

Superfluidity in Clusters of p -H₂ Molecules

Philippe Sindzingre

Laboratoire de Physique Theorique des Liquides, Université Pierre et Marie Curie, 75252 Paris, France

David M. Ceperley

National Center for Supercomputer Applications, Department of Physics, University of Illinois, Urbana, Illinois 61801

Michael L. Klein

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

(Received 1 February 1991)

Path-integral Monte Carlo calculations have been used to study small clusters of p -H₂ molecules at low temperatures. Below about 2 K, clusters of 13 and 18 molecules exhibit manifestations of superfluid behavior. However, exchange permutation of molecules is greatly suppressed in a cluster of 33 molecules, even at 1 K.

PACS numbers: 67.20.+k, 36.40.+d, 67.40.Db

The possibility that liquid parahydrogen (p -H₂) might exhibit superfluid behavior was raised some time ago [1]. Although the p -H₂ molecule obeys Bose statistics, and has a lighter mass than ⁴He, the stable low-temperature bulk phase is not a superfluid but an hcp solid. So far, attempts to produce a superfluid by supercooling the normal liquid below the triple point of 13.8 K have been unsuccessful [2]. A possible way around this problem might be to produce small clusters of p -H₂ molecules in a molecular beam [3,4]. Indeed, the analogous case of ⁴He clusters has attracted considerable interest [5-11]. Attempts to provide experimental evidence for superfluidity in clusters have so far proved to be inconclusive [11]. However, path-integral Monte Carlo calculations on small ⁴He clusters of $N=64$ and 128 atoms revealed significant superfluid fractions below $T=2$ K [8].

Here, we report the results of a low-temperature path-integral Monte Carlo study on clusters of p -H₂ molecules that specifically includes the effect of Bose statistics. The method we employ and the calculational procedures have successfully probed the superfluid transition of bulk liquid ⁴He [12], the two-dimensional counterpart [13], and the nature of ⁴He clusters [8]. Our main finding is that, below about 2 K, the superfluid fractions in clusters of $N=13$ and 18 p -H₂ molecules become large. In particular, at $T=1$ K, most of the molecules in these clusters are participating in permutation cycles analogous to those occurring in superfluid bulk liquid ⁴He. The present results complement and extend a recent variational Monte Carlo calculation which suggested that clusters consisting of up to seven p -H₂ molecules have a "quantum-liquid-like ground state" [14].

At the densities relevant to clusters, p -H₂ molecules are well described by spherical ($J=0$) rotational wave functions. Accordingly, it is sufficient for our purpose to employ a spherical interaction potential. In order to avoid having to include many-body forces we use an "effective"

pair potential that gives a good account of the equation of state of bulk solid H₂ [15].

The properties of a p -H₂ cluster are embodied in the density matrix. In the Feynman path-integral representation this is factored into M time slices, a procedure that leads to the notation of a discretized path and the possibility of utilizing a temperature factor $1/M$ lower than $\beta=kT$. The density matrix for a Bose system is obtained by summing over all permutations of particle labels [12]. A generalized Metropolis algorithm is used to carry out the integration over paths and the summation over all permutations [12]. The present calculations are technically similar to those carried out on ⁴He clusters [8]. The interested reader is referred to the literature for additional details [12,13].

Bulk liquid ⁴He is usually described in terms of the two-fluid model. The superfluid fraction can be computed either from properties of the discretized paths or from the momentum density correlation function [12]. The normal-fluid fraction can be obtained from the response of the system to an external influence. In the present case, the p -H₂ cluster is imagined to be in an external field which has cylindrical symmetry about an axis passing through the center of mass. We then consider the response of the cluster to slow rotation of the field, a procedure employed to study ⁴He clusters [8]. As in that case, the superfluid fraction can be determined by the departure of the cluster's moment of inertia tensor \mathbf{I} from its classical value \mathbf{I}^* or from the angular momentum density correlation function $\langle \mathbf{L}(r) \cdot \mathbf{L}(0) \rangle$, where \mathbf{L} denotes the total angular momentum.

