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We review the use of the path integral Monte Carlo (PIMC) methodology to the
study of finite-size quantum clusters, with particular emphasis on recent appli-
cations to pure and impurity-doped ⁴He clusters. We describe the principles of
PIMC, the use of the multilevel Metropolis method for sampling particle permu-
tations, and the methods used to accurately incorporate anisotropic molecule-
helium interactions into the path integral scheme. Applications to spectroscopic
studies of embedded atoms and molecules are summarized, with discussion of the
new concepts of local and nanoscale superfluidity that have been generated by
recent PIMC studies of the impurity-doped ⁴He clusters.

1. Introduction

Over the past 15 years, the path integral Monte Carlo (PIMC) method has evolved
into a uniquely powerful computational tool for the study of bulk and finite quantum
systems. In PIMC, one is interested in computing the thermal average of a quantum
observable $\hat{O}$ at a given temperature $T$, which can be expressed with respect to the
thermal density matrix $\rho(R, R'; \beta) = \langle R'| e^{-\beta \hat{H}} | R \rangle$:

$$\langle \hat{O} \rangle = Z^{-1} \int dR dR' \rho(R, R'; \beta) \langle R|\hat{O}|R' \rangle;$$

(1)

where $R \equiv (r_1, r_2, \ldots, r_N)$ is a point in the $3N-$dimensional configuration space
of an $N$-particle system, $\hat{H}$ is the Hamiltonian, and $\beta = 1/k_B T$. Here $Z = \int dR \rho(R, R; \beta)$ is the partition function. The multidimensional integral of Eq. (1)
can in principle be evaluated by standard Monte Carlo integration schemes, i.e. by
taking an average of $\langle R|\hat{O}|R' \rangle$ over the configurations $\{R, R'\}$ sampled from the
probability distribution $Z^{-1}\rho(R, R'; \beta)$. However, the full density matrix of an in-
teracting $N$-particle quantum system is generally not known at low temperatures.
Therefore one needs to resort to the discrete representation of the Feynman path
integral formula for a low-temperature density matrix, which will be discussed in
detail in Section 2.

The finite-temperature nature of PIMC makes this a complementary approach
to zero-temperature Monte Carlo methods, such as variational Monte Carlo, or
Green’s function-based methods such as diffusion Monte Carlo, which are reviewed
in Chapter 1 of this volume. PIMC is currently the only numerical method capable
of directly addressing finite-temperature superfluidity and the superfluid transi

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in helium. In addition, unlike the zero-temperature methods, PIMC does not require the use of a trial function, requiring as input only the particle masses, numbers, and interaction potentials, in addition to the temperature and volume. Consequently, it is a numerically exact technique, and is independent of the trial function bias problems that zero-temperature methods may suffer from. However, because PIMC provides thermodynamic averages, state-specific information is generally not available. Although in principle the density matrix contains information on the full eigenspectrum of the Hamiltonian $\hat{H}$, extracting this requires the numerical inversion of a Laplace transform. Such inversions are known to be notoriously difficult in the presence of Monte Carlo noise. Thus, to date, path integral Monte Carlo has provided only very limited dynamical information of a direct nature. Nevertheless, it has provided critical microscopic input into dynamical models for physical systems in helium droplets, and in conjunction with zero-temperature, state-specific calculations for these finite helium systems, PIMC has proven to be a powerful means of investigating the dynamic consequences of atomic scale structure of a superfluid.

Feynman first applied the path integral approach to liquid helium in 1953, and provided a consistent clarification of the role of Bose permutation symmetry in the lambda transition of liquid helium. In Feynman’s original treatment, the multidimensional integrals of Eq. (1) were approximated analytically. In the late 1980’s, Ceperley and Pollock subsequently devised a Monte Carlo scheme for the exact numerical evaluation of these multidimensional integrals, in which the combined configuration and permutation spaces were efficiently sampled using a multilevel Metropolis method. This allowed direct quantitative application of Feynman’s path integral approach to the superfluid state of helium for the first time.

Since then, the PIMC method has been applied to provide a quantitative description of numerous bulk and finite bosonic systems. In addition to extensive studies of bulk helium, PIMC has now been employed in the study of $^4$He/$^3$He mixtures, of helium and molecular hydrogen droplets, and of helium and hydrogen films on various surfaces. In this work, we focus on the application of PIMC to quantum simulations of finite helium clusters, $^4$He$_N$. Since we are primarily concerned with the bosonic isotope of helium, for the remainder of the chapter, we will denote $^4$He as simply He, unless explicitly stated. The field of helium cluster research has grown very rapidly over recent years due to new possibilities of inserting molecular probes and studying their properties. An overview of the experimental work in this area is provided in Chapter 9 of this volume. Accompanying this rise in experimental studies, there has been a correspondingly increased demand for complementary theoretical study of these finite quantum systems.

The earliest PIMC simulation of pure He$_N$ droplets, made in 1989, demonstrated superfluid behavior for sizes $N$ as small as 64. This result, together with zero-temperature calculations of the size scaling for pure cluster excitation spectra made at that time, was taken to be strong theoretical evidence that these finite-sized clusters were indeed superfluid. This was later confirmed experimentally through a series of elegant experiments with impurity-doped helium clusters.
clusters present additional technical challenges for PIMC beyond the requirements posed by a finite cluster of pure HeN. Early PIMC work with doped clusters addressed the widely studied HeN SF6 system. These studies showed that the global superfluid fraction appeared not to be significantly modified by introduction of an impurity. However, it soon became apparent that interesting new local features due to Bose exchange symmetry were present in the immediate vicinity of an impurity. This led to the recognition that a local non-superfluid density could be induced by the molecular interaction with helium. PIMC simulations of doped clusters have now been made with a variety of impurities, including OCS, HCN, benzene, H2, neutral and ionic alkali atoms, and some complexes of these molecules. As will be outlined here, these studies have revealed a broad range of properties of the dopant as well as insight into the dopant influence on the superfluid properties of the droplets. Key features that have emerged from these studies of doped droplets are the ability to analyze superfluid behavior in nanoscale dimensions, to characterize quantum solvation in a superfluid, and to probe the atomic-scale behavior of a superfluid near a molecular interface.

In this review, we first provide an overview of the Feynman path integral formalism for quantum statistical thermodynamics in Section 2. Following this introduction, we discuss the PIMC implementation of the general Feynman theory, focusing in particular on the multilevel Metropolis sampling method of Ceperley and Pollock. We then review applications of the PIMC method to the study of pure helium droplets, and of doped helium clusters containing atomic or molecular impurities in Section 3. The analysis of superfluidity in finite droplets, and concepts of nanoscale superfluids and local superfluidity are described in Section 3.4. PIMC applications to spectroscopic studies of doped helium clusters are summarized in Section 4. We conclude in Section 5 with a summary of open questions.

2. Theory

2.1. General formulation

Here we deal with a cluster of N He atoms doped with a single impurity. In many of the studies made to date, the impurity is assumed to be fixed at the origin without either translational or rotational motion. Neglect of the impurity translational degrees of freedom is not essential, but for impurity particles which are heavy relative to a helium atom, it is reasonable and often convenient to ignore the translational motion of the impurity. However, the neglect of the impurity rotational degrees of freedom should be treated with caution, especially for impurities with small principal moments of inertia. Incorporation of the rotational motion of the impurity is an area of current work. Hence for the present discussion we consider the following system Hamiltonian $\hat{H}$:

$$\hat{H} = \hat{K} + \hat{V} = -\lambda \sum_{i=1}^{N} \nabla_{i}^{2} + \sum_{i<j} V_{\text{He-He}}(r_{ij}) + \sum_{i} V_{\text{He-imp}}(r_{i}),$$ (1)
where $\lambda = h^2/2m_4$, with $m_4$ being the helium mass. The potential energy $\hat{V}$ includes a sum of He-He pair potentials, $V_{\text{He-He}}$, and He-impurity interactions $V_{\text{He-imp}}$, where the latter are most readily given in the molecular frame. If necessary, e.g. for light molecules, the impurity translational degrees of freedom can be incorporated by adding an additional term $-\lambda I\nabla_i^2$, corresponding to the impurity center-of-mass kinetic energy.

In the path integral approach, one uses the identity $e^{-(\beta_1+\beta_2)\hat{H}} = e^{-\beta_1\hat{H}}e^{-\beta_2\hat{H}}$ to express the low-temperature density matrix by an integral over all possible paths, $\{R, R_1, R_2, \ldots, R_{M-1}, R'\}$, with the weight for each path given by the product of density matrices at a higher temperature $T' = MT$:

$$\rho(R, R'; \beta) = \int dR_1 dR_2 \ldots dR_{M-1} \rho(R, R_1; \tau)\rho(R_1, R_2; \tau) \ldots \rho(R_{M-1}, R'; \tau).$$

Here $\tau \equiv \beta/M = (k_B T')^{-1}$ constitutes the imaginary time step defining the discrete representation of the path integral. For a sufficiently high temperature $T'$ or, equivalently, for a small enough time step $\tau$, there exist several approximations to the density matrix that are sufficiently accurate for this factorization to be used in numerical work. The simplest of these high-temperature approximations is the primitive approximation, which is based upon the Trotter formula:

$$\rho(R_k, R_{k+1}; \tau) \approx \int dR' \langle R_k | e^{-\tau \hat{K}} | R' \rangle \langle R' | e^{-\tau \hat{V}} | R_{k+1} \rangle.$$

The potential energy operator $\hat{V}$ in Eq. (1) is diagonal in the position representation,

$$\langle R' | e^{-\tau \hat{V}} | R_{k+1} \rangle = e^{-\tau V(R_{k+1})} \delta(R' - R_{k+1}),$$

while the kinetic term corresponds to the free particle density matrix:

$$\langle R_k | e^{-\tau \hat{K}} | R' \rangle = \rho_{0}(R_k, R'; \tau) = (4\pi \lambda \tau)^{-3N/2} e^{-\langle R_k - R' \rangle^2/4\lambda \tau}.$$  

From Eqs. (2)-(5), the path integral representation for the density matrix in the primitive approximation may be expressed as:

$$\rho(R_0, R_M; \beta) =$$

$$(4\pi \lambda \tau)^{-3N\beta/2} \int dR_1 \cdots dR_{M-1} \exp \left[-\sum_{k=1}^{M} \sum_{i,j=1}^{N} \frac{(r_{i,k} - r_{i,k-1})^2}{4\lambda \tau} - \tau \sum_{k=1}^{M} V(R_k) \right],$$

with

$$V(R_k) = \sum_{i<j}^{N} V_{\text{He-He}}(r_{i,j,k}) + \sum_{i=1}^{N} V_{\text{He-imp}}(r_{i,k}).$$

A single $R_k$ is referred to as a time slice, and $r_{i,k}$, the position of the $i^{th}$ particle at the $k^{th}$ time slice, as a bead. From here on, $i$ will denote particle index and $k$ will denote time index. Eq. (6) may be viewed as a classical configuration integral, with the exponent of its integrand corresponding to an energy function. The first term in the exponent, derived from the kinetic energy, corresponds to a spring
potential that connects beads representing the same atom at successive imaginary times, with coupling constant $\frac{2\lambda\tau}{-1}$. This chain of beads connected by springs is often referred to as a polymer. The helium-helium interaction is represented by an inter-polymer potential that has non-zero interactions only between beads located on different polymers and indexed by the same imaginary time value. This corresponds to Feynman’s original idea of mapping path integrals of a quantum system onto interacting classical polymers, with a special form of polymer interaction potential.

