Path integral Monte Carlo applications to quantum fluids in confined geometries

David M. Ceperleya)
National Center for Supercomputer Applications, Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

Efstratios Manousakisb)
Center for Materials Research and Technology, Department of Physics, Florida State University, Tallahassee, Florida 32306

(Received 18 July 2001; accepted 25 September 2001)

Path integral Monte Carlo is an exact simulation method for calculating thermodynamic properties of bosonic systems. Properties such as superfluidity and Bose–Einstein condensation are directly related to multiparticle exchange cycles of individual particle paths. Such calculations of bosonic systems in confined geometries, such as helium and hydrogen on surfaces and in droplets are reviewed.


I. INTRODUCTION

Path integral computation allows one to investigate many-body quantum systems without significant approximations, at least as concerns static properties. The methods and computers are now powerful enough that such calculations can be done with nearly the same ease as using the molecular dynamics and Monte Carlo to investigate classical systems. In this article we summarize some of the applications of the path integral Monte Carlo (PIMC) methods on superfluids in confined geometries and Bose–Einstein condensation (BEC) of very dilute atomic gases.

We do not review in detail the path integral Monte Carlo method since one of us has done that a few years ago. However, that review was focused on the theory and computation of bulk helium, particularly its superfluid properties. There have been other reviews on quantum simulation methods such as that by Schmidt and Ceperley, by Marx and Müser on quantum rotors, and Kwon et al. on helium drops.

The first part of the article is a survey of some aspects of the methods: The path integral theory for quantum systems and computational aspects. We then discuss applications to droplets and surfaces. This paper reviews our own work on films. Our work on droplets is also briefly discussed; we have not made an attempt to review a great body of work done on the subject of doped droplets. PIMC calculations on helium droplets doped with molecules have been recently summarized by Kwon et al.

II. PATH INTEGRAL METHODS

First, we describe the method as applied to distinguishable particles with neither Bose nor Fermi statistics. The fundamental idea, due primarily to Feynman, is that the quantum statistical mechanics can be written as an integral over paths. We denote a path, as a point in the time \( t \) which is in the range \( 0 \leq t \leq \beta \) with \( \beta = (k_B T)^{-1} \). An example of such a path is shown in Fig. 1. For computational purposes it is advantageous to work with discrete paths \( R_1, R_2, \ldots, R_M \) where \( M \) is the number of time slices and the time step is \( \tau = \beta / M \). The partition function is given by

\[
Z = \int dR_1 dR_2 \ldots dR_M e^{-S[R(t)]},
\]

(2.1)

where \( S[R(t)] \) is the action of a given path, \( R(t) \). The integral has the formal structure of a classical-like partition function if we interpret \( S[R(t)] \) as proportional to the classical potential energy of a path. As the number of links \( M \) gets large, we can write down explicit approximations for the "action." The simplest is the primitive form

\[
S = \sum_{j=1}^{M} \left[ \frac{(R_j - R_{j-1})^2}{4\lambda \tau} + \tau V(R_j) \right],
\]

(2.2)

As is discussed in Ref. 1, other forms of the action, such as the pair product action, can be more accurate and the resulting numerical methods, much more efficient. This is an important point since with the most efficient methods one can now simulate on a desktop computer, a quantum system containing about one hundred helium atoms at temperatures characteristic of superfluidity.

The efficiency of methods based on time slices (DPI) as described above and Fourier path (FP) methods (where the time dependence is given by an expansion in fourier components) have recently been compared. Discrete path integrals (DPI) have the advantage of easily treating statistics since those moves can be made local in imaginary time. FP methods, initially shown to be slow have been improved and are comparable in efficiency.

Having chosen the action, one must decide on how the paths are to be sampled. The most successful and general methods, are generalizations of Metropolis Monte Carlo. It is possible to simply move a single link variable. However, faster coverage of phase space is obtained by moving sections of the path since the kinetic "spring" action couples the
path integral variables. In addition to PIMC methods, one can use molecular-dynamics (MD) methods to sample distinguishable-particle path integrals, but MD methods do not readily generalize to superfluid systems.