For a classical system with density distribution $\rho(r)$, the moment of inertia is given by $I^* = m \int d\mathbf{r} \rho(r) |\mathbf{u} \times \mathbf{r}|^2$. The normal fraction is the part of the cluster that responds as a classical system, namely,

$$I/I^* = \beta \{ \langle \mathbf{L} \cdot \mathbf{L} \rangle - \langle \mathbf{L} \rangle \langle \mathbf{L} \rangle \} / I^* .$$

An appropriate estimator for the path-integral evaluation of I is required and this was developed in our previous work [8]. For a given rotation axis, the deviation of the moment of inertia from its classical value can be related to the expectation value of the square of the surface area enclosed by the Feynman paths projected onto a plane perpendicular to that axis. Alternatively, the moment of inertia, and therefore the normal fraction, may be computed from the probability that the projection of angular momentum L on an arbitrary axis has the value nh . Bosons show fewer fluctuations in angular momentum than classical particles by an amount proportional to the superfluid fraction, $(I^* - I)/I^*$.

Path-integral Monte Carlo runs were carried out on four different clusters. First, a configuration taken from a $N=64$ superfluid ^4He cluster [8] was used as a starting point to study the same number of $p\text{-H}_2$ molecules at $T=0.5$ K. Unfortunately, this cluster immediately froze into an amorphous solid structure which exhibited a very low acceptance rate for permutations. A $N=64$ cluster was therefore melted by heating to 10 K and then subsequently quenched to 1 K. Again, there was only the slightest hint of permutations occurring in the cold cluster. This finding may be of little relevance to beam experiments which attempt to achieve a "metastable liquid state" for sufficiently long times to make experiments possible *before* nucleation sets in to initiate freezing [4]. Unfortunately, an extensive study of the effects of heating and cooling the $N=64$ cluster was not possible due to the excessive demands on computer time. Accordingly, we next carried out a systematic study of a cluster with $N=33$. This was built from an icosahedral core (a central molecule abutted by two rings of five molecules and capped top and bottom), plus an outer shell of twenty additional molecules. The $N=33$ cluster was investigated at a variety of temperatures ranging up to 10 K. The temperature dependence of the energy is shown in Fig. 1

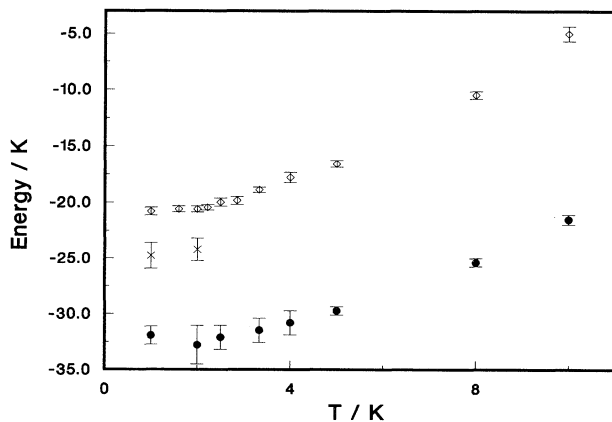


FIG. 1. Path-integral Monte Carlo results for the energy of $p\text{-H}_2$ clusters with $N=13$ (open diamonds), $N=18$ (crosses), and $N=33$ (solid circles).

and the radial density profile in Fig. 2. Some of the low-temperature runs gave hints of superfluidlike behavior (see below). Although it is compact, the chosen initial configuration, which had an atom at the center of mass, is not the ground-state structure for the $N=33$ cluster. The latter has a pentagonal bipyramidal core, as in the case of a classical $N=33$ cluster whose atoms interact with a Lennard-Jones potential [16]. This explains why below 5 K the profiles for this cluster lack density at the origin [17].

Next, we studied an icosahedral cluster with $N=13$. To our delight, around 3 K, the molecules in this cluster exhibited a significant propensity for participating in permutation cycles and this behavior increased substantially when the temperature was lowered to 1 K. Finally, we studied a cluster with $N=18$ which was formed by adding five additional molecules to the surface of the icosahedral cluster. This also exhibited superfluidlike behavior below 2 K. Figure 1 shows results for the energy as a function of temperature for the cluster with $N=13$ and two points for a cluster with $N=18$.

