Correlated Random-Chemical-Potential Model for the Phase Transitions of Helium Mixtures in Porous Media

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A lattice model is constructed for ^{3}He-^{4}He mixtures in porous media, characterized by correlated random chemical-potential differences between isotopes. Sites with high chemical-potential differences form a random connected porous structure, similar to silica strands in aerogel. We find by Monte Carlo simulation that the bulk tricritical phase diagram is replaced: The λ line extends to zero temperature, as had been theoretically predicted some time ago, and phase separation occurs within the superfluid phase. These findings and the behavior of the order parameter agree with recent experiments.

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It has been argued that the introduction of quenched bond randomness has a drastic effect on all temperature-driven first-order phase transitions [1,2]. If the first-order phase transition involves symmetry breaking, it is converted to a second-order phase transition, according to the argument. It now appears that this general prediction has been confirmed experimentally with ^{3}He-^{4}He mixtures in aerogel [3]. In the present Letter, we analyze this experiment by constructing and studying a microscopic model for ^{3}He-^{4}He mixtures in aerogel. We find that the first-order portion of the superfluid phase transition is converted to second order, as mentioned above, and that a distinct phase separation occurs within the superfluid phase, understandably within the context of the theoretical argument [1,2]. These results, as well as our calculated order parameter behavior, agree with the experiment [3].

Silica aerogel is a highly porous material composed of silica strands in a random, dilute, interconnected structure [4–6]. The high porosity allows the immersion of a fluid into a fixed randomly varying microscopic environment depending on the degree of proximity of silica strands. Thus, an ideal platform obtains to study the effect of quenched randomness on collective behavior and has already been used to examine binary-liquid [7], liquid-gas [8], and liquid-crystal [9] phase transitions. In these cases, however, the quenched randomness imposed by the aerogel couples directly to the ordering degrees of freedom, thus yielding a random-field situation [10,11]. ^{3}He-^{4}He mixtures in aerogel are qualitatively different from the aforementioned cases. The random nature of the aerogel does not couple to the ordering, namely superfluid, degrees of freedom but couples to the nonordering degrees of freedom of concentration fluctuations. Because of its higher mass, therefore lower zero-point motion, ^{4}He has a higher preference to reside close to the aerogel strands, whose random distribution thus yields a random yet correlated (by the connectivity of the strands) chemical-potential difference situation. In this problem, the chemical-potential difference is a bond type of interaction, since it is invariant under the (superfluid) symmetry that is broken at the phase transition. Thus, ^{3}He-^{4}He mixtures in aerogel yield a random-bond situation.

A microscopic model introduced for bulk ^{3}He-^{4}He mixtures (no aerogel) is the Blume-Emery-Griffiths (BEG) model [12], with Hamiltonian

$$-\beta\mathcal{H} = \sum_{<ij>} J s_i s_j + \sum_{<ij>} K s_i^2 s_j^2 - \sum_i \Delta s_i^2 , \qquad (1)$$

where $s_i = 0, \pm 1$ at each site i of a lattice and $<ij>$ indicates summation over all nearest-neighbor pairs of sites. Occupation of site i by a ^{3}He or ^{4}He atom is represented by $s_i = 0$ or $s_i = \pm 1$, respectively, with the sign in the latter case representing the superfluid degree of freedom. Under this identification, J is a potential promoting superfluidity, $K = K_{33} + K_{44} - 2K_{34}$ reflects the (small) difference in interactions between the isotopes, and Δ is the chemical-potential difference between the isotopes. All of these quantities have been rendered dimensionless by absorption of a factor of β. The results shown here for mixtures are for $K = 0$. This model yields the phase diagram for bulk ^{3}He-^{4}He mixtures [open circles in Fig. 1(a)], where the superfluid and normal fluid are separated by a second-order phase boundary (the so-called λ line) at high temperatures and high ^{4}He concentrations and by the coexistence region of a first-order phase transition at low temperatures.

We therefore model ^{3}He-^{4}He mixtures in aerogel with the BEG model, but with a chemical-potential difference that is site dependent, Δ_i, with lower values occurring along the randomly connected strands. Randomness in Δ_i does not break up-down symmetry in s_i (a.k.a. superfluid ordering symmetry) and therefore is an example of quenched bond randomness. In fact, under scale change, the other two bond strengths in Eq. (1) also become random as J_{ij} and K_{ij}, but of course no random fields are generated [13,14]. Renormalization-group calculations on the BEG model with uncorrelated quenched bond randomness have shown that the first-order transitions are converted to second-order transitions [13,14].

