Nanoscale Molecular Superfluidity of Hydrogen

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We present a microscopic quantum theoretical analysis of the nanoscale superfluid properties of solvating clusters of para-H_2 around the linear OCS molecule. Path-integral calculations with $N = 17$ para-H_2 molecules, constituting a full solvation shell, show the appearance of a significant superfluid response to rotation around the molecular axis at $T = 0.15$ K. This low-temperature superfluid response is highly anisotropic and drops sharply as the temperature increases to $T \sim 0.3$ K. These calculations provide definitive theoretical evidence that an anisotropic superfluid state exists for molecular hydrogen in this microscopic solvation layer.

Since its discovery more than 60 years ago, the phenomenon of superfluidity has been extensively studied both experimentally and theoretically. While superfluidity in the bulk is well understood today as one of the most prominent macroscopic quantum phenomena, its finite size scaling still raises fundamental questions as well as novel opportunities. The helium liquids ^{4}He (bosonic) and ^{3}He (fermionic) are the only known substances exhibiting bulk superfluidity, although much effort has been expended to find superfluidity in other systems. Molecular hydrogen is a prime candidate for this, with its light mass and the existence of a compound boson ground state ($J = 0$ parahydrogen). However, there is no known superfluid state in bulk H_2, or in any other molecular system. While H_2 is lighter than He, giving rise to a higher ideal Bose-Einstein condensation temperature of 6 K [1], it is nevertheless much more strongly bound. This characteristic results in a triple point at 13.8 K, below which the bulk material is solid. No liquid phase is therefore accessible in the region of the predicted Bose-Einstein temperature. There has been considerable experimental effort to supercool liquid H_2 below the triple point in order to produce a superfluid. Maris *et al.* have attempted several approaches to supercooling H_2–droplets [2]. Others have studied thin H_2–films on various substrates [3,4] or finite sized systems in confined geometries, for example, in porous media [5,6]. So far, however, none of these experimental directions have been successful. On the theoretical side, a number of predictions have been made. Obtaining a lower density than that in bulk solid H_2 appears essential for superfluidity (including the elusive "supersolid" phase [7]). A recent prediction that a superfluid state might be formed in a doped two-dimensional film specifically designed to have such a lower density [8] indicates that restricted dimensionality systems are promising candidates to find this elusive quantum state.

Quantum Monte Carlo calculations by our group and others predicted some years ago that small para-H_2 clusters ($M < 20$ molecules) are liquidlike [9–13], and several studies have subsequently investigated the structure of larger H_2 clusters [14–16]. Path-integral Monte Carlo calculations have shown that the very small pure H_2 clusters ($M < 20$) should be predominantly superfluid below about 1 K [10]. Analogous calculations with mixed He/H_2 clusters showed that the H_2 clusters undergo considerable compression when embedded in a larger ^{4}He$_N$ cluster, and the extent of superfluidity in the H_2 subcluster is then significantly reduced [17].

Experimental advances in the development and application of helium cluster beams have recently provided a new approach to the investigation of superfluidity in hydrogen clusters [18]. Infrared spectroscopic measurements on a linear OCS molecule "wrapped" by a small number (14 to 16) of para-H_2 molecules inside large ^{4}He droplets ($T \sim 0.38$ K) have revealed the spectral feature (Q branch) that indicates the excitation of angular momentum around the OCS molecular axis. This Q-branch feature was not observed inside the colder ^{4}He/^{3}He mixed droplets ($T \sim 0.15$ K). Disappearance of the Q branch at the lower temperature was interpreted as evidence of a novel superfluid state in molecular hydrogen when solvating a small molecule [18]. If this interpretation is valid, the hydrogenic solvation shell of the wrapped OCS molecule would constitute a new superfluid state of matter, albeit defined so far only in the nanoscale regime. Furthermore, the onset of this solvation layer superfluidity would occur at a temperature between 0.15 and 0.38 K, well below the superfluid transition temperature predicted for pure hydrogen clusters of similar size [10].

We demonstrate here that the solvation structure of para-H_2 molecules around an OCS molecule can support a superfluid state, using the path-integral Monte Carlo (PIMC) method with full incorporation of the boson permutation exchange symmetry of para-H_2. This methodology has been successfully applied to various bosonic systems, such as bulk helium, ^{4}He/^{3}He mixtures [19], helium and molecular hydrogen droplets [14,20], and