In the absence of kinetic contributions from the impurity, the helium-impurity interaction acts as an additional external field for the helium atoms, and hence for these polymers.

The thermal density matrix $\rho(R, R'; \beta) = \langle R|e^{-\beta\hat{H}}|R' \rangle$ can be expanded in terms of the eigenvalues $\{E_n\}$ and the corresponding eigenfunctions $\{\phi_n\}$ of the Hamiltonian $\hat{H}$:

$$\rho(R, R'; \beta) = \sum_n \phi_n(R)\phi_n^*(R')e^{-\beta E_n}. \quad (8)$$

This is appropriate for a system of distinguishable particles under Boltzmann statistics. For a Bose system such as He or para-H$_2$, it should be symmetrized with respect to particle exchanges. This can be done by modifying the sum in Eq. (8) to a sum over exchange-symmetrized stationary states $\tilde{\phi}_\alpha$ only:

$$\rho_B(R, R'; \beta) = \sum_\alpha \tilde{\phi}_\alpha(R)\tilde{\phi}_\alpha^*(R')e^{-\beta E_\alpha}. \quad (9)$$

A symmetrized eigenfunction $\tilde{\phi}_\alpha(R)$ can be obtained by summing a stationary wavefunction of distinguishable particles, $\phi_n(\mathcal{P}R)$, over all $N$-particle permutations $\mathcal{P}$:

$$\tilde{\phi}_\alpha(R) = \frac{1}{N!} \sum_\mathcal{P} \phi_n(\mathcal{P}R). \quad (10)$$

Inserting Eq. (10) into Eq. (9), we obtain the symmetrized density matrix for a Bose system:

$$\rho_B(R, R'; \beta) = \frac{1}{N!} \sum_\mathcal{P} \rho(R, \mathcal{P}R'; \beta). \quad (11)$$

2.2. Density matrix evaluation

In order to make PIMC calculations more tractable, one wishes to use the smallest possible number of time slices $M$ for a given temperature $T$. This means that it is essential to find accurate high-temperature density matrices at as small a value $T'$ as possible, so that the imaginary time step $\tau$ be kept as large as possible. It has been found that for the helium-helium interaction, the primitive approximation described in Eqs. (3)–(5) is accurate enough at temperatures higher than \(\sim 1000 \text{ K}\). This implies that a PIMC simulation at $T \sim 0.3 - 0.4 \text{ K}$, where the spectroscopic measurements for the impurity-doped helium clusters have been performed, would require several thousands of time slices. This computational expense can be avoided
by going beyond the primitive approximation to a more sophisticated approximation for the high-temperature density matrices. Based on the Feynman-Kac formula, the high-temperature density matrix $\rho(R, R'; \tau)$ can be approximated by a product of the free particle propagator $\rho_0(R, R'; \tau)$ of Eq. (5) and an interaction term $e^{-U(R, R'; \tau)}$:

$$\rho(R, R'; \tau) \approx \rho_0(R, R'; \tau) e^{-U(R, R'; \tau)}. \quad (12)$$

The interaction term $e^{-U(R, R'; \tau)}$ is in turn factored into contributions deriving from the helium-helium and helium-impurity interactions, $\rho_{\text{He-He}}$ and $\rho_{\text{He-imp}}$, respectively. For spherical interactions, one can generate a pair-product form of the exact two-body density matrices using a matrix squaring approach discussed in detail in Ref. 20. We use this for the helium-helium interaction, which is spherically symmetric. Such helium-helium density matrices of the pair-product form have been shown to be accurate for $\tau^{-1}/k_B \geq 40$ K, i.e., $T' \geq 40$ K. This same approach can be used for the helium-impurity interaction when this is also isotropic, and may involve complicated three-dimensional dependencies. This can be dealt with in several ways. One approach is to expand the helium-impurity interaction in spherical terms and then employ pair-product forms as above. We have found it convenient to work within the primitive approximation for the helium-impurity interaction, which allows considerable flexibility when changing impurities. The required time step for the accurate primitive helium-impurity density matrices varies, depending on the impurity molecule involved (e.g., $\tau^{-1}/k_B \geq 80$ K for He-SF$_6$ and He-OCS, $\tau^{-1}/k_B \geq 160$ K for He-benzene). This must be recalibrated, e.g., by establishing converged helium densities, for every new molecule that is studied. The same re-calibration requirement holds also for spherical expansions.

2.3. Multilevel Metropolis algorithm

For a diagonal operator $\hat{O}$ in the position representation, $\langle R | \hat{O} | R' \rangle = O(R) \delta(R - R')$, we need to consider only the diagonal density matrices for evaluation of its thermal average, Eq. (1). For the diagonal density matrix, both the sum over permutations in Eq. (11) and the multidimensional integration in Eq. (2) can be evaluated by a sampling of discrete paths which end on a permutation of their starting positions, i.e., $s = \{R_0, R_1, R_2, \cdots, R_{M-1}, R_M\}$ with $R_M = \mathcal{P}R_0$. This gives rise to an isomorphic mapping onto ring polymers. In fact, all physical quantities discussed in this review can be estimated from a set of stochastically sampled ring polymers. In the sampling process, it will be natural to choose the probability density function as

$$\pi_s = Z^{-1} \prod_{k=0}^{M-1} \rho(R_k, R_{k+1}; \tau). \quad (13)$$

The Metropolis algorithm, a widely-used Monte Carlo sampling technique, provides a route to obtain the converged distribution $\pi_s$ in the limit of many sampled config-
urations, as long as the detailed balance condition is satisfied for transitions between successive configurations:

\[ \pi_s P_{s \rightarrow s'} = \pi_{s'} P_{s' \rightarrow s}. \]  

(14)

Here \( P_{s \rightarrow s'} \) is the transition probability from a configuration \( s \) to \( s' \). This is factorized into an \textit{a priori} sampling distribution \( T_{s \rightarrow s'} \) and an acceptance ratio \( A_{s \rightarrow s'} \):

\[ P_{s \rightarrow s'} = T_{s \rightarrow s'} A_{s \rightarrow s'}. \]  

(15)

In order to speed up convergence times in a path integral simulation, in particular one involving permutation moves, it is very important to select an appropriate distribution function \( T_{s \rightarrow s'} \) for a trial move \( s' \) from \( s \). The most efficient way of doing this is the multilevel Metropolis algorithm developed by Pollock and Ceperley. \cite{20,24} Here one first chooses end points of each path by sampling a permutation \( P \). Then the paths are bisected and the configurations at the midpoints sampled. This process of bisection and midpoint sampling is repeated multiple times, resulting in a multilevel scheme that samples whole sections of the paths in a single step. The acceptance ratio at each level of this multilevel Markov process is set so that the combined process of permutation and configuration moves may lead to the probability density function \( \pi_s \) of Eq. (13). Detailed procedures are summarized as follows:

1. Initialize a configuration \( s \). Typically one starts from a \textit{classical} configuration, in which all beads representing each atom are located at the same site. So each polymer corresponds initially to a single point.
2. Choose a time slice \( k \) randomly between 0 and \( M - 1 \) and construct a table for trial permutation transitions between time slices \( k \) and \( k + n \), where \( n = 2^l \) and \( l \) is the \textit{level} of this path updating process. For the simulation of a He system, \( l = 3 \) turns out to be a good choice for the permutation moves. Trial permutations may be restricted to cyclic permutations among 2, 3, or 4 particles. The probability for permutation transitions is proportional to

\[ T_P = \exp \left[ - \frac{(R_k - PR_{k+n})^2}{4\lambda n_T} \right], \]  

(16)

\[ C_I = \sum_P T_P. \]  

(17)

Thus the transition probability for permutational moves does not depend on the potential energy. Note that one can explore the entire \( N \)-particle permutation space by repeatedly sampling cyclic permutations among a small number of particles.
3. Select a trial permutation \( P \) involving \( p \) atoms such that

\[ \sum_{P' < \mathcal{P}} T_{P'} < \chi < \sum_{P' \leq \mathcal{P}} T_{P'}, \]  

(18)

where \( \chi \) is a random number on \((0, C_I)\). This selects the permutation with probability \( T_{P}/C_I \). Then compute \( \Delta_0 = T_{P}/T_I \). After this, we will sample the
intermediate path coordinates connecting $R_k$ with $\mathcal{P}R_{k+n}$. The coordinates of the $(N-p)$ atoms not on the cycle represented by $\mathcal{P}$ will not change from their old positions. This is level 0 sampling.

4. Start a bisection algorithm by sampling a new midpoint $R'_{k+\frac{n}{2}}$. For the sampling distribution function $T(R'_{k+\frac{n}{2}}|R_k, \mathcal{P}R_{k+n}; \frac{n}{2}\tau)$, we use a multivariate Gaussian form centered at the mean position $\bar{R} = (R_k + R_{k+n})/2$ (see Eq. (5.16) of Ref. 20). Then compute

$$\Delta_1 = \frac{\rho(R_k, R'_{k+\frac{n}{2}}; \frac{n}{2}\tau)\rho(R'_{k+\frac{n}{2}}, \mathcal{P}R_{k+n}; \frac{n}{2}\tau)}{\rho(R_k, \mathcal{P}R_{k+n}; \frac{n}{2}\tau)}.$$  

Proceed to the next step with probability

$$\frac{\Delta_1 T(R'_{k+\frac{n}{2}}|R_k, \mathcal{P}R_{k+n}; \frac{n}{2}\tau)}{\Delta_0 T(R'^{'}_{k+\frac{n}{2}}|R_k, \mathcal{P}R_{k+n}; \frac{n}{2}\tau)}. \quad (20)$$

If rejected, go back to step 3 and sample a new trial permutation. This is level 1 sampling.