Here, to study ^{3}He-^{4}He mixtures in aerogel, correlations (along the strands) in the quenched random

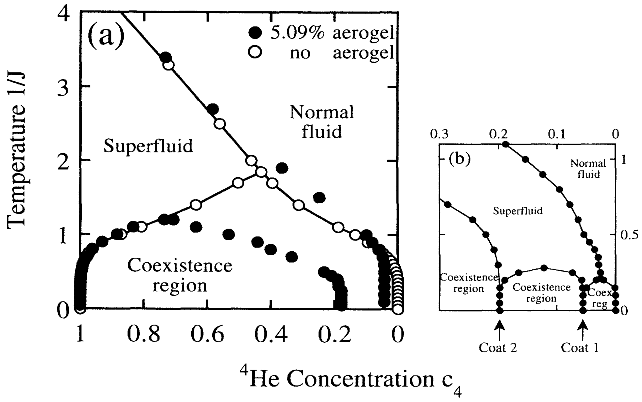

FIG. 1. (a) Calculated phase diagram for ^{3}He-^{4}He mixtures with no aerogel (open circles) and with 5.09% aerogel (dark circles) having $\varepsilon_0/J = -2.5$. The superfluid and normal fluid phases are marked. The coexistence region is characterized by superfluid-normal coexistence with no aerogel and by dense superfluid-dilute superfluid coexistence with aerogel. In the latter case, the onset of superfluidity is always via a second-order phase transition: The λ line reaches zero temperature. Phase separation occurs entirely within the superfluid phase. These results agree with the experiment of Ref. [3] and are explained by the earlier general argument of Refs. [1] and [2]. (b) Changes in the phase diagram when randomness is removed. The strands are arranged in a regular jungle-gym net and $\sigma = 0$ in Eq. (3).

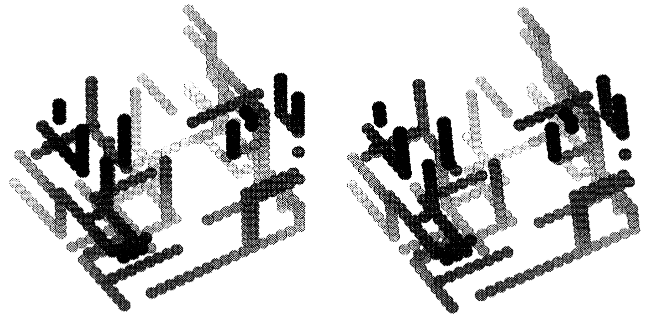

FIG. 2. Stereoscopic computer aerogel used in our study.

chemical-potential differences are used [15]. We have performed Monte Carlo simulations on $L \times L \times L$ cubic lattices, for $10 \leq L \leq 36$, with periodic boundary conditions, using the standard Metropolis importance sampling method. The first part of our analysis was to "grow" a random, connected structure that mimics the effect of aerogel in our $L \times L \times L$ lattice, using a procedure that parallels the actual laboratory procedure used to manufacture aerogel [5]. We begin with a single strand which is allowed to grow a random length between 1 and $L/2$. This strand is then branched into two strands which are each allowed to grow a random length. The process is repeated until the desired density of aerogel is achieved. This method yields a dilute, extensive, and connected structure with a random distribution of pore sizes, consistent with the experimental data on aerogels [4,6]. We have used aerogel densities ranging between 2% and 6% to match the experiment with ^{3}He-^{4}He mixtures [3]. Figure 2 depicts one of our computer aerogels.

The chemical-potential differences were taken as

$$\Delta_i = \Delta + \varepsilon_i , \tag{2}$$

where Δ is the bulk chemical-potential difference, and ε_i reflects the effects of the strands. Thus, ε_i was chosen from a Gaussian distribution

$$P(\varepsilon_i) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp[-(\varepsilon_i - \varepsilon)^2/2\sigma^2], \tag{3}$$

where the randomness reflects the atomic-scale disorder of the silica strands. We have used $\varepsilon = \varepsilon_0 \leq 0$ and $\sigma = 0.1\varepsilon_0$ on our computer-generated strands and $\varepsilon = 0.4\varepsilon_0$ and $\sigma = 0.01\varepsilon_0$ on the immediate neighbors of these strands. On all other sites, $\varepsilon_i = 0$.

In our Monte Carlo study, we calculate the densities that are the ^{4}He concentration,

$$c_4 = \left\langle \sum_i s_i^2 \right\rangle / N , \tag{4}$$

where $N = L^3$ is the number of sites, and the superfluid order parameter,

$$M = \left\langle \sum_i s_i \right\rangle / N . \tag{5}$$

Figure 3(a) shows these densities for opposite scans of the chemical-potential difference Δ at fixed temperature $1/J$, in the absence of aerogel. A first-order phase transition can be seen by the hysteresis in these densities. The actual location of the transition was determined by the crossing of free energies evaluated by integration from $J = 0$ and $\Delta = \pm\infty$. Figure 3(b) shows the same scans but with 5.09% aerogel. A first-order phase transition is again seen by the hysteresis, but with the striking feature that the superfluid order parameter M, although discontinuous at this first-order transition, is nonzero on both sides of the hysteresis loop. It goes to zero at a higher chemical-potential difference, without discontinuity, as a second-order phase transition.