III. QUANTUM STATISTICS

The situation where quantum statistics matter are the focus of this article. Bose statistics are simple to incorporate: See the description in Feynman. To take into account statistics one allows the paths to return to a permutation of their starting position after a “time” β has elapsed. An example of Bosonic paths is shown in Fig. 2. If we interpret the time as the chemical distance along a polymer, a Bose system corresponds to a classical system of cross-linking polymers. Properties relevant to superfluids always involve such a permutation or cross-linking. The two most important properties for bulk bosonic systems are the superfluid density and off diagonal long-range order, more commonly called Bose condensations. We now explain the physical and PI manifestations of these phenomena since this is important to the discussion of superfluids in confined geometries.

A. Superfluidity

A superfluid is defined by how a system responds to a slow movement of its boundaries. In the classic experiment of Andronikashvali (1946), a stack of thin, closely spaced disks, submerged in liquid–helium was gently oscillated and the amount of liquid–helium entrained by the motion was measured by the effective moment of inertia of the oscillator. On cooling through the lambda point (2.2 K) it was found that less and less of the helium moved with the disks. Experiments of higher precision have found that a few atomic layers of helium do move with the disk. The simplest explanation is that the attraction of helium to the disk causes localization of a few layers, the precise depth of this “dead” layer depends primarily on the strength of the interaction of the helium with the substrate. Other contributions arise from the roughness of the surface. This is the hydrodynamical effect discussed by Callegari et al. elsewhere in this volume. The recent experiments, described elsewhere in this volume, that measure the moment of inertia of an impurity in a superfluid helium droplet are a fantastic extension of the Andronikashvali experiment to the microscopic scale.

The definition of the normal fluid is simply the fraction of helium contributing to the moment of inertia of the disk, or equivalently, the free energy, F necessary to bring the disk to a rotational velocity ω: \( I = \frac{d^2 F}{d\omega^2} \) with \( I = I_{\text{disk}} + I_n \). The superfluid density is the relative amount of helium missing as the system is cooled through the transition.

Now let us turn to the question of evaluation of the superfluid density using path integrals. It is relatively straightforward to show that the superfluid density is given by the mean-squared area of the paths where the “area” of the paths is simply the vector defined as \( \mathbf{A} = \sum_{j=1}^{N} \mathbf{r}(t_j) \times \mathbf{r}(t_{j+1}) \). Then \( \rho_s / \rho = 4m^2(\mathbf{A}^2) / \beta \hbar^2 I_c \) where \( I_c \) is the classical moment of inertia. One can see that unless there are long exchanges, the area will be of atomic size, and the superfluid density will be nearly zero. Simulations show that the positions and correlations of atoms in the superfluid and normal fluid are virtually identical. It is the connection of the paths in imaginary time which is responsible for superfluidity.

B. Bose condensation

The other important concept of bosonic systems is that of Bose–Einstein (BEC) condensation. For noninteracting bosons, Einstein predicted that at the critical temperature, there would be a macroscopic occupation of a single quantum state. London proposed that this happens at the lambda point in liquid helium, as evidenced among other phenomena, by the closeness of the critical temperature to that of an ideal Bose gas. London’s idea for a strongly interacting liquid has won slow acceptance since it was proposed. The stron-
ggest evidence is obtained by neutron scattering experiments of the dynamical structure factor, which is an approximate measurement of the momentum distribution. BEC in weakly interacting bosonic systems is realized in lasers or, more recently, by BEC in low-density atomic vapors.\textsuperscript{12}

For bulk helium, the single particle states, by translation symmetry, must be momentum eigenstates. For an inhomogeneous system, such as a droplet, the states are obtained by diagonalizing the single particle density matrix and are the natural orbitals, familiar from the electronic structure of molecules.\textsuperscript{13} In contrast to electrons obeying fermi statistics, the occupation number in a given single particle state is not constrained by the Pauli principle, so BEC occurs when the occupation number of the lowest state becomes much greater than one, typically proportional to the number of particles in the system. To compute the single particle density matrix using PIMC, one cuts a single atom's path and allows the two ends to choose their own relative position. Without permutations present, the two ends can only be separated by a distance proportional to the thermal wavelength, typically a few Angstroms. The momentum distribution will be close to the Maxwell distribution, even if quantum effects are present. However, if long exchanges are present, the two loose ends can easily wander around the entire system and become uncorrelated. In this case the occupation number of the lowest state becomes proportional to the total volume and hence the number of atoms. Please consult Ref. 1 for detailed discussion of these issues.