5. At the second level, sample $R'_{k+\frac{n}{2}}$ and $R'^{'}_{k+\frac{n}{2}}$ by bisecting the two intervals and continue to the next level with the same procedures as used in step 4. This bisection process is repeated until we get to the final $l$-th level. At the $l$-th level, sample $R'_{k+1}, R'_{k+3}, \ldots,$ and $R'_{k+n-1}$ with the probability distribution function $T(R'_{k+1}|R'_{k+1-1}, R'_{k+1+1}; \tau)$. Proceed to the next step with probability

$$\frac{\Delta_l T(R_{k+1}|R_{k+1-1}, R_{k+1+1}; \tau)}{\Delta_{l-1} \prod_{j=k+1}^{k+n-1} T(R_{j}^{'}|R_{j-1}^{'}; R_{j+1}^{'}; \tau)}, \quad (21)$$

where

$$\Delta_l = \prod_{j=k+1}^{k+n} \frac{\rho(R'_{j-1}, R'_{j}; \tau)}{\rho(R_{j-1}, R_{j}; \tau)}.$$  

If rejected, go back to step 3. Fig. 3 depicts the structure of a multi-level sampling with $l = 3$, in a path integral containing $M = 16$ time slices.

6. Construct a new permutation table for all 2, 3, or 4 particle exchanges $\mathcal{P}'$ acting on $\mathcal{P}R_{k+n}$. Accept a new path $R_k, R'_{k+1}, \ldots, R'_{k+n-1}, \mathcal{P}R_{k+n}$ with probability $C_l/C_{\mathcal{P}'}$, where $C_{\mathcal{P}'} = \sum_{\mathcal{P}'} T_{\mathcal{P}'}$. If rejected, go again back to step 3.

7. After replacing old coordinates and permutation table with new ones, repeat steps 3 to 6.

8. After attempting several hundreds or thousands of permutation moves between times slices $k$ and $k+n$, followed by the bisection procedures to update the midpoints of all $l$ levels, we select a new time slice $k$ and repeat steps 2 to 6.

One can check that the multilevel bisection algorithm described here satisfies the detailed balance condition in Eq. (14). Note that $P_{s \rightarrow s'}$ is the total transition probability to go through all $l$ levels.
2.4. Estimators for some physical quantities

With the generalized Metropolis sampling of the permutation symmetrized density matrix $\rho_B(R, R; \beta)$, the thermal average of an observable $\hat{O}$ diagonal in the position representation can be estimated by taking an arithmetic average of $\langle \hat{O} \rangle = \langle R | \hat{O} | R \rangle$ over the paths sampled. For instance, the helium density distribution around an impurity molecule can be estimated by

$$
\rho(r) = \frac{1}{M} \sum_{k=0}^{M-1} \sum_{i=1}^{N} \langle \delta(r - \vec{r}_{i,k}) \rangle.
$$

(23)

Note that all time slices in ring polymers can be considered as equivalent. Unlike importance-sampled diffusion Monte Carlo methods, the PIMC calculation of structural properties such as the density distribution does not involve any trial function bias.

There are many ways to compute the energy in PIMC, discussed in detail in Ref. [24]. Most of the PIMC applications discussed here employ the direct estimator obtained by directly applying the Hamiltonian operator to the density matrix in the position space. For calculations neglecting the impurity translational and rotational degrees of freedom, the kinetic energy average is expressed in the path integral representation as

$$
\langle K \rangle = \left\langle \frac{1}{M} \sum_{k=0}^{M-1} \left[ \frac{3N}{2\tau} - \frac{(R_k - R_{k+1})^2}{4\lambda \tau^2} \right] \right\rangle
$$

(24)
\[-\frac{(R_k - R_{k+1})}{\tau} \cdot \nabla_k U_k + \lambda \nabla_k^2 U_k - \lambda (\nabla_k U_k)^2 \bigr) \bigr],

where \( \nabla_k = \partial/\partial R_k \) is the 3N-dimensional gradient operator, and \( U_k \equiv U(R_{k-1}, R_k; \tau) \) is the interaction for link \( k \), \( k \) being for the spring connecting beads \( k-1 \) and \( k \) (see Eq. (12)). Computation of the potential energy is straightforward since this is diagonal in the position representation:

\[
\langle V \rangle = \frac{1}{M} \sum_{k=0}^{M-1} \langle V(R_k) \rangle.
\]

(25)

As noted earlier, the inter-polymeric potential acts only between beads defined at the same imaginary time.

One of the most interesting properties of bulk and finite He systems is their superfluid behavior. For bulk systems superfluid estimators are generally derived from linear response theory, \( \text{i.e.} \) by considering the helium response to boundary motion. Pollock and Ceperley showed how to derive momentum density correlation functions that quantify the superfluid response of bulk systems with periodic boundary conditions. Sindzingre et al. subsequently developed a global linear response estimator for finite helium clusters with free boundaries. This estimator is based on the response to a rotation of continuous angular frequency, \( \text{i.e.} \) to a classical rotation such as might be appropriate to a macroscopic droplet. Consider the Hamiltonian in a coordinate frame rotating about an axis with frequency \( \omega \),

\[
\hat{H}_{\text{rot}} = \hat{H}_0 - \hat{L} \cdot \omega,
\]

(26)

where \( \hat{L} \) is the total angular momentum operator. For a classical fluid, in the limit of an infinitesimally small rotation the entire fluid should rotate rigidly with classical moment of inertia \( I_{\text{cl}} \). But in a Bose superfluid, only the normal component responds to the rotation, resulting in an effective moment of inertia

\[
I = \left. \frac{\partial \langle \hat{L} \rangle}{\partial \omega} \right|_{\omega=0}.
\]

(27)

Note that this is to be evaluated in the limit \( \omega \to 0 \), appropriate to rotation of a macroscopic system. In a homogeneous system the normal fraction can be defined as

\[
\rho_n = \frac{I}{I_{\text{cl}}},
\]

(28)

and the complementary superfluid fraction is then given by

\[
\rho_s = 1 - \frac{\rho_n}{\rho} = \frac{I_{\text{cl}} - I}{I_{\text{cl}}}.
\]

(29)

For \( \omega = \omega \hat{z} \), this linear response estimator can be expressed in the path integral representation as

\[
\frac{\rho_s}{\rho} = \frac{4m^2 \langle \hat{A}^2 \rangle}{\beta \hbar^4 I_{\text{cl}}}.
\]

(30)
with the vector quantity $A$ defined as

$$A = \frac{1}{2} \sum_{i,k} (\mathbf{r}_{i,k} \times \mathbf{r}_{i,k+1}).$$

(31)

Here the summation runs over particle $i$ and imaginary-time slice $k$. The vector quantity $A$ is the directed total area of closed imaginary-time polymers spanned by all $N$ particles, e.g., $A_z$ is the projection of $A$ on the $\hat{z}$-direction. The average size of a single polymer is given by its thermal de Broglie wavelength $\Lambda = (\beta \hbar^2 / m)^{1/2}$. This becomes negligible in the high-temperature limit, and thus the corresponding superfluid fraction $\rho_s/\rho$ goes to zero (although the projected area can remain finite at the microscopic level). At low temperatures, when the de Broglie wavelength becomes comparable to the inter-polymer spacing, particle exchanges cause polymers to cross-link and form larger ring polymers. The projected area $A$ increases correspondingly and the helium system attains an appreciable superfluid fraction.

We discuss the application of this finite-system superfluid estimator in detail in Sec. 3, together with analysis of how this can be decomposed into local contributions for an inhomogeneous system.

3. Superfluidity and quantum solvation of atoms and molecules in bosonic helium clusters

Spectroscopic studies of impurity-doped clusters have allowed experimental investigation of a variety of excitations in helium clusters. The relevant temperature range currently accessible is $T \sim 0.15 - 0.5$ K. Thus, the incorporation of Bose symmetry is essential in simulation of these systems. In this section, we focus on the application of finite-temperature PIMC to bosonic helium clusters. We begin by briefly reviewing studies of pure clusters in Sec. 3.1, and then focus on the more recent work for the clusters doped with various impurities in Secs. 3.2–3.4. Secs. 3.2–3.3 summarize the structural and energetic aspects, while Sec. 3.4 deals with the microscopic analysis of superfluid properties of the doped clusters.

3.1. Pure clusters

Most of the previous theoretical studies involving pure clusters are based on zero-temperature methods, and have focused on the cluster elementary excitation spectrum, which qualitatively retains the phonon-roton features characteristic of bulk He II. Current work in this area aims to understand the physical nature of the roton excitations. Zero- and finite-temperature calculations for pure helium clusters have been reviewed previously, and so we shall provide only a brief outline of the finite-temperature results here. The first studies were made by Cleveland et al., using the path integral molecular dynamics approach in which exchange is neglected. This allowed structural analysis, which was used to study the changes in droplet density and diffuseness as a function of size. Permutation exchange symmetry was incorporated by Sindzingre et al. in a study of the temperature and size
dependence of the global superfluid fraction in finite He$_N$ clusters. These calculations employed the area estimator discussed in Sec. 2.4 and showed that a broad transition to a predominantly superfluid state occurs at a temperature depressed from the bulk superfluid transition temperature, in accordance with expectations from scaling of phase transitions for finite systems. The extent of depression increased as the cluster size decreased. For $N = 64$, the onset of the transition occurs just below $T = 2$ K, and the transition appears complete at $T = 0.5$ K, with about 90% or more of the cluster being superfluid at that temperature. A qualitative examination of the relative contribution of long exchange path lengths to the density revealed that the long exchange path contribution was largest in the interior of the droplets.

3.2. Atomic impurities

Neutral and ionic atomic impurities constitute the simplest dopants. For ground electronic states, the helium-impurity interatomic potential can be calculated with fairly high accuracy using standard quantum chemistry methods, and the helium-helium interatomic potential is well-known. Thus, within the two-body approximation, it is possible to construct accurate potential energy surfaces for the ground electronic state. The interactions of excited electronic states with helium are, by comparison, less well-characterized and only a few calculations of electronically excited potential energy surfaces have been even attempted. To date, PIMC calculations have been made for the neutral alkali metal impurities Li, Na, K, and for the ionic impurity Na$^+$. In general, the solvation characteristics of each impurity are controlled by a balance between different energetic factors. These include the helium-impurity interaction strength, the helium-helium interaction strength, the impurity kinetic energy (and thus impurity mass), and the free energy change due to the loss of exchange energy for helium atoms adjacent to the impurity.

The He-Li, He-Na, and He-K ground state potentials typically have well depths of $\sim 1 - 2$ K, smaller than the He-He well depth of $\sim 11$ K. By considering these potential energy factors alone, one would qualitatively expect that the atomic impurities would reside on the droplet surface in order to minimize the total energy. The PIMC studies, made at $T = 0.5$ K, indicate that the neutral alkali impurity species are indeed surface-attached for cluster sizes of $N \leq 300$. In all cases, the perturbation on the cluster structure due to the presence of the impurity is weak. The neutral impurity atom induces small but distinct modulations in the helium density, starting at the surface and decaying into the interior of the droplet. While no zero-temperature microscopic calculations of these systems have been made to date, it is expected that this behavior would persist to lower temperatures and is therefore also applicable to the experimental studies of these alkali-doped systems that are made at $T = 0.38$ K.