helium and hydrogen films on various surfaces [8,21]. In this study of OCS-doped para-H_2 clusters, hydrogen molecules are treated as spherical particles interacting with each other and with a nonrotating OCS molecule whose center of mass is fixed at the origin. A three-dimensional *ab initio* calculation of the anisotropic OCS-H_2 potential has recently been made with fourth-order Møller-Plesset perturbation theory [22]. Integration over the H_2 angular coordinate yields a two-dimensional representation which we fit to a Legendre expansion. This OCS-H_2 potential has a very similar structure to that of the previously reported He-OCS potential [23], possessing a global minimum of -208 K at $r = 3.35$ Å and $\theta = 106°$, where r is the distance from the OCS center of mass and θ the polar angle from the sulfur side of the OCS molecular axis. For the H_2-H_2 interaction, we use the spherical part of the empirical potential proposed by Buck *et al.* [24]. In the path-integral representation, the low-temperature density matrix, whose exact form is not known in general for a many-body system, is factored into M high-temperature density matrices with *imaginary* time step $\tau = (Mk_BT)^{-1}$. We employ here values $\tau^{-1}/k_B \geq 40$ K. In the high-temperature density matrix, the H_2-H_2 interaction is incorporated with the pair-product form of the exact two-body density matrices, and the OCS-H_2 interaction with the *primitive* approximation [25].

Within the Feynman path-integral analysis, the super-fluidity of a Bose system can be quantified in terms of exchange-coupled paths that are comparable to the system size. In the linear response regime, the global super-fluid fraction of an anisotropic system can be evaluated by a tensor estimator written in terms of the projected area of the Feynman paths [25]:

$$f_{ij}^s = \frac{4m^2 \langle A_i A_j \rangle k_B T}{\hbar^2 I_{ij}^{cl}}. \tag{1}$$

Here A_i is the area of a Feynman path projected onto a plane perpendicular to the axis $\hat{x}_i$, and I^{cl} is the classical moment of inertia tensor. This quantity can be defined independent of the number of Bose particles, and provides a valid estimator of the superfluid response to rotation for both bulk and finite size systems in the linear response regime [25]. Since our system has cylindrical symmetry, there are only two distinguishable principal values of f^s, namely, $f_\parallel^s$ and $f_\perp^s$ for rotations around axes parallel and perpendicular to the OCS molecular axis, respectively. Additional insight is gained by decomposing the local density into contributions from paths of differing exchange lengths [26] or of differing projected area [27]. We focus here on the temperature dependent correlation between changes in the global superfluid fractions and the topology of the local exchange path densities of the solvating H_2 layer.

Our path-integral calculations show that 17 hydrogen molecules are required to form a complete solvation shell around OCS. Additional calculations embedding this sol-

vated $OCS(H_2)_{17}$ in a larger cluster of ^4He (39 ^4He atoms) [28], show that 17 H_2 molecules suffice to expel all ^4He atoms from the immediate vicinity of the OCS molecule and $N = 17$ thus also constitutes exactly one solvation layer when the hydrogen-wrapped molecule is inside a helium cluster. The total density is found to change little over the temperature range $T = 0.15$–2.5 K studied here and does not change with addition of helium. It shows a persistent structure of four distinct annular bands around the molecular axis, illustrated in Fig. 1. The most intense band is located over the global potential minimum and contains 6 H_2 molecules. Two secondary bands, one with 4 H_2 molecules and the other with 6 H_2 molecules, are located in the saddle point regions of the H_2-OCS interaction potential, and a single H_2 molecule is located in the secondary minimum at the sulfur end of the molecule. This structure is found to be stable to further decreasing the time step τ, which causes small changes in the shape of the most intense band but does not affect the distribution of H_2 molecules among the four bands. These four annular bands of hydrogen density are separated by regions of very low density. They appear to be very strongly packed, according to a balance between the topography of the OCS-hydrogen interaction potential, and the repulsive H_2-H_2 interaction that restricts the number of H_2 molecules in each band. The packing in the angular degree of freedom is much stronger here than in the previously studied $He_N OCS$ system, where, despite a similar topology of the molecule-helium interaction potential, higher delocalization of the helium results in less pronounced annular structures around the OCS molecule [20].

The temperature dependence of the global superfluid fraction components $f_\parallel^s$ and $f_\perp^s$ for hydrogen is shown in Fig. 2. A strong anisotropy in the superfluid fraction is
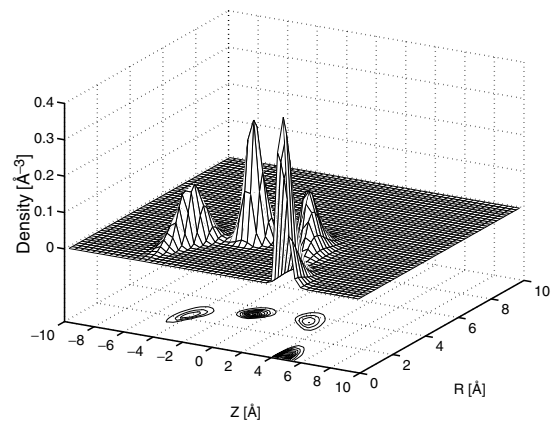

