Collective Excitations of Helium Clusters

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The excitation spectra of compressional modes of ^4He_N, $N=20$, 70, and 240, clusters at 0 K are calculated by treating the cluster as a quantum liquid drop. The spectrum of $N=240$ strongly resembles that of liquid helium with a visible roton structure, while for $N=20$ no roton minimum is seen and $N=70$ shows a weak minimum. Implications of these findings for superfluidity in helium clusters are discussed.

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The possibility of observing superfluidity in isolated ^4He_N clusters has generated some experimental activity, but the evidence so far is inconclusive.[1,2] Such experiments are important because superfluidity has been observed in ^{4}He thin films, finite pores, and other restricted geometries, and hence may occur in clusters too. An important difference, however, is that true superfluid behavior has so far been discovered in systems in which at least one dimension is macroscopic, whereas all three dimensions are finite in clusters. However, considerable experimental difficulties lie in the search for superfluidity in helium clusters, because these are very weakly bound species. Experiments with high-pressure helium confined to nonconnected cavities in copper foil showed anomalous specific-heat-capacity behavior at about 2 K.[3] These thermodynamic measurements constitute the most suggestive experiments so far, although they do not give direct evidence for superfluid flow in these systems. In macroscopic systems a crucial criterion for superfluidity is the existence of a finite-velocity barrier for exciting the fluid. Knowledge of the excitation spectrum of a cluster is thus an essential prerequisite for determining if superfluidity is possible in these finite systems, and how this may be probed.

Previous theoretical studies of helium clusters have yielded extensive information on the ground states.[4,5] In this first study of the excitation spectra of these quantum liquid clusters, we model the cluster as a liquid drop of radius R and constant density ρ_0. The liquid-drop model has been successfully employed in nuclear physics for the study of collective modes. This model is much more appropriate for liquidlike helium clusters, which are bound by weak interatomic forces closely resembling those in molecular liquids. In addition, the ground-state energies of ^4He_N for $N \geq 20$ are accurately fitted by liquid-drop formulas and the calculated density profiles are uniform inside a surface region.[4] The theory described below utilizes the liquid-drop model together with ground-state wave functions determined from full microscopic calculations. We also report microscopic calculations for the first few excited states using a Bijl-Feynman approach, which confirm the liquid-drop results.

The low-lying excitations of these clusters are treated as quasiparticles characterized by momenta k_{ln} and energy ϵ_{lmn}, where l, m, and n are the radial and angular quantum numbers characteristic of the excitation. The quasiparticle momenta k_{ln} are defined by the condition $j_l(k_{ln}R)=0$, where R is the equivalent sharp radius. This ignores the very slight movement of the surface while defining k_{ln}.[6] If the quasiparticles are noninteracting, the complete excitation spectrum consists of one branch for each l,m pair, each branch being characterized by a unique relationship between k_{ln} and ϵ_{lmn}. The ground-state energy of a helium cluster is the static potential energy of the unperturbed cluster, together with the zero-point energy associated with these quasiparticles. The general cluster Hamiltonian is expanded as a functional of the density,[7]

$$H[\rho]=H[\rho_0]+\tfrac{1}{2}\rho_0\int \mathbf{v}^2(\mathbf{r})d^3r + \tfrac{1}{2}\int \phi(\mathbf{r}_1,\mathbf{r}_2)\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)d^3r_1 d^3r_2 , \quad (1)$$

where $\mathbf{v}$ is the velocity field, ρ_0 is the equilibrium ground-state mass density, $\delta\rho$ is the zero-point density fluctuation, and ϕ is the deformation potential energy associated with the density fluctuations at two different points. We have retained terms up to second order in $\delta\rho$ in Eq. (1). We now expand $\delta\rho$, $\mathbf{v}(\mathbf{r})$, and ϕ in terms of spherical Bessel functions,

$$\delta\rho(\mathbf{r})=\sum_{lmn}\rho_{lmn}j_l(k_{ln}r)Y_{lm}(\hat{\mathbf{r}}) , \quad (2)$$

$$\mathbf{v}(\mathbf{r})=\sum_{lmn}v_{lmn}\nabla[j_l(k_{ln}r)Y_{lm}(\hat{\mathbf{r}})] , \quad (3)$$

$$\phi(\mathbf{r}_1,\mathbf{r}_2)\simeq\frac{1}{4\pi}\sum_n\phi_{0n}j_0(\tilde{k}_{0n}|\mathbf{r}_1-\mathbf{r}_2|) . \quad (4)$$