It is important to realize that:

(i) A rigorous definition of BEC is possible even in a very strongly interacting system. BEC is not a concept tied to weakly interacting bosons;
(ii) BEC and superfluidity are not the same property even though they both are a consequence of macroscopic exchange. The PIMC calculations of the condensate fraction estimate that about 10\% of the helium atoms have precisely zero momentum, in agreement with experimental estimates.\textsuperscript{14} In contrast, the superfluid density in bulk liquid $^4$He approaches 100\% at low temperature;
(iii) Numerically straightforward procedures exist to compute both properties using path integral methods.

\section{C. Fermi statistics}

Sampling permutations of the paths, so successful for bosons, is very inefficient for fermions. This is because paths with an odd permutation count negatively, those with an even permutation positively. This can be shown\textsuperscript{15} to make the direct PIMC method very inefficient at low temperatures or for large system sizes since the probability of a negative permutation is only slightly smaller than that of a positive permutation. There is, however, an efficient procedure, known as the fixed-node or restricted path method based on the fact that there exists a rule to restrict the paths to those having a positive sign.\textsuperscript{16}

A simple example\textsuperscript{14} is provided by the rotational states of molecular hydrogen. Parahydrogen has a rotationally symmetrical state: It corresponds to Bose statistics in the angular degree of freedom and the appropriate paths are of two types: Closed paths on a sphere, or paths that start at the north pole and end at the south pole. Ortho-hydrogen corresponds to fermi statistics in that the wave function is antisymmetric with respect to inversion. Hence, one subtracts the contributions of these two types of paths. For restricted PIMC, one uses only the paths which stay in a single hemisphere. One can show that these give the exact quantum properties, since symmetry determines the path restrictions. For general Fermion systems, the restriction, though constrained by theory, essentially has to be determined self-consistently, and it is unlikely to ever be known precisely, so that effectively the restricted path procedure is a super-variational method. Problems with minus signs also arise in bosonic systems, for computations in excited quantum states, e.g., with a nonzero value of linear or angular momentum.

\section{IV. CALCULATIONS ON 3D SYSTEMS}

Recently\textsuperscript{17} the limits of superfluidity for low-density hard spheres has been computed with PIMC. The interest is in how the transition temperature evolves from the region of helium densities to the low density region probed by the atomic BEC. The overall phase diagram is shown in Fig. 3. At normal helium density the transition temperature is a factor of 2 below that of the ideal gas, because of caging effects in the liquid (or equivalently the larger effective mass). Over the years, there have been many analytical attempts to calculate how the transition temperature approaches the ideal gas temperature. Using PIMC, we found an enhancement of $T_c$ with respect to density of roughly 7\% at $\rho a^3 = 0.01$. The enhancement of the transition temperature is likely due to the homogenization of the density caused by the repulsive interaction which allows the long exchange to propagate more easily across the system. The slope at $\rho a^3 = 0$ is still contro-
versial. The theoretical analysis is much complicated by cross-over effects from the interacting to the noninteracting fixed point.” See Ref. 18 for recent citations.

The calculation of the transition temperature has been extended to a random “jungle gym” geometry, similar to the situation for helium absorbed inside vycor.19 These calculations did not include the attraction of helium atoms to the silica strands, but were only concerned with the effect of the excluded volume on the superfluid properties. It was found that the transition temperature is depressed by a relatively small amount by the randomness. The superfluid transition in three-dimensional (3D) is robust: As long as the atoms remain in a liquid state, they will become superfluid at approximately the same temperature. However, the superfluid density no longer goes to unity at low temperatures. Experimentally, it is known that one can characterize the response of an inhomogeneous geometry by a tortuosity factor which takes into account that superflow must wind around the obstacles presented by the pores. Although, one might call this a “normal” component of the liquid, equivalently one can regard this as a hydrodynamical effect induced by the boundaries of the liquid. The reduction of the superfluid density within path integrals arises from the fact that atoms next to the walls can only exchange or permute with a fraction of the atoms that those in the middle of a pore can, thus the reduction.