FIG. 1. Total density distribution of hydrogen molecules in $OCS(H_2)_{17}$ at $T = 0.375$ K. Z is the OCS molecular axis with sulfur in the positive direction, R the radial distance from the Z axis, and the coordinate origin located at the center of mass of the molecule. The density peaks represent annular bands containing four, six, six, and one hydrogen molecule, respectively, from left to right. A contour plot is shown below the mesh plot.
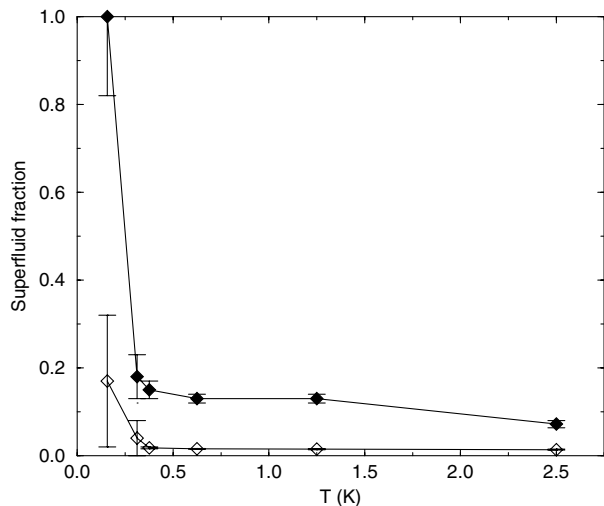
FIG. 2. Hydrogen superfluid fraction in $OCS(H_2)_{17}$ as a function of temperature. Solid symbols show the parallel response $f_\parallel^s$, open symbols the perpendicular response $f_\perp^s$.

evident, with the parallel component $f_\parallel^s$ being significantly larger at all temperatures considered. As the temperature decreases from $T = 2.5$ K to $T \sim 0.3$ K, $f_\parallel^s$ initially shows a very weak increase to a value of ~ 0.18 at $T \sim 0.3$ K, and then rises sharply to reach unity at $T = 0.15$ K. This onset of significant superfluid response at $T \sim 0.3$ K is considerably lower than that predicted for either pure clusters of para-H_2 [10] or H_2 films [8]. Furthermore, the two-stage nature of the rise in $f_\parallel^s$ at low temperatures is distinctly different from the shape of analogous transitions in pure clusters. This can be partially attributed to the differences in dimensionality. Pure $(H_2)_N$ is a finite three-dimensional system, while H_2 films are two dimensional. In contrast, these solvating H_2 clusters wrapped around a linear molecule constitute quasi-one-dimensional annular bands. As we see below, the permutation exchanges responsible for the superfluid response occur primarily within one of these one-dimensional annular bands in the higher temperature regime, while exchanges between bands become facile at the lower temperature, introducing two-dimensional character. The reduced phase space accessible to the H_2 molecules in this highly anisotropic layer structure relative to that in films or in three-dimensional clusters results in a lower temperature for manifestation of superfluid phenomena.

The perpendicular component $f_\perp^s$ shows a small increase as the temperature drops below $T \sim 0.3$ K but remains much weaker than $f_\parallel^s$, reaching a value of only ~ 0.17 at $T = 0.15$ K. While small, $f_\perp^s$ is, nevertheless, nonzero at this low temperature where the parallel component reaches unity. This implies that there is some extent of permutation exchange occurring between H_2 molecules that are located on the different annular bands along the molecular axis. Consequently, it also suggests that the unit value of superfluid fraction seen for the

parallel response component at the lower temperature is not solely due to exchanges within each of the (three) annular bands containing four and six molecules, but that this parallel response also now has contributions from exchanges between bands.