Our calculated phase diagram for ^{3}He-^{4}He mixtures in 5.09% aerogel is given by the dark circles in Fig. 1(a). The onset of superfluidity always occurs as a second-order phase transition: This phase boundary, the so-called λ line, stretches from high temperatures and high ^{4}He concentrations to zero temperature and very low ^{4}He concentrations. A phase separation, terminating at an isolated critical point, occurs inside the superfluid phase. The open circles in Fig. 1(a) show, for comparison, our calculated phase diagram of ^{3}He-^{4}He mixtures with no aerogel. The two features mentioned above merge, to give the well-known phase diagram with the λ line terminating at a finite-temperature tricritical point and the onset of superfluidity at lower temperatures occurring with

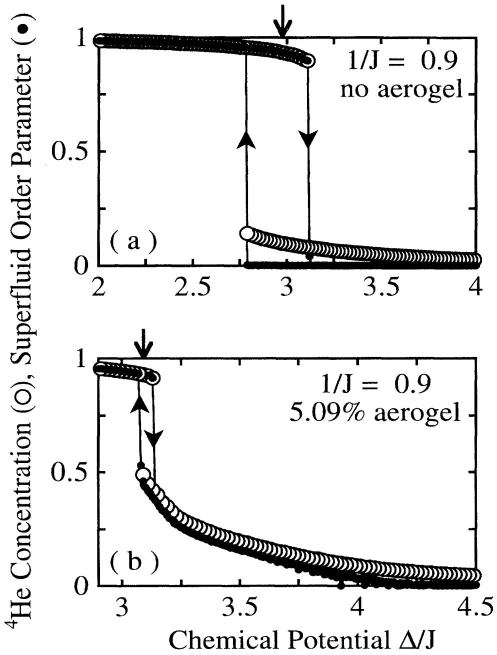

FIG. 3. Calculated ^{4}He concentrations c_4 (open circles) and superfluid order parameters M (dark circles) in ^{3}He-^{4}He mixtures for opposite scans in chemical-potential difference Δ at fixed temperature $1/J$. The arrows at the top indicate the actual locations of the first-order transitions causing the hysteresis loops, determined by the crossing of free energies evaluated by integration from $J = 0$ and $\Delta = \pm\infty$. (a) With no aerogel. (b) With 5.09% aerogel: Note the nonzero superfluid order parameter on both sides of the hysteresis loop.

phase separation. All of these findings are in complete agreement with experiment [3].

The features of the phase diagram for ^{3}He-^{4}He mixtures in 5.09% aerogel can be understood from general results for quenched randomness: (1) The superfluid transition at low temperatures and low ^{4}He concentrations occurs in the vicinity of the aerogel strands. This transition of the ^{4}He atoms in the vicinity of the aerogel strands is subject to quenched bond randomness, due to both the random chemical-potential differences and the random connectivity of the strands. General arguments [1,2] indicate that symmetry-breaking temperature-driven first-order phase transitions are converted to second-order by infinitesimal quenched bond randomness for spatial dimensions $d \leq d_c$ and by a threshold amount of such randomness for $d > d_c$. The crossover dimension is $d_c = 2$ for all transitions [16]. The threshold is needed to overcome the interfacial free energy increase due to the formation of ordered islands inside disordered regions and vice versa. The system of ^{4}He atoms in the vicinity of the aerogel strands is tenuously connected, so that the interfacial free energy increase is low, and understandably the randomness present in the system is above the small threshold for the conversion from first-order to second-order phase transitions. (2) The phase separation phenomenon occurs away from the aerogel strands. For this transition, the order parameter is the ^{4}He concentration, and a quenched random-field situation exists due to the random chemical-potential differences at the peripheral aerogel strands. A phase transition is eliminated [17] by infinitesimal quenched field randomness for $d \leq d_c$, but a threshold amount of such randomness is needed [18,19] for $d > d_c$. For a one-component order parameter, as is the case here, $d_c = 2$. The phase transition occurs in the quasibulk system of ^{3}He-^{4}He away from the aerogel strands, while the field randomness comes from the tenuous peripheral aerogel strands. Understandably, this randomness is below threshold: The transition is depressed in temperature, but not eliminated.