Krauth20 has simulated hard spheres in a droplet geometry appropriate to the experiments on dilute atomic vapors and determined transition temperature and the Bose condensate fraction for a system of several thousand hard spheres.

V. SUPERFLUID FILMS

Gordillo and Ceperley (GC)21 using PIMC and the Aziz potential for the He–He interaction have determined the phase diagram of pure helium confined in two-dimensions. The full phase diagram in the temperature-density plane is shown in Fig. 4. At low temperatures there is a liquid–gas coexistence region, a superfluid phase, a fluid–solid coexistence region and a triangular solid at high density. The upper dashed line is determined from the peaks of the specific heat. The lower dashed lines are the spinodal lines.

A. Helium films

Wagner and Ceperley (WC)22,23 have studied helium on a molecular hydrogen solid (1,1,1) surface using PIMC. Calculations with two layers of dynamic H2 substrate were also performed. They have computed the binding energy of 4He to the H2 surface as a function of the 4He coverage as well as density profiles perpendicular to the interface. The latter shows that the helium film grows layer by layer in a well defined manner up to several layers of helium. WC also studied the zero-point motion and the effective mass of 4He parallel to the substrate surface. The superfluid density versus coverage was also computed and it was found that it is non-zero even for submonolayer coverages and it grows with coverage and it becomes flat as a function of coverage at a value of about 80% its maximum value much before first layer completion.

Helium on graphite provides a very useful realization of thin quantum films.24–27 The atom–atom interaction and the atom–graphite interaction are of comparable strength and this allows an interesting competition between a number of phases including commensurate solid, incommensurate solid, striped domain wall, and superfluid phases. The study of these phases, as well as the coexistence between them as a function of substrate coverage can shed light on the physics of growth of quantum films and on the physics of other strongly correlated two-dimensional (2D) systems. For example, high-temperature superconductors are similar systems, in that there are similar phases or phases of similar origin such as stripes, phase separation and superconductivity.

The growth of 4He on graphite can be experimentally studied layer by layer and the coverage per unit surface area for layer promotion can be accurately determined.28 Pierce and Manousakis (PM)29–33 using PIMC, the Carlos–Cole34 helium–graphite interaction and the Aziz helium–helium potential have found that these promotion coverages can be reproduced within a few percent up to the fifth layer. The first layer phase diagram as a function of coverage and temperature has a $\sqrt{3}\times\sqrt{3}$ commensurate solid at 1/3 coverage.35 Below this density down to zero density, clusters of such a commensurate solid are formed on the surface. Figure 5 shows contour plots of the probability density for density 0.0424 Å$^{-2}$ and at commensurate density as calculated by PM. Figure 6 shows the experimental specific heat36 as a function of temperature for the commensurate density 0.0636 Å$^{-2}$ and at density 0.0367 Å$^{-2}$ below the commensurate density. Greywall and Busch36 had attributed the specific heat maximum at low density at arising from the onset of a superfluid phase of an assumed low-density two-dimensional (2D) liquid. In Fig. 6 the results of the PIMC simulations of PM at similar densities are shown for comparison. Notice that in this calculation there is a specific heat peak at the low coverage corresponding to the melting of...
commensurate solid clusters and it arises as the evolution as a function of density of the peak that corresponds to the melting of the commensurate solid at 1/3 coverage. The results of PM\textsuperscript{31,32} are in disagreement with the interpretation given by Greywall and Busch\textsuperscript{36,37} but are in agreement with the earlier interpretation (see Ref. 38 and references therein). Notice that there are torsional oscillator measurements by Reppy \textit{et al.}\textsuperscript{39} in which there is no period shift due to first layer superfluidity.

At densities above the commensurate density the first layer undergoes transitions into a phase with domain walls and at higher density, closer to the completion density, the system forms an incommensurate solid. PM find\textsuperscript{32} in agreement with the experimental promotion density that above 0.120 Å\textsuperscript{2} an ad-atom becomes a building block of the next layer.