The ionic impurity Na$^+$ interacts much more strongly with helium and consequently gives a markedly stronger structural perturbation of the local helium den-
Helium density profiles relative to the impurity center, at $T = 0.625$ K. The left panel (a) shows the radial density profiles for $\text{He}_{100}\text{Na}^+$ (dashed lines) and $\text{He}_{64}\text{SF}_6$ (solid lines), where an isotropic $\text{He-SF}_6$ interaction was used. The right panel (b) shows anisotropic helium densities for $\text{SF}_6$ (solid lines) from a calculation using an anisotropic $\text{He-SF}_6$ interaction, viewed along the molecular $C_3$ (higher values) and $C_4$ (lower values) axes. This is compared to anisotropic radial density profiles for $\text{He}_{39}$-benzene (dotted-dashed lines), viewed along the molecular $C_6$ axis (higher peak) and along the C–H bond (lower peak). The $\text{He}_{100}\text{Na}^+$ profile is reproduced from Ref. 32.

sity. The $\text{He-Na}^+$ well depth is 407 K, about 40 times larger than the $\text{He-He}$ well depth. Here the finite-temperature PIMC studies indicate that the $\text{Na}^+$ ion resides in the center of the cluster, and the strength and range of the $\text{He-Na}^+$ interaction induces a tightly packed helium “snowball” around the ion. In Fig. 2a, the radial helium density profile for the $\text{He}_{100}\text{Na}^+$ system at $T = 0.625$ K is shown. This is compared with the $N = 64$ radial density profile around the molecular impurity $\text{SF}_6$, at the same temperature using an isotropic $\text{He-SF}_6$ interaction. There is a very strongly modulated layer structure around the $\text{Na}^+$ ion, with a high first coordination shell peak followed by a second peak of lower density. Similar structural features have been seen in variational shadow function calculations for $\text{Na}^+$ and $\text{K}^+$ in bulk He, although quantitative differences exist in comparison with those results. In the variational calculations the local angular ordering within the coordination shells was also examined, leading to more conclusive evidence of solid-like structure in the first two shells. These studies indicate that there definitely exists a more strongly layered shell structure in the helium density around an impurity ion than around neutral atomic species, with more solid-like character. This feature can be further explored in the imaginary-time path integral representation by examining the permutation exchanges of helium atoms at specific locations. For the $\text{He}_{100}\text{Na}^+$ cluster at $T = 0.8$ and 1.25 K, the atoms in the first coordination shell rarely partic-
ipated in permutations with other particles, and thus are well-localized in the PIMC sense. In the second solvation shell, some atoms are involved in long exchanges at the lower temperature, while in the outer third shell most atoms are involved in long exchanges. From this, it was inferred that the third shell is superfluid, while the second shell has an intermediate, temperature-dependent character. Such an analysis has been made in more quantitative detail for the molecular impurities, which we discuss next.

3.3. Molecular impurities

Molecular impurities introduce an additional level of complexity because molecules have internal structure and usually possess an anisotropic interaction with helium. Especially for the larger molecules, there is a severe lack of accurate two-body molecule-helium interaction potentials. Nevertheless, the study of molecular impurities in helium clusters is currently of great interest, with an increasing number of experiments being performed on a variety of molecules. Even with simple models for the molecule-helium interaction, analysis of these experiments in terms of the perturbation of the helium environment on the molecular internal degrees of freedom has provided much insight into the quantum fluid nature of these clusters. It is important to recall that to date, all PIMC work involving molecular impurities in helium have not explicitly incorporated the impurity rotational kinetic energy. This is not an essential restriction, and has been so far made for convenience rather than for any fundamental limitations. Since zero-temperature DMC calculations have recently shown that the helium densities around small molecules may be sensitive to the rotational motion of the molecule, it would be desirable to incorporate the rotational degrees of freedom in future path integral studies. Only for the heaviest rotors can molecular rotation be justifiably omitted. Several studies have also justified neglecting the translational motion of the molecular impurity, in which case the helium atoms may be regarded as moving in the external potential field of the molecule in the molecular body-fixed frame, given by the Hamiltonian of Eq. (1). The validity of this assumption can be assessed with the comparative study of molecular delocalization as a function of molecular mass and binding energy shown in Fig. 3. There, the probability of finding a molecule at some distance \( r \) from the cluster center-of-mass is shown for a series of molecules. As expected, the heaviest dopants such as SF\(_6\) and OCS are well-localized near the center of the cluster, and thus it is a reasonable approximation to neglect their translational motion. On the other hand, H\(_2\) is much more delocalized throughout the interior of the cluster, due to its comparatively smaller mass and weaker helium-impurity interaction, and therefore requires that its translational motion be properly incorporated.

To date, the most extensively studied molecular impurity is the octahedral SF\(_6\) molecule. Early PIMC work on SF\(_6\) in helium clusters employed isotropic molecule-helium interaction potentials, and was later extended to include anisotropic in-
Fig. 3. Radial distribution for several impurity molecules (H₂, HCN, SF₆, and OCS) relative to the cluster center-of-mass, shown as \( P(r) = 4\pi r^2 \rho(r) \) such that \( \int P(r) \, dr = 1 \). All calculations were made from PIMC at \( T = 0.312 \) K, and include the impurity translational kinetic energy. Isotropic interaction potentials were used, and Bose permutation symmetry was not included. The H₂ and HCN distributions were obtained from a calculation with \( N = 128 \) He, while the SF₆ and OCS distributions correspond to a cluster of \( N = 100 \) He. Data courtesy of D. T. Moore.

The helium structure around SF₆ from an isotropic calculation is shown in Figs. 3a and 3b. The anisotropic He-SF₆ potential surface has a global minimum of \(-84\) K, considerably deeper than that of the He-He interaction. Thus, SF₆ is expected to reside at the center of the cluster. This has been verified by both zero-temperature DMC and by finite-temperature PIMC calculations. For the He₆₄SF₆ cluster in the temperature range of \( T = 0.3 - 0.75 \) K, there is an anisotropic layering of the helium density around the SF₆. Integration of the helium density over the first solvation shell yields about 23 atoms, independent of whether isotropic or anisotropic interactions are employed. The strength and range of the molecule-helium interaction pins the helium density in the first solvation shell to a total density comparable to that of the more strongly bound He₉-Na⁺ system. Detailed analysis of the helium density distribution around the molecule shows that while the angular average of the density in the first solvation shell is independent of temperature below \( T = 1.25 \) K, there is a small increase in the extent of anisotropy as the temperature is lowered. This is illustrated in Fig. 4 with a comparison of the densities along different molecular symmetry axes for an \( N = 64 \) cluster at temperatures \( T = 0.625 \) K and \( T = 0.312 \) K. As the temperature is increased above \( T = 1.25 \) K, this trend to an increasingly isotropic distribution is further modified by the onset of evaporation of helium atoms. Evaporation begins with atoms in the second solvation shell, is clearly evident at \( T = 2.5 \) K, and is essentially complete...
at $T = 5.0$ K (Fig. 5).

![Fig. 4. Comparison of the helium density distribution around the octahedral SF$_6$ molecule in a $N = 64$ cluster at $T = 0.625$ K and $T = 0.312$ K. Solid lines show the lower temperature densities and dashed lines the higher temperature densities. Panel (a) shows the angular-averaged density $\rho_0$, for which the profiles at two different temperatures are identical. Panels (b), (c), and (d) show the densities along the three symmetry axes of the molecule $C_2$, $C_3$, and $C_4$, respectively. The higher temperature profiles show consistently smaller peak values in the first solvation shell, indicating a decrease in the anisotropy of the distribution as temperature increases.]

Since the first experiments for doped clusters that employed SF$_6$ as a probe species, a broad array of molecular impurities have been studied by spectroscopic means. The infrared spectral regime has provided a particularly rich field of study. Vibrational spectra in the infrared at $T \sim 0.4$ K show rotational fine structure in $^4$He droplets, but not in $^3$He droplets, providing evidence that quantum statistics play an important role in the spectral properties of the dopant. There is now an increasing collection of experimental data available for the rotational dynamics of molecules possessing varying symmetries and a range of values for the gas phase rotational constant. To date, PIMC has been used to make theoretical stud-
Fig. 5. Helium evaporation for the SF$_6$He$_{39}$ cluster. The lower panel plots a snapshot of imaginary time paths at $T = 1.25$ K. At this temperature the helium atoms are bound to the cluster. In the middle panel, at $T = 2.5$ K, the cluster begins to dissociate, losing helium atoms. In the upper panel, at $T = 5.0$ K, the cluster has completely evaporated.
ies of the linear rotors OCS, HCN, the planar aromatic molecule benzene (C₆H₆), the linear (HCN)₃ complex, and the OCS-(H₂)ₘ complex. From these studies the notion of two different dynamical regimes has emerged, namely that of heavy molecules such as SF₆ that are characterized by gas phase rotational constants \( B_0 < 0.5 \text{ cm}^{-1} \), and a complementary regime of lighter molecules possessing larger gas phase values of \( B_0 \). This division into two dynamical regimes based on rotational constants emerges from analysis of the helium solvation density and energetics derived from path integral calculations.

The OCS impurity lies in the regime of relatively heavy molecules, with \( B_0 = 0.20 \text{ cm}^{-1} \). The He-OCS potential has a global minimum of \( \sim 64 \text{ K} \), which is only about two-thirds that of the He-SF₆ potential. It is important to consider the anisotropy of the intermolecular potential in addition to its strength when assessing the quantum solvation structure. In this respect the linear OCS molecule has lower symmetry than the octahedral SF₆. The minimum angular barrier for rotation of the OCS about an axis perpendicular to the molecular axis (i.e., the angular adiabatic barrier for rotation) is 41.9 K. This barrier is markedly higher than the corresponding value 20.7 K for SF₆, and consequently gives rise to stronger angular modulations in the solvating density. As shown in Fig. 6, PIMC calculations for the He₆₄OCS cluster at \( T = 0.312 \text{ K} \) reveal a strongly structured helium density, forming approximately elliptical solvation shells around the OCS impurity. The first shell integrates to \( \sim 17 \) atoms. Because of the axial symmetry of the He-OCS potential, the density at the global minimum forms a ring around the OCS molecular axis, consisting of about 6 helium atoms.

The benzene molecule (C₆H₆) also lies in the heavy regime. The benzene \( \pi \)-electron character leads to a highly anisotropic interaction with helium, with two deep, equivalent global potential minimum located on the six-fold axis of symmetry above and below the plane of the molecule. A PIMC study of benzene-doped clusters has shown a highly anisotropic helium structure around the impurity molecule that reflects this six-fold symmetry. The sharpest density peak is located along the C₆-axis, at the two equivalent locations of the global potential minima. These two global density maxima are higher than the local density maxima viewed along the in-plane directions by more than a factor of four, reflecting the marked anisotropy of the He-benzene interaction potential. The extreme density anisotropy is summarized in Fig. 2b, where the dotted-dashed lines show density profiles along the C₆-axis and along one of the in-plane directions. Integration over any one of the two equivalent global density maxima gives exactly one helium atom. We see an interesting effect of near complete localization of these two helium atoms located at the two global potential minima on either side of the molecular plane. As noted in Ref. 37, this phenomenon can be viewed as a precursor form of helium adsorption onto a molecular nanosubstrate. Extending these studies to larger polyaromatic molecules will allow contact to be made with PIMC studies of helium adsorption on graphite.