In a Monte Carlo calculation, there is always a chance that molecules will evaporate during a simulation at finite temperature, a problem that is particularly acute for He but less so for the more strongly bound $p\text{-H}_2$ clusters. To prevent possible evaporation at the highest temperatures we restricted the Feynman paths to lie within a radius R_c from the center of gravity of the paths [8]. The present choice was $R_c = 10, 12,$ and 14 \AA , for the clusters with $N=13, 18,$ and 33 , respectively. The density in the tail of the profiles shown in Fig. 2 increases slightly with temperature but is always very small, even at 10 K. Above 5

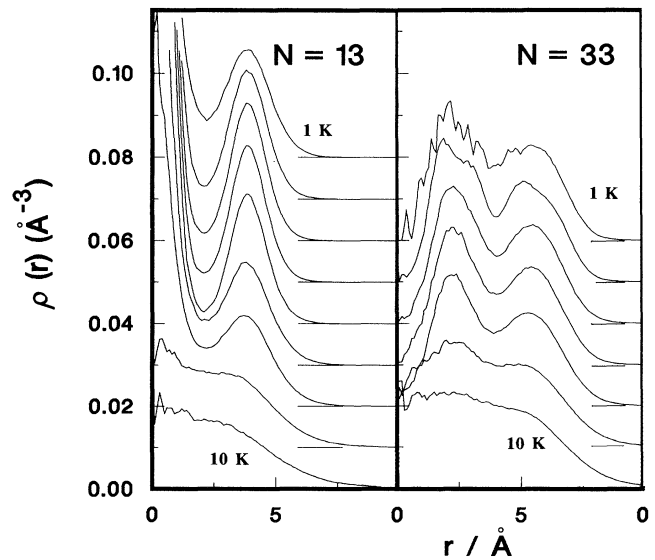


FIG. 2. Radial density profiles for $p\text{-H}_2$ clusters. From top to bottom the curves correspond to $T=1, 1.6, 2, 2.2, 2.8, 4, 5, 8,$ and 10 K for $N=13$ and $T=1, 2, 3.3, 4, 5, 8,$ and 10 K for $N=33$, respectively.

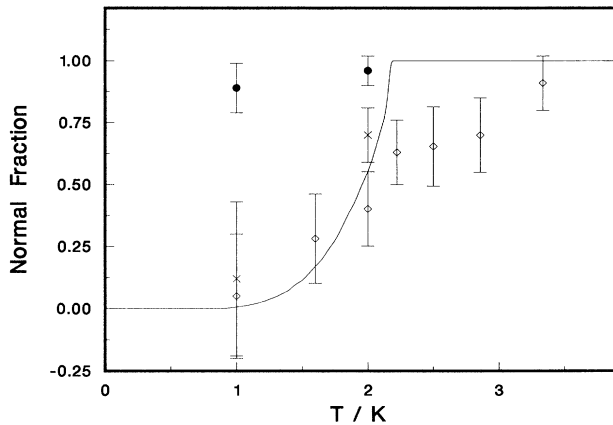


FIG. 3. Temperature evolution of the normal fraction in the p -H₂ clusters with $N=13$ (open diamonds), 18 (crosses), and 33 (solid circles), respectively. The solid curve is the experimental result for bulk ⁴He.

K, the profiles appear liquidlike. Indeed, in the core region the density is essentially identical to that of superfluid ⁴He clusters [8]. Below this temperature a well-defined shell structure is present that changes very little as the temperature is lowered. We have verified by independent calculation that below 5 K physical exchange of particles occurs even in the absence of Bose statistics [17]. This observation explains why there is little variation in the density profiles below 5 K and why the profiles for $N=13$ do not fall to zero between the two peaks.

The calculated temperature dependence of the normal fraction in each cluster is shown in Fig. 3. For the $N=13$ and 18 cases values significantly less than 1 occur at a higher temperature than previously found for ⁴He clusters [8]. Since the number densities of the p -H₂ and ⁴He clusters are approximately the same, a corresponding-states argument implies that the superfluid transition temperature should scale with the particle mass [1,2]. The results in Fig. 3 therefore suggest a slightly enhanced effective mass for p -H₂, compared to ⁴He, no doubt due to the deeper interaction potential [15].