The contribution of permutation exchanges can be analyzed in more detail by evaluating the local exchange path densities, i.e., the contribution to the hydrogen density from paths of variable exchange length. The contributions from all exchange paths, i.e., from exchanges involving two or more H_2 molecules, are plotted in Fig. 3 at temperatures $T = 0.375$ K (a) and $T = 0.15$ K (b). Detailed analysis shows that at the higher temperature, $T = 0.375$ K, predominant contributions to this local exchange density come from two- and four-molecule exchanges within the secondary band that is located between oxygen and carbon (negative z axis), in the flat part of the interaction potential. This is the least strongly bound part of the molecule-hydrogen interaction potential, and so the four hydrogen molecules located around the molecular axis here experience the weakest attraction to OCS. They are, consequently, the first to initiate permutation exchanges as the temperature is lowered. It is notable that at the higher temperature, the exchange permutations do indeed occur within a single
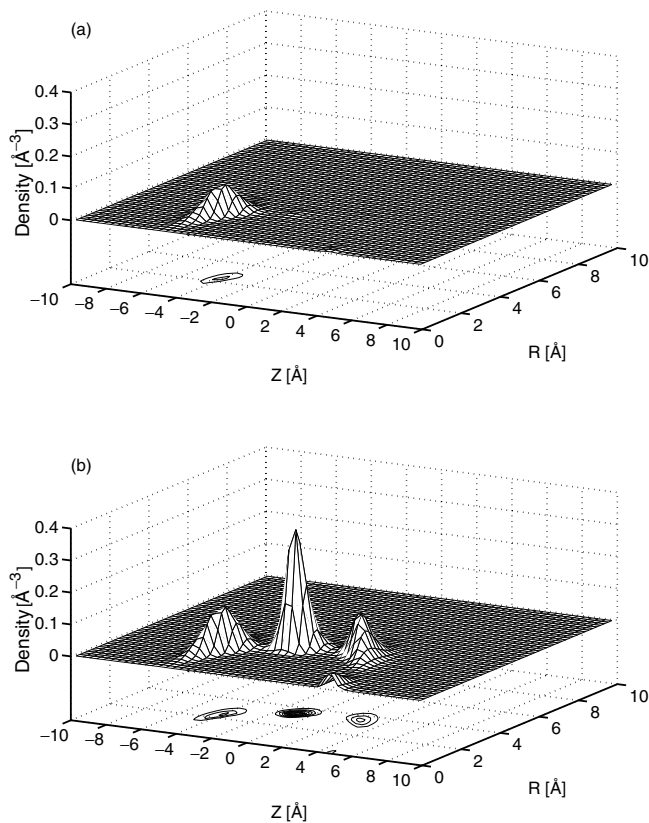

FIG. 3. Local exchange density deriving from all hydrogen exchange permutations in $OCS(H_2)_{17}$, shown at temperatures of (a) 0.375 K, and (b) 0.156 K. Molecular orientation as in Fig. 1. Contour plots are shown below the mesh plots.

annular band. In contrast, at the lower temperature, $T = 0.15$ K, permutation exchanges of all lengths are found to now contribute to the local exchange density. Furthermore, these permutation paths primarily involve exchanges of atoms *between* the annular bands rather than exchanges *within* a single band, which is illustrated by the fact that the 4-molecule density band in Fig. 1 contributes significantly to five- and six-molecule exchanges.

These results show that a nanoscale superfluid state of molecular hydrogen can exist in a cluster constituting a molecular solvation layer, with the specific example of OCS studied here showing essentially complete superfluid response to the rotation around the molecular axis at $T = 0.15$ K. This molecular superfluidity is characterized by a highly anisotropic response function that is controlled by the molecule-hydrogen interaction potential. This external potential provides a template for the molecular hydrogen to form a low-dimensional confined layer structure. Consequently, the position and shape of the transition to the state of superfluid response is quite different in these solvating hydrogen clusters than in their pure hydrogen analogs. The nanoscale superfluidity of hydrogen seen here also appears very different from that of helium seen in OCS solvated by ^{4}He [20,29]. Helium is less strongly localized around the OCS molecule, and consequently its exchange paths extend from the first solvation layer out into the surrounding helium liquid.

These manifestations of superfluidity reflect a paucity of states for the H_2 cluster to rotate about the molecular axis, and provide quantitative insight to the coupling between the H_2 cluster and the OCS rotational excitations. In particular, the high parallel superfluid response implies that there can be no angular momentum excitation in the H_2 parallel to the molecular axis, and hence there is no possibility of a Q branch corresponding to $\Delta J = 0$ transitions in the coupled $OCS(H_2)_N$ system. The calculations presented here for a complete solvation shell, $N = 17$, imply that a similar nanoscale superfluid response will be present for any number of H_2 molecules sufficient to form at least two of the three larger annular bands around the OCS molecule, i.e., $N > 10$. They therefore provide a microscopic explanation for the absence of a Q branch in experimental spectra for $N \gtrsim 11$ [18], quantitatively confirming the suggestion that this anomaly in the rotational spectra is due to the onset of a superfluid state in the surrounding H_2 clusters. The finding of a finite perpendicular superfluid response at $T = 0.15$ K also implies that the measured rotational constants will be higher than expected from rigid coupling of the H_2 density to the end-over-end OCS rotation.

In general terms, these results demonstrate the existence of a new form of superfluidity in the nanoscale regime, one that provides opportunities to tune the local hydrogenic superfluid response by systematic modification of the molecular impurity and of its solvating environment. In particular, it will be important to examine how this nanoscale superfluidity varies when the molecule-hydrogen interaction is weakened, as well as how it is affected by the addition of successive solvation layers or of other impurities.

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