In contrast to this highly structured quantum solvation observed around the
Fig. 6. Total helium density around HCN (top panel) and OCS (bottom panel) for a $N = 64$ cluster at $T = 0.312$ K. The origin is set at the impurity center-of-mass. The OCS is oriented with the oxygen end directed towards the $-\hat{z}$ direction, and the HCN is oriented with the nitrogen end directed towards the $-\hat{z}$ direction.

Heavier molecules such as OCS and benzene, the linear HCN molecule falls into the light molecule regime, with a significantly larger gas phase rotational constant. For HCN, $B_0 = 1.48$ cm$^{-1}$. The He-HCN potential is both weaker (its global minimum is $-42$ K) and less anisotropic than the He-OCS potential. While there is clearly still an ellipsoidal layering of the helium density around the HCN, within each solvation shell there is now a noticeable lack of angular structure, in contrast to the situation with OCS (Fig. 6). For such a light rotor, neglect of the molecular rotational kinetic energy now becomes a more serious concern. From DMC studies assessing the effect of molecular rotation, the expectation here is that the helium density will become more diffuse when molecular rotation is explicitly incorporated into PIMC.

Self-assembled linear chains of polymeric (HCN)$_M$ have been detected experimentally in helium droplets. The helium structure around such linear chains has recently been addressed with a study of the properties of helium droplets with up
to \(N = 500\) atoms that contain (HCN)\(_2\) dimers and (HCN)\(_3\) trimers. Like the monomeric molecules discussed above, the HCN polymers are found to be located at the center of the droplet and to induce a layering of the helium density. Draeger et al. have analyzed the structure of the first solvation shell around the linear polymer in terms of a two-dimensional film, estimated the effective confinement potential for displacement away from the droplet center, and made calculations for vortex formation in these droplets. It has been suggested earlier that the presence of a linear impurity species might stabilize the formation of a vortex line in helium droplets. The expectation here is that a vortex line could be pinned along the molecular axis of a linear molecule such as HCN, or more likely, along the axis of a linear polymeric chain such as (HCN)\(_M\). While the physics of vortices constitute an essential feature of bulk He II, and ways of producing and detecting vortices during helium droplet formation have been the subject of much discussion (see Ref. and therein), no experimental evidence has been found so far for existence of vortices in finite helium droplets. Theoretically, vortices have been shown to be unstable in pure droplets, and the situation with regard to doped droplets is still controversial. The energy for formation of a vortex, \(\Delta E_V\), is defined as

\[
\Delta E_V = E_V - E_0,
\]

where \(E_0\) is the ground state cluster energy and \(E_V\) is the energy of the cluster with a vortex line present. Within the fixed-phase approximation, the PIMC estimate for this vortex formation energy is \(\sim 30\) K for a He\(_{500}\)(HCN)\(_M\) cluster at \(T = 0.38\) K, where \(M = 0 - 3\). In this case, the vortex formation energy is found not to be significantly affected by the presence of a linear impurity. In comparison, density functional calculations made for a range of impurities and cluster sizes give values of \(\Delta E_V\) that are larger than the fixed-phase PIMC estimates by a factor of 3, and that are reduced by \(\sim 5 - 10\) K in the presence of an impurity. An exact estimator for the energy of a cluster in an angular momentum state \(m\) relative to \(m = 0\) has been derived using angular momentum projection methods. Application of this estimator at \(T = 2.0\) K indicates that the presence of an impurity actually results in a slight increase in the vortex formation energy. More work is required in this direction, in particular the systematic examination of the cluster size and temperature dependence of \(\Delta E_V\) obtained from the angular momentum projection estimator.

Many other complexes have now been synthesized in helium droplets. Indeed, these droplets are proving to be a remarkably versatile quantum matrix environment for synthesis of unusual or metastable aggregates. Of particular interest from a fundamental point of view are the complexes of OCS with molecular hydrogen, \(H_2\). Recent spectroscopic measurements on OCS(\(H_2\))\(_M\) complexes inside He\(_N\) clusters have shown an interesting feature that has been interpreted as evidence of nanoscale hydrogen superfluidity. Initial PIMC studies of these systems have been carried out using accurate pair potentials of OCS with He and with \(H_2\). Since the \(H_2\)-OCS potential surface has a similar angular modulation as that for He-OCS,
but a deeper minimum, the OCS molecule is expected to bind preferentially to H\(_2\) over He. Calculations for the OCS(H\(_2\))\(_5\) complex in the He\(_{39}\) cluster showed that approximately six helium atoms, which would normally occupy the region of the global potential minimum in the absence of H\(_2\), are completely displaced by five H\(_2\) molecules. These H\(_2\) molecules form a complete ring encircling the linear OCS molecule at the region of lowest potential energy. The helium density is pushed either to either the secondary peaks in the first shell, or outwards from first to second shell region.

### 3.4. Exchange permutation analysis and impurity-induced non-superfluidity

In addition to providing structural and energetic information, PIMC is currently the only numerical method capable of providing information on finite-temperature superfluidity in He systems. At high temperatures an N-body system may be described by Boltzmann statistics, i.e. in the path integral representation, only the identity permutation is important. At low temperatures however, permutations must be included in the path integral representation for the thermal density matrix. In particular, for liquid helium near the lambda transition, Feynman qualitatively showed that the presence of long exchange cycles gives rise to the sharp increase in the heat capacity, but due to the analytical approximations made in his analysis he was not able to correctly identify the order of the transition. Further refinements in this and numerical PIMC simulations have quantitatively confirmed both the transition temperature and its order.

The area estimator of Eq. (30) gives a scalar value for the global superfluid fraction \(\rho_s/\rho\). This provides a complete description for homogeneous helium systems. However, a finite cluster of nanoscale dimensions necessarily contains inhomogeneity deriving from the surface, and atomic and molecular dopants provide additional sources of inhomogeneities. In this situation Eq. (30) may be interpreted as providing an estimate of the global superfluid fraction averaged over all sources of inhomogeneity. It is notable that the impurity molecule does not significantly perturb this global superfluid fraction. For neutral Na-doped clusters, the area estimator yields a global superfluid fraction of about 95%, consistent with the very weak perturbation of the density noted earlier. For more strongly bound systems such as He\(_N\)SF\(_6\) and He\(_N\)Na\(^+\), it is found that \(\rho_s/\rho\) is similarly large, approaching unity for \(N > 100\) at \(T = 0.625\) K. Thus to see a molecular effect on superfluidity, one needs to examine the local solvation structure on microscopic length scales. Here, the density \(\rho\) is no longer uniform, particularly in the neighborhood of an inhomogeneity. Thus, the superfluid fraction \(\rho_s/\rho\) is expected to be dependent on position. Some indirect indications of this have also been found in analyses of helium films.

A simple way to qualitatively estimate the local dependence of superfluid character is to examine the probability \(\Pi_p(r)\) of a particle at a position \(r\) to participate in an imaginary-time exchange cycle of length \(p\). As discussed previously, Bose su-
perfluidity is associated with the existence of exchange cycles of long $p$. In a pure cluster, the single source of inhomogeneity is the cluster surface. For a pure cluster, $\Pi_{p \geq 6}(r)$ goes to zero as the radial distance $r$ approaches the surface. In the presence of an impurity, the examples discussed in Secs. 3.2 and 3.3 show that an embedded molecule can significantly modify the total density distribution $\rho(r)$. Consequently one also expects changes in the local superfluid character. Kwon and Whaley have systematically examined $\Pi_p(r)$ for helium clusters doped with a single SF$_6$ impurity. They define a local superfluid density by

$$\rho_s(r) = \sum_{p \geq p'}^N \Pi_p(r) \rho(r)$$

where $\rho(r)$ is the total density at $r$, and $p'$ is a cutoff value for the permutation cycle length. This does not account for the tensor nature of the superfluid response, providing a three-dimensional anisotropic representation of a scalar, that may be viewed as an average over the set of tensorial response functions. For a molecule with high symmetry such as a spherical top, this will not be a serious limitation. For linear molecules it will introduce some uncertainty. For clusters of $N > 50$, most of the polymers sampled involve either one or two atoms ($p = 1, 2$) or many atoms (large $p$). Thus in this size regime a clear cutoff exists. For these sizes, Kwon and Whaley used a value of $p' = 6$. For small clusters ($N < 50$), a clear distinction between short and long exchange cycles cannot be made, which implies that in the small cluster regime a two-fluid interpretation of the density cannot be applied.

For the octahedral SF$_6$ molecule, the local superfluid estimator of Eq. (2) yields an anisotropic superfluid solvation structure around the impurity molecule, whose density modulations are similar to those of the total density $\rho(r)$. The local non-superfluid density $\rho_n(r) = \rho(r) - \rho_s(r)$ does depends weakly on temperature, which implies that $\rho_n(r)$ consists of thermal contribution and a molecule-induced component. Fig. 7 shows a three-dimensional representation of the local non-superfluid distribution around the octahedral SF$_6$ molecule. The red areas of highest non-superfluid density are located at the octahedral sites of strongest binding to the molecule, reflecting the origin of this as a molecule-induced non-superfluid. This is in contrast to the thermal normal density of bulk He II in the Landau two-fluid description of a homogeneous superfluid. The molecule-induced density component depends on the strength and range of the helium-impurity interaction potential, and is expected to persist at $T = 0$. Detailed analysis shows that it is non-zero only in the first solvation layer around the molecule.

An analysis using the local estimator of Eq. (2) has been applied to a number of different molecular impurities in helium clusters, including the linear molecules OCS and HCN, and benzene. These systems exhibit a similar layering in both local superfluid density $\rho_s(r)$ and local non-superfluid density $\rho_n(r)$ around the molecule. The non-superfluid density shows slightly stronger modulations, resulting in a weakly anisotropic local superfluid fraction in addition to the component densities themselves. In the more strongly bound He-OCS case, the maximum
Fig. 7. Local non-superfluid density $\rho_n(r)$ around SF$_6$ in a $N = 64$ cluster at $T = 0.312$ K, as measured by the exchange path decomposition of the density. The color scale goes from red for highest values of $\rho_n(r)$, to blue for the lowest values of $\rho_n(r)$. The size of the ball corresponds to a distance from the SF$_6$ molecule of $r = 9.0$ Å. The two cuts display the density in two equivalent planes containing $C_3$ and $C_2$ axes. The strong binding to the octahedral sites located along the $C_3$ axes is evident, with 4 of the 8 octahedral sites visible here.

of the non-superfluid component is roughly $\sim 50\%$ of the total density, while for the weakly bound He-HCN, the non-superfluid, or short-exchange path, component is only $\sim 20\%$. We note that the molecule-induced non-superfluid density is also present around an impurity possessing an isotropic interaction with helium, i.e., it is not essential to have an anisotropic interaction. In fact the existence of a molecule-induced non-superfluid density was first seen in calculations of the SF$_6$ molecule with isotropic interactions potentials, summarized in Fig. 8.