The probability that a p -H₂ molecule is part of a permutation cycle involving p molecules can be used to provide a local measure of the degree of superfluidity, if p is not too small [12]. In Fig. 4 we show the temperature dependence of $\Pi(r)$, the fraction of the radial density profile due to molecules involved in permutation cycles of six or more. The calculated probability for large permutation cycles increases significantly below 2 K for the $N=13$ and 18 clusters. This measure of the superfluid density indicates that initially mostly the surface molecules are involved in large permutation cycles. This phenomenon is greatly suppressed in the $N=33$ cluster. Moreover, only at the lowest temperature does the central molecule in the $N=13$ cluster participate. As mentioned above, physical exchange of the particles including the

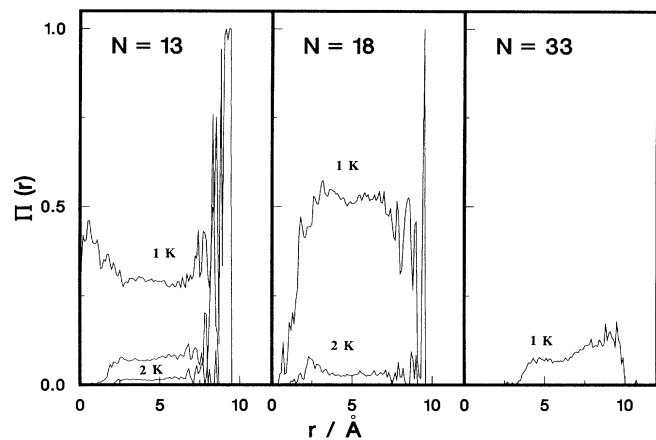


FIG. 4. Evolution with temperature of the fraction of the radial density profile due to permutation cycles involving six or more molecules. The curves correspond to 2, 1.6, and 1 K for $N=13$, 2 and 1 K for $N=18$, and 1 K for $N=33$.

central molecule occurs above 2 K. In view of the structured nature of the low-temperature radial density profile shown in Fig. 2, the $N=13$ cluster might perhaps be thought of as a “supersolid” rather than a superfluid [18]. Figure 5 compares snapshots of typical Feynman paths for the $N=13$ cluster at 2 and 1 K. Clearly, at the lower temperature this cluster is a highly quantum object.

In summary, at sufficiently low temperatures, small clusters of p -H₂ molecules have been found to indeed exhibit properties characteristic of a Bose-condensed system [3,4]. Experimental verification of the present findings will no doubt provide an extremely challenging task. The use of a nozzle beam would seem to be a natural way to attempt to produce such clusters [4]. However, the “superfluid” behavior comes about, in part, because the density of the clusters is about 30% less than that of the bulk solid. It might therefore prove informative to once

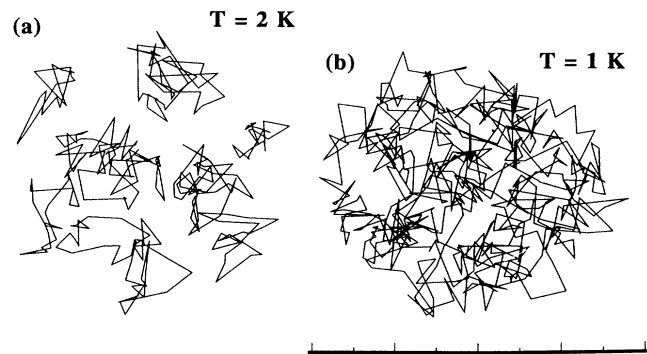


FIG. 5. Snapshots of typical Feynman paths projected onto an arbitrary plane taken from the simulation of the $N=13$ cluster at (a) 2 K and (b) 1 K. The indicated scale spans 12 Å.

again investigate p -H₂ molecules at low temperature on a surface [1,19] or in a porous solid [20].

The research outlined above was supported by the National Science Foundation under Grants No. CHE-8722481, No. CHE-8815130, No. DMR 88-08126, and No. DMR 88-19885. We thank Daphna Scharf, Giacinto Scoles, and Birgitta Whaley for helpful discussions and for freely communicating their ideas before publication.