We are neglecting the effect of the boundary surface by approximating the deformation potential as a function of $|\mathbf{r}_1-\mathbf{r}_2|$, while retaining its nonlocal character. This is consistent with the liquid-drop assumption. Since $|\mathbf{r}_1-\mathbf{r}_2|$ takes values from 0 to $2R$, $\tilde{k}_{0n}$ is given by the boundary condition $j_l(2\tilde{k}_{0n}R)=0$. We now use hydrodynamic continuity in the interior to relate the coefficients v_{lmn} and ρ_{lmn}:

$$v_{lmn}=\dot{\rho}_{lmn}/\rho_0 k_{ln}^2 . \quad (5)$$

To calculate the kinetic-energy (KE) part of Eq. (1),

we define a velocity potential as

$$\psi=\sum_{lmn} v_{lmn} j_l(k_{ln} r) Y_{lm}(\hat{\mathbf{r}}) , \tag{6}$$

with $\mathbf{v}(\mathbf{r})=\nabla\psi$. After some tedious algebra and use of the integral indentity,

$$(2l+1)\int_0^R j_l(k_{ln} r) j_l(k_{ln'} r)\,dr = k_{ln}\int_0^R r j_l(k_{ln'} r) j_{l+1}(k_{ln} r)\,dr + k_{ln'}\int_0^R r j_l(k_{ln} r) j_{l+1}(k_{ln'} r)\,dr , \tag{7}$$

we find[8]

$$\mathrm{KE}=\tfrac{1}{2}\rho_0\sum_{lmn} v_{lmn}^2 k_{ln}^2 v_{ln} , \tag{8}$$

where

$$v_{ln}=\tfrac{1}{2}R^3[j_l'(k_{ln}R)]^2 .$$

To calculate the potential energy (PE) part of Eq. (1), we first expand j_0 of Eq. (4) as[9]

$$j_0(\tilde{k}_{0n}|\mathbf{r}_1-\mathbf{r}_2|)=4\pi\sum_{lm} j_l(\tilde{k}_{0n} r_1) j_l(\tilde{k}_{0n} r_2) \times Y_{lm}(\hat{\mathbf{r}}_1) Y_{lm}(\hat{\mathbf{r}}_2) . \tag{9}$$

Substitution of

$$j_l(\tilde{k}_{0n} r_i)=\sum_{n'}\frac{1}{v_{ln'}}\gamma_{nn'}^l j_l(k_{ln'} r_i) , \tag{10}$$

where

$$\gamma_{nn'}^l=\int_0^R j_l(\tilde{k}_{0n} r) j_l(k_{ln'} r) r^2\,dr \tag{11}$$

into Eq. (9) yields for the potential energy

$$\mathrm{PE}=\tfrac{1}{2}\sum_{lmn'n''}\rho_{lmn'}\rho_{lmn''}\sum_n \phi_{0n}\gamma_{nn'}^l\gamma_{nn''}^l \tag{12}$$

$$\simeq\tfrac{1}{2}\sum_{lmn}\phi_{0n}\rho_{lmn}^2 v_{ln}^2 . \tag{13}$$

The diagonal terms make the largest contribution to the summation over n' and n'' in Eq. (12), justifying the omission of off-diagonal terms in (13). We thereby obtain

$$H[\rho]=H[\rho_0]+\sum_{lmn}\left(\frac{1}{2}\frac{|\dot{\rho}_{lmn}|^2}{\rho_0 k_{ln}^2}v_{ln}+\frac{1}{2}\phi_{0n}|\rho_{lmn}|^2 v_{ln}^2\right) . \tag{14}$$