Nakayama and Yamashita have pursued a similar analysis of the local superfluid density for the He$_N$Na$^+$ cluster, which exhibits a triple-layer structure for $N = 100$. While they did not explicitly compute the local quantities $\rho_s(r)$ or $\rho_n(r)$ in their PIMC study, they observed that the helium atoms in the first solvation shell ($r < 4$ Å) rarely participate in long exchanges. This observation, combined with the pair distribution functions computed with respect to atoms in the first shell, led them to conclude that the first shell is solid-like.
As discussed previously, an even more anisotropic impurity-helium interaction potential is provided by the benzene molecule. For the He$_{39}$-benzene cluster at $T = 0.625$ K, the two atoms corresponding to the two total density maxima localized at the two global potential minima, undergo less than 2% permutation exchanges with the surrounding helium. This implies that they are effectively removed from the superfluid, i.e., constitute a true "dead" adsorbed pair of atoms. This near-complete removal of individual helium atoms in the solvation shell from participation in permutation exchanges of nearby helium atoms has not been seen for other molecules to date. It provides an extreme case of the local non-superfluid density, $\rho_n(r)$, in which there is no longer any partial exchange of helium atoms between the non-superfluid and superfluid densities. These features of the helium solvation around a benzene molecule are expected to appear also in clusters containing larger polyaromatic molecules such as tetracene and naphthalene. A systematic analysis of the effect in planar aromatic molecules of increasing size, making the transition from a molecular to a micron-scale substrate, would be very useful.

Recently another local estimator of superfluidity has been proposed that decomposes the projected area into contributions from each local density bin. This decomposition allows the anisotropy of the response tensor to be evaluated explicitly. Application of this local estimator to the linear HCN trimer embedded in helium droplets has confirmed that the superfluid density is reduced in the first solvation layer, consistent with the presence of a local non-superfluid density induced
by the molecule-helium interaction, as first established by Kwon and Whaley. Furthermore, this new estimator shows that there is an asymmetry between the helium response to rotation about the molecular axis, versus rotation about an axis perpendicular to the molecular axis. Draeger et al. find that the superfluid response is reduced more for rotation about the perpendicular axes than for rotation about the molecular axis. In both cases it is less than unity, implying that there is a non-superfluid component both when rotation is accompanied by variation in potential energy, and when there is no variation in potential energy. This finding supports the existence of a local non-superfluid induced by an isotropic helium-impurity interaction, using the exchange path analysis of Kwon and Whaley (Fig. 3). Thus the local non-superfluid is not dependent on the presence of anisotropy, but derives primarily from the stronger attraction of helium to the molecule than to itself.

These studies of various molecules embedded in He\textsubscript{N} clusters employing different estimators of local superfluidity all point to the existence of a molecule-induced non-superfluid density in the first solvation shell around a molecule. While the details of this non-superfluid density may be somewhat dependent on how it is defined, it is evident from the studies of OCS, benzene, and HCN polymers made to date, that this local non-superfluid component is a general phenomenon to be expected for all heavy molecules. It therefore appears to be one of the defining features of quantum solvation in a superfluid. The extent of exchange between non-superfluid and superfluid densities exhibits a dependence on the strength of the helium interaction with the molecule. Benzene provides an interesting extreme case of negligible exchange between non-superfluid and superfluid density components, while less anisotropic molecules such as SF\textsubscript{6} still possess considerable exchange between local non-superfluid and local superfluid. Thus, both the interaction strength with the molecular impurity and the symmetry of this interaction are important. The benzene example indicates that there are useful analogies with the well-known “dead” or “inert” layer of helium adsorbed into bulk solid surfaces, which will be valuable to pursue in future studies.

4. PIMC and the connection to cluster spectroscopy

4.1. Electronic spectra in He\textsubscript{N}

Calculations of electronic spectra typically require accurate potential energy surfaces for both ground and excited electronic states. This is particularly challenging for excitations in condensed phases. To date, theoretical work in this area has been limited to relatively simple systems, where the helium-impurity ground and excited state pair potentials can be computed to good accuracy using standard \textit{ab initio} electronic structure methods. Thermally-averaged electronic absorption spectra for the \textit{2}P \leftarrow \textit{2}S transition have been computed for neutral alkali impurities at \( T = 0.5 \) K, using a modification of the semi-classical Frank-Condon expression
for the electronic lineshape, \[ I(\omega) \propto |M|^2 \int dR \rho(R, R; \beta) \delta[V_e(R) - E_g(R) - \hbar\omega], \] where \( M \) is the electronic transition dipole moment, and \( V_e \) is the potential in the electronic excited state. The quantity \( E_g \) is a local ground state energy, which is assumed to take the form
\[ E_g(R) = T_{\text{imp}}(R) + \sum_{i=1}^{N} V_{\text{He-imp}}(r_i) + \sum_{i<j}^{N} V_{\text{He-He}}(r_{ij}), \]
and explicitly incorporates the kinetic energy of the impurity atom \( T_{\text{imp}} \). The terms \( V_{\text{He-imp}} \) and \( V_{\text{He-He}} \) correspond to the helium-impurity and helium-helium ground state pair potentials, respectively. The electronic excited state potential \( V_e \) is obtained from the diatomics-in-molecules (DIM) model,
\[ V_e(R) = V_{e-\text{imp}}^{\text{ad}}(R) + \sum_{i<j}^{N} V_{\text{He-He}}(r_{ij}), \]
where the first term \( V_{e-\text{imp}}^{\text{ad}} \) is the adiabatic energies of the alkali atom in the \( ^2P \) manifold interacting with the \( N \) helium atoms, and the remaining helium-helium pair potentials \( V_{\text{He-He}} \) are taken to be identical to the ground state. Thus, the thermal absorption profile \( I(\omega) \) can be computed by sampling this energy difference of Eq. (1) from a PIMC simulation. As discussed in Sec. 3.2, the neutral alkali impurities reside on the droplet surface, and the resulting perturbation on droplet properties is weak. The electronic lineshape is therefore most sensitive to the details of the surface structure near the alkali atom. The PIMC calculations for neutral Li, Na, and K on helium clusters of size \( N = 100 - 300 \) give good qualitative agreement with experiment. The doublet structure \( (^2P, ^2P \rightarrow ^2S) \) observed in the experimental spectra for Na and K on helium droplets can be seen in the PIMC calculations. However, while both experiment and theory show that these transitions are shifted to the blue relative to the experimental gas phase values, the absolute value of these shifts is in general much more difficult to obtain from theory. Due to weak spin-orbit coupling for Li, the doublet splitting is small relative to the linewidth, and thus also difficult to resolve. The PIMC absorption spectra for the He\(_N\)Li system exhibits a weak red shift and a long tail towards the blue, both of which are consistent with the experimental spectra.

### 4.2. Vibrational shifts in infrared spectroscopy of molecules in He\(_N\)

The first spectroscopic experiment made on a doped helium cluster measured the infrared absorption spectrum of the octahedral SF\(_6\) molecule. This low resolution spectrum, obtained with a pulsed CO\(_2\) laser, revealed that the \( \nu_4 \) vibrations of SF\(_6\) molecule are red-shifted from the gas phase value by about 1–2 cm\(^{-1}\). They also
appeared to show that the three-fold degenerate absorption for these vibrational modes is split into two peaks. The split peaks were interpreted as implying that the SF$_6$ molecule resides on the cluster surface where the three-fold degeneracy would be expected to be split into parallel and perpendicular modes. However, DMC calculations made at that time showed that the molecule should be located at the cluster center. This was later confirmed by PIMC calculations and verified by subsequent experimental investigations. These include high resolution spectra made with diode lasers, which showed a single vibrational absorption, red-shifted by $\Delta \nu = -1.6 \text{ cm}^{-1}$ and having no splitting of the vibrational degeneracy, and analysis of ionization products of SF$_6$-doped helium clusters. Calculations of the spectral shifts of these triply degenerate intramolecular $\nu_3$ vibrations of SF$_6$ were made with both PIMC and DMC, using the instantaneous dipole-induced dipole (IDID) mechanism originally proposed by Eichenauer and Le Roy to calculate the vibrational spectra of SF$_6$ inside argon clusters. PIMC allows the calculation of the thermally averaged spectral shift at finite temperatures, while DMC gives the ground state, $T = 0 \text{ K}$ value of the spectral shift. Ref. provides a discussion of the difficulties in calculating spectral line shapes (and hence extracting line widths) from a finite-temperature path integral calculation. The IDID approach is taken because the intramolecular vibrational dependence of the He-SF$_6$ interaction potential is not known, and it is therefore necessary to approximate this. In the IDID model, the origin of the spectral shift is assumed to be the dipole-dipole interaction between the instantaneous dipole moment of the SF$_6$ $\nu_3$ vibration and the induced dipole moments of the surrounding helium atoms. The average shift of the $\nu_3$ absorption estimated from the IDID model within PIMC calculations are red-shifted, in agreement with experiment, but the magnitudes of the calculated shift ($\Delta \nu = -0.84 \text{ cm}^{-1}$) is somewhat smaller than the experimental value of $\Delta \nu = -1.6 \text{ cm}^{-1}$. Overall, the agreement of the spectral shift value to within a factor of two is quite reasonable, but it is evident that for a proper understanding of the spectral shift of SF$_6$ inside helium, one needs to also incorporate the contribution from the repulsive part of the He-SF$_6$ interaction that is neglected in the IDID model.

Recently Gianturco and Paesani have calculated vibrationally adiabatic He-OCS potentials for various internal vibrational states of OCS, which allow for a more fundamental approach to the calculation of vibrational shifts. These vibrationally adiabatic potentials are derived by evaluating the interaction potentials as a function of both external coordinates and an internal vibrational coordinate using $ab\initio$ electronic structure methods, and then averaging over the internal vibrational wavefunctions. In particular, they have provided vibrationally adiabatic potentials $V_{00}$ and $V_{11}$ that are averaged over the ground state and first excited state of the asymmetric stretching motion of the molecule, respectively. The shift of an intramolecular vibrational mode inside the helium cluster can be estimated within an adiabatic separation of the fast intramolecular vibrational mode from the slow He-He and He-molecule degrees of freedom. In this approach, the spectral shift
results from computing the average of the difference between $V_{00}$ and $V_{11}$ over the finite-temperature ensemble sampled in the PIMC simulation. Recent PIMC calculations for He$_{39}$-OCS at $T = 0.3$ K find a red-shifted asymmetric vibration, with the shift of $\Delta \nu = -0.87(1)$ cm$^{-1}$. The sign of the shift is in agreement with that seen in experimental measurements for OCS made in larger clusters involving more than 1000 helium atoms at $T = 0.38$ K, but its magnitude is somewhat larger than the experimental value of $\Delta \nu = -0.557(1)$ cm$^{-1}$. Detailed analysis indicates that these discrepancies are likely due to small errors in the vibrationally averaged adiabatic potentials.