-
- [1] V. L. Ginsburg and A. A. Sobyenin, *Pis'ma Zh. Eksp. Teor. Fiz.* **15**, 343 (1972) [*JETP Lett.* **15**, 242 (1972)].
- [2] H. J. Maris, G. M. Seidel, and T. E. Huber, *J. Low Temp. Phys.* **51**, 471 (1983); G. M. Seidel, H. J. Maris, F. I. B. Williams, and J. G. Cardon, *Phys. Rev. Lett.* **56**, 2380 (1986); H. J. Maris, G. M. Seidel, and F. I. B. Williams, *Phys. Rev. B* **36**, 6799 (1987).
- [3] G. Scoles, in *Proceedings of the Trento Meeting on Quantum Clusters*, 1989 (unpublished); (private communication).
- [4] E. L. Knuth, B. Schilling, and J. P. Toennies, in *Proceedings of the Seventeenth International Symposium on Rarefied Gas Dynamics*, Aachen, 1990 (unpublished).
- [5] V. R. Pandharipande, J. G. Zabolitzky, S. C. Pieper, R. B. Wiringa, and U. Helmbrecht, *Phys. Rev. Lett.* **50**, 1676 (1983); R. Melzer and Z. G. Zabolitzky, *J. Phys. A* **17**, L565 (1984).
- [6] S. C. Pieper, R. B. Wiringa, and V. R. Pandharipande, *Phys. Rev. B* **32**, 3341 (1985); V. R. Pandharipande, S. C. Pieper, and R. B. Wiringa, *Phys. Rev. B* **34**, 4571 (1986); D. S. Lewart, V. R. Pandharipande, and S. C. Pieper, *Phys. Rev. B* **37**, 4950 (1988).
- [7] S. Stringari and J. Treiner, *J. Chem. Phys.* **87**, 5021 (1987); M. Casas and S. Stringari, *J. Low Temp. Phys.* **79**, 135 (1990).
- [8] Ph. Sindzingre, M. L. Klein, and D. M. Ceperley, *Phys. Rev. Lett.* **63**, 1601 (1989).
- [9] M. V. Rama Krishna and K. B. Whaley, *J. Chem. Phys.* **93**, 746 (1990); *Phys. Rev. Lett.* **64**, 1719 (1990); *Mod. Phys. Lett. B* **4**, 895 (1990).
- [10] S. A. Chin and E. Krotscheck, *Phys. Rev. Lett.* **65**, 2658 (1990).
- [11] D. Eichenauer, A. Scheidemann, and J. P. Toennies, *Z. Phys. D* **8**, 295 (1988); A. Scheidemann, J. P. Toennies, and J. A. Northby, *Phys. Rev. Lett.* **64**, 1899 (1990).
- [12] E. L. Pollock and D. M. Ceperley, *Phys. Rev. B* **30**, 2555 (1984); **36**, 8343 (1987); D. M. Ceperley and E. L. Pollock, *Phys. Rev. Lett.* **56**, 351 (1986); *Can. J. Phys.* **65**, 1416 (1987).
- [13] D. M. Ceperley and E. L. Pollock, *Phys. Rev. B* **39**, 2084 (1989).
- [14] M. V. Rama Krishna and K. B. Whaley, report, 1990 (to be published).
- [15] I. F. Silvera and V. V. Goldman, *J. Chem. Phys.* **69**, 4209 (1978); J. van Straaten and I. F. Silvera, *Phys. Rev. B* **37**, 1989 (1988).
- [16] M. R. Hoare and P. Pal, *Adv. Phys.* **20**, 161 (1971); **24**, 646 (1975); J. D. Honeycutt and H. C. Andersen, *J. Phys. Chem.* **91**, 4950 (1987).
- [17] D. Scharf, G. Martyna, and M. Klein (to be published).
- [18] A. F. Andreev and L. M. Lifschitz, *Zh. Eksp. Teor. Fiz.* **56**, 2057 (1969) [*Sov. Phys. JETP* **29**, 1107 (1969)]; G. V. Chester, *Phys. Rev. A* **2**, 256 (1970); A. J. Leggett, *Phys. Rev. Lett.* **25**, 1543 (1970).
- [19] P. R. Kubick and W. N. Hardy, *Phys. Rev. Lett.* **41**, 257 (1978); J. Cui, S. C. Fain, H. Freimuth, H. Wiechert, H. P. Schildberg, and H. J. Lauter, *Phys. Rev. Lett.* **60**, 1848 (1988).
- [20] A. P. Y. Wong and M. H. W. Chan, *Phys. Rev. Lett.* **65**, 2567 (1990).