind of ''width'' for the distribution. Note that the number operator n_i has eigenvalues of 0 or 1 in the case of both bosons (B) and spinless fermions (SF) in the limit of infinite intrasite repulsion ($U=\infty$). The heat capacity for a given set of $\{t_i,\ i=1,\ldots,8\}$ can be obtained by

$$C(n,T,\{t_i\})=(\langle E^2\rangle-\langle E\rangle^2)/k_B T^2. \qquad (5)$$

In Eq. (5), the thermal averaging $\langle E^p\rangle$ is done with the help of the exact partition function.

Next, one must perform the configurational averaging for disorder. Let $f(t_i,\sigma)$ be the distribution function for the random variable t_i with σ denoting its width. We have chosen Gaussian distributions for the random tunneling parameters: $f(t_i,\sigma)=\sigma\sqrt{\pi}\,\exp[-(t_i-t_0)^2/\sigma^2]$. These distributions are symmetric around $t_i=t_0$. We have also used a uniform distribution in our calculations. The heat capacity for the canonical ensemble may be configurationally averaged over the disorder as follows:

$$C(n,T)=\int_{-\infty}^{+\infty}\cdots\int_{-\infty}^{+\infty} C(n,T,t_1\cdots t_8)\times f(t_1,\sigma)\cdots f(t_8,\sigma)dt_1\cdots dt_8, \qquad (6)$$

The integration is performed numerically by using Gaussian quadrature. This gives the disordered averaged heat capacity for a *fixed* value of n, i.e., for a canonical ensemble.

To obtain the heat capacity as a function of $\langle n\rangle$ rather than a fixed n, we need an appropriate grand canonical ensemble distribution function for the disordered system. We have to generalize the distribution function $P(n,T_0,\mu)$, defined in Sec. II, to the disordered case. Let this function be $P(n,T_0,\mu,\{t_i\})$. One obtains $\langle n\rangle$ and $C(\mu,T)$ as functions of μ after replacing $P(n,T_0,\mu)$ by $P(n,T_0,\mu,\{t_i\})$ in Eqs.

(2) and (3), and integrating over the distribution functions for t_i's as in Eq. (6) above. Eliminating μ between $\langle n \rangle$ and $C(\mu,T)$ gives $C(\langle n \rangle,T)$ for the disordered system. Although straightforward, in principle, this is an extremely involved procedure in practice. We have made a simplifying assumption where we replace $P(n,T_0,\mu,\{t_i\})$ by $P(n,T_0,\mu,\{t_i=t_0,\forall i\})$ which corresponds to the distribution function for a system without disorder (mean ensemble) and with all tunneling matrix elements equal to t_0. We have tested the adequacy of this approximation in a few cases and find it to be reasonable. Physically this implies that the effect of disorder on number fluctuation is much less compared to that on the low-energy thermal excitations and hence the heat capacity for fixed n.

IV. RESULTS AND DISCUSSIONS

Before presenting our results for the eight-site system appropriate to the He atoms inside *K-L* zeolite let us discuss a simpler system consisting of four sites and two spinless ^{3}He atoms. This will help us elucidate the nature of the tunneling states in this system. In the absence of tunneling ($t=0$), and $V=-24$ K as estimated in Ref. 3, the ground state is fourfold degenerate corresponding to bound pairs with two He atoms occupying the pairs of ring sites (1,2), (2,3), (3,4), and (4,1). The excited state is twofold degenerate corresponding to the unbound pairs (1,3) and (2,4). The energy splitting between the ground and the excited state is 24 K, quite large. The energy is measured in units of the Boltzmann constant k_B. In the presence of nonzero t, the ground-state degeneracy is lifted partially. The spectrum now consists of three doublets which, for $t=-7$ K, have energies -30.44, -24, and $+6.4$ K, respectively. The lowest energy gap reduces dramatically from 24 to 6.44 K. One can physically think of this splitting as resulting from tunneling of a bound pair from one configuration to another. This lowest energy gap depends on t in a nonlinear fashion. For example, the three values of the gap corresponding to $t=-7$, -14, and -20 K are, respectively, 6.44, 18.46, and 29.76 K. Thus for a distribution of t, one expects to see smaller energy gaps and hence an increased heat capacity at low T.

Next we present the numerical results for the eight-site system. Since in Ref. 3 we concentrated on the spinless fermion model we will discuss in detail the effects of disorder for this system. Although we have carried out numerical calculations with both uniform and Gaussian distributions it suffices to discuss results for the latter case only because the qualitative results are similar for both the distributions. We kept the intersite attraction parameter V to be the same as in the nondisordered case and varied the mean value of the tunneling parameter t_0 and the width of the Gaussian distribution σ to get an optimal fit with experiment for different values of $\langle n \rangle$ and T. The parameter values for which we present our results are $t_0=-17$ K, $V=-24$ K, and $\sigma=7$ K. The ratio of the disorder parameter to the mean band width is about 0.2 which looks quite reasonable. Figure 1 gives the results of temperature dependence of the heat capacity for specific values of $\langle n \rangle$ without [Fig. 1(a)] and with [Fig. 1(b)] disorder. As we can see, the effect of disorder is to *enhance* the low-T heat capacity. Figure 2 gives the results of $\langle n \rangle$ dependence of the heat capacity without [Fig. 2(a)] and with [Fig. 2(b)] disorder. Agreement with experiment for values of $\langle n \rangle$ less than 6 is quite good but there is a large discrepancy between our calculations and the experiment for $\langle n \rangle$ larger than 6. We do not understand the reason for this rather large discrepancy. In summary, the effect of including disorder clearly improves the agreement with experiment although detailed quantitative agreement is still lacking. We have carried out similar calculations for the Bose system and also find dramatic improvement vis-a-vis experiment at very low temperatures.

ACKNOWLEDGMENTS

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