4.3. Rotational spectra of molecules embedded in He$_N$

The experimental observation of rotational fine structure for infrared spectra of vibrational transitions in the bosonic $^4$He clusters but not in the corresponding fermionic $^3$He clusters at the operative temperature of $T = 0.38$ K, led to the conclusion that superfluidity is essential for observation of a free rotor-like spectrum. This has been explained as a result of the weak coupling of molecular rotations to the collective excitations of superfluid He II, compared to the much stronger coupling to particle-hole excitations in the Fermi fluid $^3$He. Consequently, the rotational lines are considerably broadened in the fermionic clusters, and the fine structure of rovibrational transitions is washed out. This is consistent with the results of direct calculations of rotational energy levels of $^4$He clusters containing rotationally excited molecules, using zero-temperature DMC-based methods. These direct calculations show that the bosonic nature of the $^4$He is critical in ensuring a free rotor-like spectrum of rotational energy levels of the molecule when embedded in a helium droplet. The corresponding rotational energy levels in fermionic helium droplets have not yet been calculated, and would constitute an interesting theoretical topic for future study. Path integral calculations have not provided any information on the dynamical differences resulting from solvation in fermionic versus bosonic helium droplets so far, since fermionic PIMC simulations have not been made for these systems.

A major feature of the rotational spectra of molecules in $^4$He droplets is the appearance of free rotor-like spectra with increased effective moments of inertia. In principle, any helium-induced change in the molecular moment of inertia should be directly related to a change in the global superfluid fraction, according to Eqs. (29) and (30) (assuming that linear response measures are applicable to the quantized rotation of the molecule). Furthermore, a highly anisotropic molecule would be expected to result in some anisotropy in the helium response for rotation around different axes, yielding anisotropy in the tensor of global superfluid response. However, as noted earlier, the global superfluid estimator is relatively insensitive to the presence of an impurity and the statistical errors mask small changes. It is possible that for significantly larger, and more anisotropic molecules than those theoretically studied to date, e.g., for the planar aromatic molecules such as tetracene
and phthalocyanine that have already been studied experimentally, the global superfluid response may be more affected and yield information. For the relatively small molecules and complexes studied so far however, it has proven necessary to examine the local perturbations of the helium superfluidity in order to develop an understanding of the coupling between this and the molecular rotational dynamics.

The microscopic two-fluid description of the quantum solvation of molecules in He that is provided by path integral calculations has led to a detailed analysis of the effective moments of inertia of molecules solvated in a bosonic superfluid, and hence to a quantitative understanding of the effective rotational constants measured in the infrared and microwave spectroscopy experiments. Since the path integral calculations carried out to date do not explicitly incorporate the molecular rotational degrees of freedom, the connection between the path integral densities and the molecular moments of inertia has to be made within a dynamical model. Kwon and Whaley have proposed a quantum two-fluid model for calculating the effective moment of inertia. The main features of this model are summarized below. As will be evident from the assumptions of this quantum two-fluid model for superfluid helium response to molecular rotation, it is applicable only to the regime of heavier molecules, i.e., those possessing gas phase rotational constants less than \( \sim 0.5 \text{ cm}^{-1} \). Excellent agreement with spectroscopic measurements is obtained for the two instances in which the He-molecule interaction potential is best known, SF\(_6\) and OCS. The theoretical values of rotational constant calculated from the quantum two-fluid model are 0.033 cm\(^{-1}\) and 0.067 cm\(^{-1}\), for SF\(_6\) and OCS respectively, compared with the corresponding experimental values 0.034(1) cm\(^{-1}\) and 0.073 cm\(^{-1}\). Draeger et al. have recently tested this quantum two-fluid model for the linear trimer (HCN)\(_3\). They also find excellent agreement between the predictions of the quantum two-fluid model and the experimentally measured rotational constant. While the HCN monomer lies in the regime of light molecules, the trimer is sufficiently massive to fall within the heavy regime, possessing a gas phase rotational constant of \( B_0 = 0.015 \text{ cm}^{-1} \).

The quantum two-fluid model of Kwon and Whaley is a microscopic two-fluid continuum theory for the spectroscopic response of a molecule rotating in superfluid He. It is to be distinguished from the phenomenological two-fluid theory of Landau for bulk He II. The Kwon and Whaley model examines the helium response to rotation of an embedded molecule that, starting from the local two-fluid decomposition of the molecular solvation density into non-superfluid and superfluid components. Unlike the Landau two-fluid theory for bulk He II, it does not make a two-fluid decomposition of the current densities, but deals only with decomposition of the helium density near an impurity on an atomic length scale, into a non-superfluid component induced by the molecular interaction and the remaining superfluid. This constitutes a significant difference between the well-known phenomenological theory for bulk, homogeneous He II, and the microscopic two-fluid model for molecular rotational dynamics in an inhomogeneous superfluid solvation situation. For the remainder of this section we shall interchangeably use the terms
two-fluid model, microscopic two-fluid model, and quantum two-fluid model to refer to the Kwon/Whaley model.

The starting point for the quantum two-fluid model for helium response to molecular rotation is the local two-fluid density decomposition of the molecular solvation density that results from path integral calculations. As described in Sec. 3.4, consistent evidence for the existence of the local non-superfluid density in the first solvation shell around the molecule, induced by a strong molecular interaction with helium, has now been obtained from two different estimators of the local superfluid response. The second feature of the model is the assumption of adiabatic following of some or all of the solvating helium density with the molecular rotation. Adiabatic following means that the helium density follows the molecular rotational motion. Quantitatively, complete adiabatic following of the helium density would imply that when viewed in the rotating molecular frame, the helium density appears stationary. Thus, in the molecular frame it is independent of rotational state. This applies to both classical and quantum descriptions of the molecular rotation. In a classical description the helium density is analyzed as a function of continuous molecular rotation frequency, while for a quantum description it is analyzed as a function of quantum rotational state of the molecule.

The accuracy of the adiabatic following assumption, as well as quantification of the extent of adiabatic following by helium, has been the subject of several studies by Whaley and co-workers. Within a classical description of molecular rotation, Kwon et al. provided a criterion for adiabatic following, namely that the kinetic energy of rotation associated with a particular helium density (total, non-superfluid, or superfluid) be less than the potential energy barrier to rotation around the molecule. This criterion is applicable to densities deriving from any number of helium atoms, and allows simple estimates using either barriers to rigid rotation, or barriers to adiabatic motion between potential minima associated with different molecular orientations. Application of this criterion to the molecules OCS, SF6 and HCN, for which the molecule-helium interaction potentials are very well characterized, showed that for both OCS and SF6 it is energetically feasible for the entire helium density to adiabatically follow the molecular rotation. However, for the lighter HCN molecule, it is not energetically feasible for any density component, whether non-superfluid, superfluid, or total, to adiabatically follow the molecular rotation. In a classical sense, the molecular rotation is then too fast for the helium to follow. The consequence of this lack of adiabatic following is that the helium density distribution is more diffuse when viewed in the molecular frame. This cannot be seen directly in the PIMC densities, since molecular rotation is not included in these. However, it can be seen directly in diffusion Monte Carlo calculations of excited rotational states of the molecules in He clusters. In these calculations, made with an importance sampling algorithm for rotational degrees of freedom, the helium density (or wave function) is projected into the rotating molecular frame and compared with the corresponding density (wave function) from a calculation performed without molecular rotation. Explicit analysis of the dependence on
rotational state can also be performed, although comparison between rotating and non-rotating cases is already very revealing. The original application of this analysis showed that the extent of adiabatic following decreases for lighter molecules, with the helium density in the molecular frame becoming more diffuse as the rotational constant of the molecule increases. Kwon et al. showed recently how this comparison may be quantified by evaluation of a quality factor $Q$ that measures changes in the ratio of densities along directions corresponding to strong and weak binding, as a function of molecular rotational state. Complete adiabatic following is measured by $Q = 1$, provided the molecular interaction potential is anisotropic. (For an isotropic interaction with helium, adiabatic following is not applicable, and $Q \equiv 1$ by definition.) Application to the series of molecules, OCS, SF$_6$, and HCN, shows that $Q \sim 0$ for HCN, and $Q \sim 0.7$ for both OCS and SF$_6$. This confirms the prediction of the energetic criterion for HCN, i.e., there is negligible adiabatic following around this molecule. The $Q$-value results for the heavier molecules are quite significant, implying that the extent of adiabatic following is not complete, even for the most strongly bound case of a single He atom attached to SF$_6$. So only a fraction of the helium density can adiabatically follow the molecular rotation, even for a heavy, strongly bound molecule.

The next stage of the quantum two-fluid model is to consider the consequences of adiabatic following for both the local non-superfluid and local superfluid density around a dopant molecule. These two density components show very different response to adiabatic following, deriving essentially from the different spatial extent that results from their corresponding underlying exchange permutation paths. The molecule-induced non-superfluid density is localized close to the molecule, within the first solvation layer, and is composed of very short permutation exchange paths. In order to satisfy adiabatic following, such a localized density must rotate rigidly with the molecule. There is no other obvious way in which a density that is spatially localized within a few angstrom can remain constant in a rotating molecular frame. This results in an increment of moment of inertia from the local, molecule-induced non-superfluid that is given by

$$ I_n = m_4 \int_V d\mathbf{r} \rho_n(\mathbf{r}) r_\perp^2, $$

(4)

For the heavy molecules SF$_6$, OCS, and the linear trimer (HCN)$_3$, the PIMC values for $\Delta I_n$ amount to 100%, 90%, and $\sim 81\%$ of the corresponding experimentally observed moment of inertia increments, $\Delta I$. It is interesting that for the highly symmetric SF$_6$ molecule, a very similar result ($\Delta I_n \sim 98\%$ of $\Delta I$) is obtained from calculations with only an isotropic interaction potential. While there is no adiabatic following with an isotropic interaction and hence no mechanism for rigid coupling of the non-superfluid helium density to the molecular rotation, the high symmetry of the octahedral SF$_6$ molecule nevertheless results in the integrated non-superfluid density in the first shell being very similar in anisotropic and isotropic calculations. In fact, the finding that the isotropic non-superfluid density could account
quantitatively for $\Delta I$ was obtained prior to calculations of the anisotropic local non-superfluid density. While this result did not have the theoretical justification of rigid coupling as a result of adiabatic following at that time, it was the first indication that a local two-fluid description was dynamically relevant and prompted the application of a microscopic Andronikashvili analysis of experimental rotational spectra for the case of OCS in He.