The ground-state expectation value of Eq. (14) is a sum of harmonic-oscillator energies, with frequencies given by

$$\omega_{lmn}^2=\phi_{0n}\rho_0 k_{ln}^2 v_{ln} . \tag{15}$$

Following Pitaevskii, ϕ_{0n} can now be eliminated by applying the virial theorem to the ground state[7] to finally obtain

$$\epsilon_{lmn}=\frac{\hbar^2 k_{ln}^2}{2mS_{lm}(k_{ln})v_{ln}} , \tag{16}$$

where

$$S_{lm}(k_{ln})=\frac{\langle|\rho_{lmn}|^2\rangle}{mN\rho_0}=\frac{1}{mN\rho_0 v_{ln}^2}\int\int d^3r_1\,d^3r_2\, j_l(k_{ln} r_1) j_l(k_{ln} r_2) Y_{lm}^*(\hat{\mathbf{r}}_1) Y_{lm}(\hat{\mathbf{r}}_2)\langle\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)\rangle \tag{17}$$

is the Fourier-Bessel transform of the ground-state density-fluctuation–density-fluctuation correlation function of the cluster. Equation (16) is the finite cluster analog of the Bijl-Feynman-Pitaevskii result for the excitation spectrum of bulk He II, and allows one to compute the excited-state energies directly from the ground-state generalized static structure function of the cluster, Eq. (17). We can rewrite Eq. (17) as a sum of expectation values of spherical Bessel functions. For $l=0$ we obtain

$$S_0(k_{0n})v_{0n}=\frac{m}{4\pi\rho_0 v_{0n}}\left[\left\langle\sum_{i\le N} j_0^2(k_{0n} r_i)\right\rangle-\left\langle\sum_{i\le N} j_0(k_{0n} r_i)\right\rangle^2\right]+2\left\langle\sum_{i<j\le N} j_0(k_{0n} r_i) j_0(k_{0n} r_j)\right\rangle , \tag{18}$$

where r_i and r_j are the coordinates of the particles i and j, respectively. The expectation values in Eq. (18) are defined with respect to the N-particle ground-state wave function of the cluster, Ψ_N. By writing this equation slightly differently we can show that it has a natural physical interpretation as the quantum dispersion of a quasiparticle, if we define the quasiparticle coordinate to be $q_k=\sum_i j_0(kr_i)$.

We calculated the $l=0$ compressional spectra for He_N, $N=20$, 70, and 240, using Eqs. (16) and (18). The normalized structure functions defined by Eq. (18) were calculated using 100000, 80000, and 35000 configurations generated according to the relative probability $|\Psi_N|^2$, for $N=20$, 70, and 240, respectively. The ground-state wave function Ψ_N contained one-, two-, and three-particle correlation terms.[8] Optimization of the wave-function parameters was carried out by variational Monte Carlo simulation to yield binding energies per particle within 0.002–0.06 K of those reported in Ref. 4. The first sum in Eq. (18) contributes unity for a true sharp surface liquid drop. Explicit evaluation of these integrals confirms that this is true to a high accuracy for $N=240$ (1.00), while for $N=70$ and 20 the approximation is less accurate (0.98 and 0.89, respectively). The excitation spectra for $l=0$ are shown in Fig. 1(a). These