The second layer is even more interesting because of the appearance and then disappearance of superfluidity as coverage is increasing. Figure 7 shows the low temperature phase diagram of the second layer of helium on graphite as determined by PM.\textsuperscript{29,30} At low density there is coexistence between the liquid (L) and a vapor (G) phase and the equilibrium density is 0.175 atom/Å\textsuperscript{2}. Above the density the 2D liquid is compressed by the presence of the substrate van der Waals interaction which holds the atoms on the first layer. At coverage of 0.1996 Å\textsuperscript{2} PM find the phase shown in Fig. 8 which is a $\sqrt{7} \times \sqrt{7}$ solid commensurate\textsuperscript{48} (denoted by C in Fig. 7) with the first layer of $^3$He. For higher densities, near the second layer completion density, an incommensurate triangular solid is formed (IC). In addition to these pure solid structures there are regions, shown in Fig. 7, where coexistence between two such phases exists. In Fig. 7 the superfluid response as a function of coverage is also plotted as solid squares. This was inferred from the period shift of the torsional oscillator experiments.\textsuperscript{39} Notice that it starts becoming significant at the start of the liquid phase, it peaks inside the liquid phase and superfluidity goes to zero at higher coverages inside the region where the liquid phase coexists with the $\sqrt{7} \times \sqrt{7}$ commensurate phase. PM using the PIMC simulation calculated the superfluid density for the coverage where the liquid is formed and found that the superfluid den-
sity is close to the ideal 2D superfluid. Experimentally, the superfluid response is significantly smaller as compared to that of a 2D superfluid. This has been attributed to the grafoil substrate inhomogeneities which create only “patches” of superfluid.

The second layer of helium on graphite at completion is a compressed 2D triangular solid. This is the last layer that is solid at completion. The third layer is far enough from the substrate surface that the van der Waals attraction is not strong enough to compress the third layer to form a solid at completion. This experimental fact is also seen in the PIMC simulation of PM. While the simulation indicates that third layer remains liquid at completion, an increased spatial order is observed indicating that the layer at completion is near solidification. While the coverage is continually increased and the fourth layer liquid is built, atoms are observed to go to the third layer. It is also seen experimentally, that the formation of a new layer squeezes the previous layer further. This effect can cause solidification of the third layer during the construction of the fourth layer, explaining a new peak which appears in the experimental specific heat as a function of temperature for densities which correspond to fourth layer coverage. Moreover the tendency for increased spatial order near layer completion can explain the plateaus in the superfluid density as a function of coverage observed by torsional oscillator experiments. PM have calculated the superfluid density and they also find a suppression of it near and after third layer completion.

There is another recent calculation of helium on a very different substrate, namely, metallic lithium.

B. Molecular hydrogen films

Molecular hydrogen has quantum fluctuations nearly as important as helium. The H₂–H₂ interaction is approximately a factor of three stronger than the He–He interaction, while the H₂ mass is a factor of two smaller. Nevertheless, bulk H₂ becomes solid at 13.8 K, because the H₂ zero pressure density is 30% higher than ⁴He because of the stronger interaction. One may anticipate that in 2D, where due to reduced coordination number quantum fluctuations become more important, H₂ might not be a solid at zero temperature. However, H₂ confined onto a two-dimensional surface without corrugations forms a triangular solid with an equilibrium density which depends on the strength of the confining potential. For strictly 2D H₂ the equilibrium density is found to be 0.064 Å⁻². PIMC calculations for H₂ on graphite without corrugations give an equilibrium density 0.0705 Å⁻². This can be understood by the fact that the strict 2D confinement increases the zero-point motion along the surface and that causes melting of the solid at a lower density. A similar effect was observed when H₂ was placed on a helium surface and on a solid hydrogen surface. Below this equilibrium density H₂ is in solid–gas coexistence.