In contrast to the local non-superfluid density, the superfluid density, while also modulated around the molecule, is not restricted on an angstrom length scale within the quantum solvation structure. By its very definition, consisting of long exchange paths, the superfluid density extends far from the molecule. Thus the equation of continuity can applied to this density over long distances. Kwon et al. have shown that for a classical molecular rotation, determined by a continuous frequency $\omega$, the condition of adiabatic following, if satisfied, can be combined with the equation of continuity to eliminate the explicit time dependence of the density and to arrive at an equation for the superfluid velocity:

$$\nabla \cdot [\rho_s(\mathbf{r}, t) \mathbf{v}_s(\mathbf{r}, t)] = \nabla \rho_s(\mathbf{r}, t) \cdot (\omega \times \mathbf{r}).$$ \hspace{1cm} (5)

The irrotational nature of a superfluid may be used to replace $\mathbf{v}_s$ by $(\hbar/m_4)\nabla u(\mathbf{r}, t)$, to arrive at a second-order partial differential equation for the superfluid velocity potential $u(\mathbf{r})$:

$$\nabla \cdot [\rho_s(\mathbf{r}) \nabla u(\mathbf{r})] = \left(\frac{m_4}{\hbar}\right) \nabla \rho_s(\mathbf{r}) \cdot (\omega \times \mathbf{r}).$$ \hspace{1cm} (6)

This equation, discussed in detail in Ref. 5, was first proposed in 1997 before full anisotropic superfluid densities in three dimensions were calculated.

A similar equation was recently presented by Callegari and co-workers, together with the somewhat different assumption that the entire local solvation density is superfluid. Solution of these hydrodynamic equations leads to a hydrodynamic moment of inertia increment $\Delta I_h$ that is derived from the excess fluid kinetic energy associated with the flow pattern of $\mathbf{v}_s$. Callegari et al. solved the hydrodynamic equations for several linear or rod-like molecules for which the equations become two-dimensional, using total densities derived from density functional calculations.

The full solution for a molecule showing true three-dimensional anisotropy was made recently for SF$_6$ using PIMC densities. Draeger et al. have applied the hydrodynamic treatment to the (HCN)$_3$ trimer, using their PIMC densities and also assuming the total density to be superfluid, for the purpose of comparison. It appears that very different results are obtained for different molecules within the hydrodynamic treatment. For octahedral SF$_6$, the value of $\Delta I_h$ is small, irrespective of whether the total density or superfluid density is used as input to the hydrodynamic calculations (6% and 9% of $\Delta I$, respectively). For the linear (HCN)$_3$ trimer, Draeger et al. find an upper bound of $\Delta I_h \sim 0.7\Delta I$, when the total density is assumed superfluid ($\Delta I_h = 850$ amu $\text{Å}^2$, compared with an experimental value of $\Delta I = 1240$ amu $\text{Å}^2$). The calculations of Callegari et al. for rod-like molecules yielded between $\Delta I_h \sim 67\%$ and 98% of the experimentally measured increments.
These studies differed from those for SF\(_6\) and (HCN)\(_3\) in that input densities were obtained from density functional calculations rather than from PIMC, in some cases using simple estimates from pairing rules to construct interaction potentials when no empirical or \textit{ab initio} potentials were available.

The hydrodynamic treatment of the local superfluid density derived from PIMC has a number of questionable aspects. Firstly, the treatment of the molecular rotation as a classical rotation characterized by a continuous frequency \(\omega\) must be reconciled with the intrinsic quantized nature of spectroscopic transitions between quantum rotational states. The response to classical rotation necessarily gives rise to angular momentum generation in the superfluid, analogous to the rotation of bulk superfluid in a superleak. Kwon \textit{et al.} have calculated the angular momentum generation by absorption of a photon within a semiclassical analysis, and shown that significant values of \(\Delta I\) result in large fractions of the photon angular momentum being transferred to the superfluid density component. This contradicts conclusions of a number of zero-temperature DMC-based calculations that indicate there is negligible transfer of angular momentum to the fluid on rotational excitation. Kwon \textit{et al.} resolved this by adding quantum constraints to the hydrodynamic formulation, and concluding that violation of these indicates invalidity of the hydrodynamic contribution. This in turn may derive from lack of complete adiabatic following, for which considerable evidence now exists, as outlined above, or from the intrinsic lack of applicability of hydrodynamics to the motions of a superfluid on the atomic length scale. An indicator of this breakdown is the fact that the solutions to the hydrodynamic equations with density inputs of atomically modulated helium solvation densities around an embedded molecule, show variations over length scales of 1 to 2 Å. Such variations on a distance comparable to or less than the coherence length \(\xi\) of helium imply that a hydrodynamic solution is at its limits of validity here, at best, and should be interpreted with great caution.

The overall conclusions of the quantum two-fluid model for the response of helium to rotation of an embedded molecule are thus that the primary contribution to the increased molecular moment of inertia is a rigid coupling to the local non-superfluid density in the first solvation shell. This yields 100%, 90%, and \(\sim 81\%\) of \(\Delta I\) for the heavy molecules SF\(_6\), OCS, and (HCN)\(_3\), respectively. The accuracy of these estimates is dependent on the accuracy of the underlying molecule-helium interaction potentials. In contrast, there appears to be negligible contribution from the superfluid, whose response must be restricted by angular momentum constraints. This is consistent with the findings of only partial adiabatic following of the total helium density. It appears reasonable that only the non-superfluid density adiabatically follows the molecular rotation, while the superfluid density, which is defined over much longer length scales, cannot effectively adiabatically follow. For heavy molecules, this two-fluid model provides a complete dynamical picture.

For light molecules such as HCN, the zero-temperature calculations have shown that adiabatic following is questionable even for the non-superfluid density. Consequently, in this situation the two-fluid model cannot be used to estimate effective
moments of inertia. At this time, the zero-temperature DMC-based direct calculations of rotational energy levels of doped clusters provide the only route to microscopic theoretical understanding of spectroscopic measurements of rotational transitions for such light molecules in helium droplets. This will hopefully change in the future, when molecular rotational motions are explicitly incorporated into the PIMC.

5. Conclusions and future directions

The path integral approach has provided a powerful theoretical tool for investigating the superfluid properties of finite helium droplets. Path integral Monte Carlo calculations have shown that these systems constitute nanoscale superfluids and offer a unique route to probing the structure and response of a Bose superfluid on a microscopic length scale. They also provide examples of inhomogeneous superfluid density, with the unique feature that this inhomogeneous, nanoscale superfluid density can be probed by molecular and atomic dopants.

The microscopic calculations show that such impurities introduce a local quantum solvation structure into the otherwise smoothly varying helium density. The numerical path integral Monte Carlo method has allowed this quantum solvation structure in a superfluid to be analyzed in terms of the boson permutation exchange properties, and conversely, the effect of the molecular interaction on the superfluid to be quantified. PIMC calculations show that a strongly bound impurity induces a non-superfluid density in the first solvation shell, whose extent is determined by the strength of the molecular interaction. Similar conclusions are derived from analysis of the permutation exchange path lengths into short, strongly localized paths, and long, delocalized paths, and from decomposition of the linear response estimator for global superfluidity. The existence of this local non-superfluid component in the solvation layer around microscopic impurities therefore seems to be a general feature of molecular solvation in superfluid He clusters. Response of this local two-fluid density to the rotation of a molecular impurity gives rise to increments in the molecular moment of inertia, but does not otherwise modify the effective free rotation of the molecule in the superfluid.

These path integral studies of doped helium droplets open the way to study of several intriguing questions. One is the effect of the molecular rotation on the quantum solvation structure in the superfluid local environment. As noted in this article, all PIMC studies to date have not explicitly incorporated the molecular rotational degrees of freedom. We now know from zero-temperature calculations of the quantum rotational excitations that the molecular rotation does result in a smearing out of the angular anisotropy in the quantum solvation structure. This implies less than perfect adiabatic following of the helium density, even in the rotational ground state. Given the significance of the adiabatic following assumption for models of the helium response and hence for the analysis of rotational spectra of doped molecules, developing a direct route to the solvation density around a
rotating molecule is highly desirable. This can be done by incorporating the molecular rotational kinetic energy in the path integral representation. A key question with spectroscopic implications is then how the local two-fluid density decomposition is modified. We noted earlier that the moment of inertia increment of the non-superfluid density around SF$_6$ is approximately independent of the anisotropy of the interaction potential. This suggests that even if the two-fluid densities are modified with rotation, becoming less anisotropic, the effective moment of inertia of the molecule in $^4$He will be unchanged. This remains to be verified.

A second direction departing from the analysis of molecular solvation structure in a superfluid is the investigation of localization of helium atoms and their removal from the superfluid state, as a function of the binding to organic molecules of increasing size. In the study of benzene, the key feature responsible for the localization phenomenon was identified as the strong and highly anisotropic interaction of helium with the $\pi$-electron system. Systematically varying the extent of the $\pi$-electron system by going to larger planar, polyaromatic molecules will allow the transition from a nanosubstrate to a microsubstrate that begins to mimic a bulk solid surface to be investigated. We expect that the "inert" layers familiar from studies of thin films of helium on graphite will evolve from these localized atoms, but the manner in which this happens will depend on the role of lateral confinement and permutation exchanges in the presence of an extended $\pi$-electron system.

A third, novel direction is provided by extension of these ideas to nanoscale clusters of molecular hydrogen, H$_2$. In its rotational ground state, the H$_2$ molecule is a boson, but bulk superfluidity is preempted by the occurrence of the triple point at $T = 13.6$ K. However, finite-size and reduced dimensionality systems are offer ways of bypassing this solidification of hydrogen by allowing lower densities and thereby moderating the effects of strong interactions. Path integral calculations have already been used in several instances in the search for a superfluid state of molecular hydrogen. Thus, very small finite clusters of (H$_2$)$_N$ ($N \leq 18$) have been shown with PIMC to be not only liquid-like but also to show a limited extent of superfluidity. Two-dimensional films of hydrogen have been shown to allow a stable superfluid phase at low temperatures provided that an array of alkali atoms is co-adsorbed, providing stabilization of a low density liquid phase. Given these low-dimensional antecedents, it appears possible that a relatively small solvating layer of hydrogen wrapped around a molecule might also show some superfluid behavior. Path integral calculations are now in progress to examine the extent of permutation exchanges in cycles around different axes of a linear molecule wrapped with variable numbers of H$_2$ molecules. Such studies will provide microscopic theoretical insight into the quantum dynamics underlying recent spectroscopic experiments showing anomalies in the molecular moment of inertia that are consistent with a partial superfluid response of the solvating hydrogen layer.

In summary, the path integral Monte Carlo approach provides a unique tool for analysis of these degenerate quantum systems in finite geometries and with chemically complex impurity dopants. The insights into nanoscale superfluid properties
that have resulted, and the interplay between physical and chemical effects afforded by calculations on doped helium droplets offer promise of new opportunities for analysis and manipulation of superfluid at the microscopic level.

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