For comparison, we have repeated our calculations after removing randomness from the system: The strands were arrayed in a regular jungle-gym pattern and the distribution widths σ in Eq. (3) were set to zero. Figure 1(b) shows the changes in the phase diagram. As before, the ^{4}He atoms preferentially aggregate along the strands, which provide connectivity across the system, so that superfluidity is achieved even on the ^{4}He-poor side of phase separation [20]. At the lowest temperatures and concentrations, the ^{4}He-poor system undergoes a succession of first-order phase transitions that correspond to ^{4}He coatings around the strands, up to the bulk phase separation. In Fig. 1(b), the coexistence regions of two such transitions are seen to the right of the markings of coats 1 and 2. Across each of these two coexistence regions, a partially filled coating (1 or 2) is completed as c_4 is increased. There are only two here, because a potential ε is used only for the strand sites and, more weakly, for their nearest-neighbor sites. Thus we conclude, of the two new phase-diagram phenomena, that the critical point occurrence inside the superfluid phase is due to the "internal surface" provided by the aerogel, in direct analogy to the same phenomenon seen previously with a usual external surface [20], and that the continuation of the λ line to the lowest temperature that we have checked [see Fig. 1(a)] is due to quenched bond randomness, as predicted by previous theory [1,2].

Alternately to complete fillings of aerogel with ^{3}He-^{4}He mixtures, incomplete fillings with pure ^{4}He were used in several experimental scans, resulting in qualitatively different superfluidity behaviors as a function of temperature [3]. Our model is also immediately applicable to the latter experiments, with $s_i = 0$ now representing the vacuum. This physical system requires larger $|\varepsilon_i|$, representing the full binding energy of ^{4}He rather than the effective binding energy difference between the isotopes, and a larger $K = K_{44} + K_{00} - 2K_{40} = K_{44}$, which represents the full ^{4}He-^{4}He van der Waals interaction rather than the interaction differences between isotopes. Our calculated temperature scans at fixed low ^{4}He concentration for both experiments are plotted together in Fig. 4.

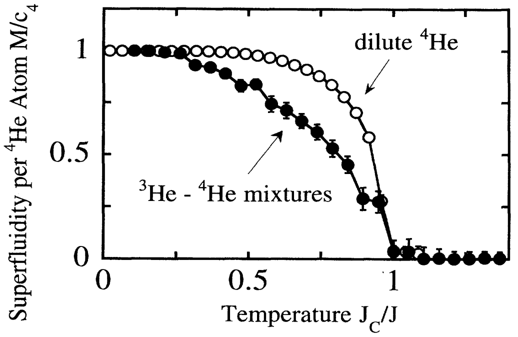

FIG. 4. Calculated superfluid order parameter per ^{4}He atom, M/c_4, as a function of temperature $1/J$ at fixed low ^{4}He concentration c_4 in 5.09% aerogel. Dark circles are for ^{3}He-^{4}He mixtures with $K = 0$, $\varepsilon_0/J = -2.5$, and $c_4 = 0.12$. Open circles are for dilute pure ^{4}He with $K/J = 4$, $\varepsilon_0/J = -15$, and $c_4 = 0.05$. The qualitative difference between the two situations can be understood from the microscopic model.

It is seen that the decay of superfluidity sets in at low temperatures and is much more gradual for the mixture, in agreement with the experiment. The microscopic explanation is apparent from our model: At these low concentrations of ^{4}He, most of the ^{4}He atoms are found in the vicinity of the aerogel strands, and superfluidity occurs through these ^{4}He atoms maintaining connectivity along the strands. As temperature is increased, a ^{4}He atom could be "boiled" away from the vicinity of the strands, decreasing superfluidity, at the energy increase of $qJ + qK - \varepsilon_i$, where q is an effective coordination number of the order of 5. As explained above, K and ε_i reflect the isotopic differences for the mixtures and the full energies for dilute pure ^{4}He. The latter constitute a much higher energy price and the process does not occur. Superfluidity disappears much more abruptly, in standard order parameter behavior at a phase transition, through the dephasing of the connected ^{4}He.

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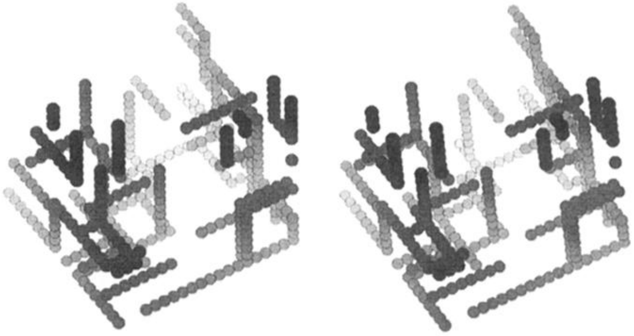

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