Wagner and Ceperley (WC) using PIMC have studied melting of H₂ surfaces. They studied the growth of several layers of H₂ on the surface of solid H₂. The zero-point motion due to reduced coordination is not strong enough to keep the surface layer in liquid state down to zero temperature which would have implied a 2D superfluid. The surface melting temperature is at most 6 K for a complete surface layer which is less than half the bulk critical temperature of 13.8 K. For an incomplete layer, this melting temperature is reduced to as low as 3 K. In the surface layer, vacancies were evident, in agreement with experimental estimates of the vacancy activation energy of 25 K.

Gordillo and Ceperley (GC) considered another possibility to reduce the tendency for solidification. They added impurities (alkali metal atoms) onto a metal surface to frustrate the long-range spatial order. GC using PIMC simulated a 2D H₂ system in which the alkali atoms form a regular lattice. They found that the presence of such alkali metals can wipe out solidification thus opening the door for superfluidity. In Fig. 9 the superfluid fraction is shown as a function of coverage at T=1 K for three different systems: A rectangular lattice of K atoms with 4 K atoms per simulation cell shown as ×’s and solid line. In addition shown as squares (diamonds) and dashed (dotted) line is the superfluid fraction for H₂ on a 2D surface with K (Cs) atoms forming a triangular lattice with 4 K (Cs) atoms per simulation cell. Notice that for all these cases the superfluid fraction has a significant value around a H₂ coverage of 0.04 Å⁻². Figure 10 shows the temperature dependence of the superfluid fraction for a system of 4 K impurities on a rectangular lattice with H₂ coverage of 0.04 Å⁻². The solid line corresponds to a rectangular lattice arrangement while the more suppressed denoted by dashed line corresponds to the triangular lattice. Notice that this is a typical 2D superfluid response with the well-known associated finite-size effects that go along with a Kosterlitz–Thouless transition. Therefore, this is a novel case scenario where impurities can cause a solid to superfluid transition in molecular hydrogen in reduced dimensionality. GC have discussed a physical realization of this mechanism on a surface of Ag with adsorbed atoms of Cs or K impurities forming a triangular lattice.
VI. DROPLETS: HELIUM AND HYDROGEN

Other authors in this volume and elsewhere have reviewed the extensive literature on doped helium droplets. Here, we only discuss calculations on pure droplets of helium and hydrogen. Such droplets were considered early on primarily as simple boson models of nuclei. Schmidt and Ceperley have reviewed aspects of this early work. Sindzingre, Ceperley, and Klein did the first computation of the superfluid properties of the droplets using PIMC. They determined that for droplets of size 64 or greater, the droplet is almost entirely superfluid, and this happens at a temperature only a little lower than the transition temperature of the bulk. In contrast to the bulk, there is not a sharp transition to the superfluid state, since sharp transition only occurs in the thermodynamic limit (or at zero temperature). Because of surface effects, the superfluid density does not equal unity at zero temperature. Lewart, Pandharipande, and Pieper have computed the occupation numbers of the single particle states using zero temperature quantum Monte Carlo methods.

SCK also consider parahydrogen droplets. As discussed above, hydrogen is very close to being a liquid and superfluid, but in the bulk or at a surface a solid is the stable low temperature structure. However, in a small hydrogen droplet, the cluster geometry frustrates the formation of a localized state. SCK discovered that clusters with fewer than 32 molecules have significant exchange at temperature less than 1 K and thus exhibit partial superfluid properties. In larger clusters, the density of the cluster increases enough so that the core of the cluster becomes localized. It is not known how much of the surface would become superfluid; that would depend on the precise cluster size and geometry. Very recently experimental evidence for hydrogen ring exchanges has been found.

VII. FINAL REMARKS

The field of boson superfluidity is healthy and moving away from its roots in liquid–helium. There are prospects of other materials where statistics are important such as hydrogen and low-density gases. PIMC methods allow for an unambiguous confrontation between theory and experiments and give us a different point of view concerning superfluidity, enabling one to use methods from classical statistical mechanics to investigate highly quantum many-body systems.

ACKNOWLEDGMENTS

The writing of this article was supported by the NSF Grant No. DMR98-03373, by NASA Grant Nos. NAG8-1773 and NAG8-1926 on fundamental physics in microgravity, and by the Department of Physics at the University of Illinois Urbana-Champaign.

42 K. Nho and E. Manousakis (in preparation).