Bose-Einstein Condensation of Molecular Hydrogen in Nanotube Bundles

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We evaluate the effects of heterogeneity on the density of states of H\textsubscript{2} molecules inside interstitial channels within bundles of carbon nanotubes. As temperature (T) falls, the density increases within those tubes having the greatest binding energy. At T \approx 10 mK, the molecules undergo Bose-Einstein condensation, exhibiting a singular heat capacity.

The subject of adsorption within bundles of carbon nanotubes has received considerable attention recently, owing to both its fundamental interest and potential applications (e.g. gas storage and isotope separation). One focus of the research is one-dimensional (1D) and quasi-1D phases of matter. These include condensing and crystallizing phases of buckyballs within tubes, He and H\textsubscript{2} within the interstitial channels (IC’s) between tubes and various gases within grooves on the outside of the nanotube bundles \cite{1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11}. Most analyses (including those of our group) have assumed that the tubes are identical and parallel, forming an ordered lattice. Real nanotube bundles, in contrast, consist of a disordered array of tubes with a distribution of radii. A logical question arises: how reliable are predictions that ignore such a variable environment? Shi and Johnson have recently shown that predictions incorporating heterogeneity agree better with adsorption data than do the idealized models \cite{12}. Stimulated by their work, we have explored the behavior of quantum fluids (He and H\textsubscript{2}) in such a nonuniform environment at low temperature (T). In this paper, we describe an intriguing result: Bose-Einstein condensation (BEC) of H\textsubscript{2} molecules occurs as a consequence of the heterogeneity. This paper makes predictions about this phenomenon that are testable experimentally. Similar behavior is expected for various gases within grooves on the outside of the nanotubes, ignoring corrections from more distant tubes and many-body effects associated with the screening of van der Waals interactions by the adjacent tubes \cite{18}. Although these approximations introduce some errors in the values of \( E_i \) they do not affect the key predictions of this work, which are sensitive to the variation of \( E_i(R) \). The potential from each neighboring tube was derived with

\[
N(E) = \sum_{R,p} \delta[E - E(p, R)]
\]

\[
= \frac{L}{\hbar \pi} \left( \frac{m}{2} \right)^{1/2} \int_0^E dE_i \frac{g(E_i)}{\sqrt{E - E_i}}
(1)
\]

where \( g(E_i) \) is the density of states for the transverse oscillation problem and \( L \) is the length of the tubes. If the length is not constant, the variation can be included in \( g(E_i) \).

The energy \( E_i(R) \) is evaluated from the potential energy \( V(r, R) \) of the molecule at position \( r \). To compute \( V \), we add contributions from the three neighboring tubes, ignoring corrections from more distant tubes and many-body effects associated with the screening of van der Waals interactions by the adjacent tubes \cite{18}. Although these approximations introduce some errors in the values of \( E_i \) they do not affect the key predictions of this work, which are sensitive to the variation of \( E_i(R) \). The potential from each neighboring tube was derived with
the method of Stan et al. \[19\]. Because \(V(\mathbf{r}, \mathbf{R})\) varies rapidly with \(\mathbf{r}\), values of \(E_t(\mathbf{R})\) include large anharmonic and small anisotropic contributions.

The form of \(N(E)\) for a given collection of nanotube bundles depends on sample preparation. A sample is represented by an ensemble of points (one for each IC) in \(\mathbf{R}\) space. The density of points in \(\mathbf{R}\) space, a function \(f(\mathbf{R})\), is defined so that \(f(\mathbf{R})d\mathbf{R}\) is the number of IC’s within an infinitesimal volume \(d\mathbf{R} = dR_1dR_2dR_3\), centered at \(\mathbf{R}\). The function \(f\) enters the transverse density of states through this expression:

\[
g(E) = \int d\mathbf{R} f(\mathbf{R}) \delta(E - E_t(\mathbf{R}))
\]  

(2)

At very low \(T\), we need the value of \(f(\mathbf{R})\) only in the immediate vicinity of the global minimum of the energy \((E_m\text{ at }\mathbf{R}_m)\), but at higher \(T\) the specific experimental distribution affects the results quantitatively. Here, we have assumed that the IC’s are uniformly distributed in \(\mathbf{R}\) space within a radius spread of width 3 Å near \(\mathbf{R}_m\). More general results will be described in a complete report of this work. We find, as one might expect, that \(\mathbf{R}_m\) occurs along the diagonal, symmetry line \((R_1 = R_2 = R_3)\). Along this line, which we call the \((1,1,1)\) line, there occurs a global minimum \(E_m = -1052.97\text{ K at }R_m = 9.95\text{ Å}\). To derive \(g(E)\), it is important to know the variation of \(E_t(\mathbf{R})\) near this minimum. Consider a particular displacement (in the \(R_2-R_3\) plane) from \(\mathbf{R}_m\) to a neighboring point for which \(R_1\) has the same value, while \(R_2\) and \(R_3\) are slightly different: \(R_2 = R_1 + \delta\) and \(R_3 = R_1 - \delta\). This change, parallel to the \((0,1,-1)\) direction, yields an extremely small increase in the \(H_2\) energy, indicative of a very slow variation of the function \(E_t(\mathbf{R})\) near \(\mathbf{R}_m\). This behavior, shown in Fig.1 reveals a long valley of low energy states in this direction; the same behavior occurs along the five equivalent directions, e.g. \((1,0,-1)\).

The transverse density of states \(g(E)\), from Eq. 2, is shown in Fig. 2. Note that \(g(E)\) is proportional to \(\sqrt{E - E_m}\) for small \(E - E_m\); the prefactor is determined by the principal axes of curvature of the function \(E_t(\mathbf{R})\). This square root behavior is identical to that found near a van Hove singularity in the phonon density of states of a 3D system near a minimum in the Brillouin zone, for the same reason- phase space topology \[20\]. At higher energy, instead, the behavior of \(g(E)\) switches to \(1/\sqrt{E - E_m}\). This \((-1/2)\) power law follows from the fact that the higher energy displacements from \(\mathbf{R}_m\) are quasi-1D. As seen in Fig.1, the iso-energy contours are perpendicular to the diagonal, so that the energy gradient in \(\mathbf{R}\) space is along the diagonal, with essentially constant transverse variation, a 1D situation.

Fig. 2 also presents \(N(E)\), derived with Eq. 1, which convolutes the transverse spectrum with the 1D motion along the axis. The resulting power law behavior can be
understood from realizing that if \( g(E) \) is proportional to \( (E - E_m)^n \), for some \( n \), then \( N(E) \) is proportional to \( (E - E_m)^{n+1/2} \). Hence, we find that \( N(E) \) is proportional to \( (E - E_m) \) near threshold. This linear behavior is that characteristic of a 4D gas in free space; the result implies that this system exhibits 4D gas behavior at low \( T \). For \( E > 20 \text{ mK} \) above threshold, instead, \( N(E) \) becomes approximately constant, corresponding to the density of states of a 2D gas. Thus, there arises a dimensionality crossover originating from the anomalous transverse density of states. We emphasize that the 4D regime is a direct consequence of the existence of a minimum in the function \( E_n(R) \), a result that is not sensitive to the details of the calculation [21].

The thermodynamic behavior of the system is derived with the usual bose gas theory. For a given number of molecules, \( N \), the chemical potential \( \mu \) is determined from the relation

\[
N = \int dE \frac{N(E)}{e^{\beta(E-\mu)} - 1} \tag{3}
\]

At a specified \( T = 1/(k_B\beta) \), this relation yields a maximum value \( N_{\text{max}} \) when \( \mu = \) the lowest energy of the system, \( E_m \), at which point BEC begins. That is, a macroscopic fraction of the molecules fall into the lowest energy state when \( N > N_{\text{max}} \). Equivalently, at fixed \( N \), BEC occurs when \( T \) falls below the inverse function \( T_c = T(N_{\text{max}}) \). The resulting dependence on \( N \) of \( T_c \) is shown in Fig. 3. As seen there, \( T_c \) is of order 10 mK, which is experimentally accessible. Fig. 4 shows the specific heat \( C_N(T) \), calculated from the energy as a function of \( \mu \) and \( T \). The novel behavior observed in the figure is a result of the unusual form of \( N(E) \). At low \( T \), \( C_N \) is proportional to \( T^2 \), a consequence of the 4D (linear) variation of \( N(E) \) at low \( E \). Note the presence of singular behavior of \( C_N(T) \) as one approaches the transition from above and a cusp at \( T_c \) itself. At relatively high \( T \), \( C_N(T)/(NK_B) \) is essentially unity because \( N(E) \) is 2D-like at high \( E \); a nondegenerate 2D gas has \( C_N(T)/(NK_B) = 1 \). Behavior for \( T > 0.2 \text{ K} \), not shown, is very sensitive to the distribution of nanotube radii.

Discussions of these results with colleagues have led to several questions concerning the transition. One is this: since each IC contributes a density of states characteristic of a 1D system, why does non-1D behavior arise here? The answer is that particles can exchange between different IC’s because of their common access to the vapor region. In practice, this may be a very slow process, leading to nonequilibrium behavior. The presence of breaks or holes in the tubes may alleviate this kinetic problem without invalidating the model, since heterogeneity is an essential aspect of the model. Another question is whether similar behavior occurs for other bose gases. Indeed, BEC of \(^4\text{He} \) is predicted by a similar analysis to occur if the sample’s distribution of tubes includes those with some near its energy minima in \( \mathbf{R} \) space, which occur near 8.5 Å. Finally, one might wonder about the effects of interparticle interactions, which have been ignored up to this point [22]. Indeed, some previous studies of \(^2\text{H}_2 \) in IC’s have found that a liquid-vapor condensation occurs at a higher temperature \( (\approx \text{K}) \) (in the absence of heterogeneity) [11]. A very recent study, however, found that nanotubes’ screening of the intermolecular interaction reduces \( T_c \) to about 10 mK [15]. However, that calculation omitted the role of heterogeneity, which is relevant, according to the Harris criterion, since the 3D specific heat critical exponent is positive [23]. We expect that this condensation temperature is further reduced by disorder, enabling the BEC transition to occur.

We summarize our results as follows. Heterogeneity alters the qualitative behavior of the low energy spectrum...
of H$_2$ molecules. The lowest-lying states of the system are those of particles in that channel. As $T$ falls, particles aggregate in the (essentially 4D) space of quantum states, (R,p), with Bose statistics having a dramatic effect, i.e. BEC, below a transition temperature of order 20 mK. Anomalous behavior is predicted for the specific heat, a consequence of the unusual density of states, which is 4D-like at very low energy and 2D-like at somewhat higher energy. An experimental probe of the real-space molecular density should reveal the needle-like concentration, below $T_c$, of a macroscopic fraction of the particles within the lowest energy channel.

Most intriguing to us is that this transition is a direct consequence of disorder, since the perfectly uniform system of identical nanotubes yields strictly 1D, non-singular behavior. Such a dramatic effect of heterogeneity occurs elsewhere in low temperature physics. Examples include the spin-glass transition [24], the effect of tunneling states on thermal behavior of glasses [25] and the effects of disorder on monolayer films [26].

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