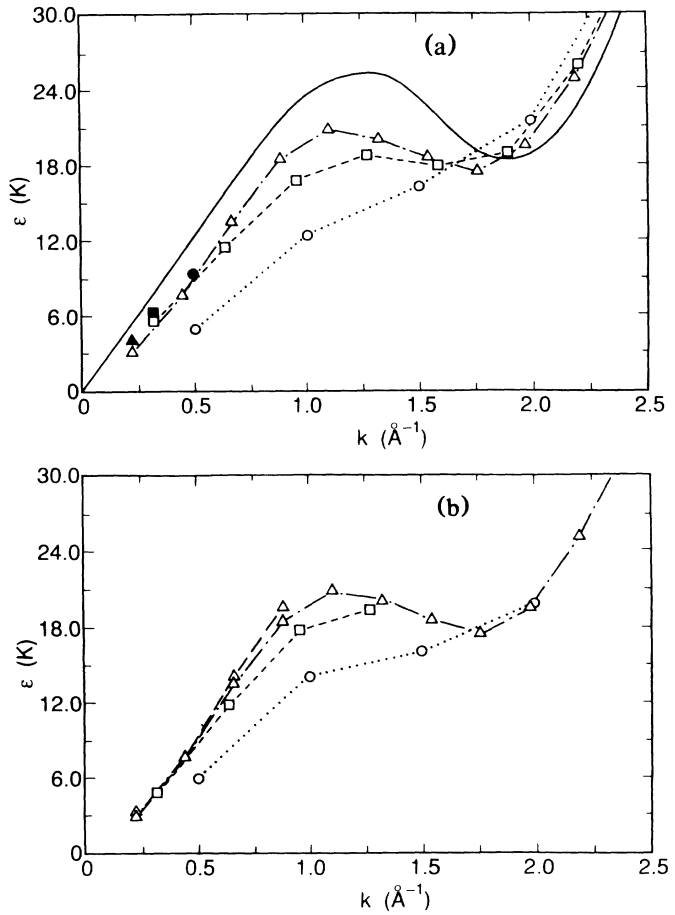

FIG. 1. (a) The $l=0$ compressional spectra of $N=20$ (open circles), 70 (open squares), and 240 (open triangles) helium clusters, calculated using Eq. (16). The solid line is the Bijl-Feynman spectrum for bulk He II. The solid circles show the lowest breathing-mode energies of these clusters predicted by the classical SSLD model (Ref. 10). (b) The first four $l=0$ compressional excitation energies of the same clusters, calculated using Eq. (20). The spectrum of He_{240} from (a) is also reproduced here for comparison purposes.

spectra show rapid evolution towards bulk behavior in the region of the roton excitations as the cluster size increases, with the He_{240} cluster showing a pronounced roton minimum, while He_{20} shows no minimum. A classical sharp-surface liquid-drop (SSLD) treatment of the excitations[6] would yield a pure phonon spectrum linear in k for all cluster sizes, and hence would be qualitatively completely incorrect. The quantum liquid-drop energies are also considerably lower than the SSLD predictions based on the velocity of sound in bulk liquid helium.[10] The SSLD values for the lowest breathing mode are shown in Fig. 1(a) as solid symbols.

An important feature of the quantum liquid-drop theory developed above is the ability to obtain the entire excitation spectrum with the same amount of effort as that needed for the lowest-energy mode, and to obtain size dependence of the crucial features such as the roton structure. We verified these liquid-drop calculations using the Bijl-Feynman wave functions

$$\psi_e = F\Psi_N \tag{19}$$

for the excited states. The excitation energies in this formulation are given by

$$\epsilon = \frac{\hbar^2}{2m}\left\{\frac{\langle\Psi_N|\sum_i|\nabla_i F|^2-(1/N)|\sum_i\nabla_i F|^2|\Psi_N\rangle}{\langle\Psi_N|F^*F|\Psi_N\rangle}\right\}, \tag{20}$$

without any sharp-surface assumption. We evaluated these energies by Monte Carlo sampling over $|\Psi_N|^2$. For the nth excited state, F is chosen to be $F_n = \sum_i j_0(k_{0n}r_i)$. Since such a simple operator does not project out orthogonal excited states, we further employ a Gram-Schmidt orthogonalization procedure to obtain fully orthogonal excited states.[8] The energies of the first four excited states are plotted in Fig. 1(b), where they are seen to show a similar trend with size as the liquid-drop energies. Agreement of the lowest energy is within 0.3 K for $N=240$, and within 1.5 K for $N=70$ and 20. For $N=240$, the quantum liquid-drop lowest breathing-mode frequency of 3.16 K is in excellent agreement with both the theoretical estimates based on a different Bijl-Feynman wave function,[10] and recent density-functional RPA calculations.[11] In particular, we note that all three methods show the same size dependence of the lowest breathing-mode energy. Overall we found that the results based on the quantum liquid-drop model are in good agreement with those based on the Bijl-Feynman approach. The Bijl-Feynman approach is more flexible than the quantum liquid-drop theory and is relatively straightforward to apply for the first excited state.[10] However, the computational complexity involved in successive orthogonalization of the excited-state wave functions grows extremely rapidly for higher states, so that obtaining a complete spectrum becomes very difficult. An important feature of the liquid-drop theory is therefore its prediction of the entire excitation spectrum from the microscopic ground-state information.

Despite the presence of the boundary surface, these spectra for clusters with as few as 70 atoms do show the roton excitations characteristic of liquid helium. From the excitation spectrum of He_{240} one can determine a Landau critical velocity for exciting this cluster of $\simeq 49$ m/s. The existence of such a velocity barrier analogous to that in bulk He II leads us to expect superfluid behavior to be manifested in these clusters. Similar conclusions have been reached in a recent finite-temperature path-integral Monte Carlo simulation.[12]

Establishing superfluidity in ^4He_N is a difficult problem experimentally, requiring a weak microscopic probe. The combination of microscopic wave-function calculations and quantum liquid-drop theory for excitations demonstrated here for pure ^4He_N now presents a power-

ful tool for the microscopic study of embedded atoms and molecules and exploration of their use as spectroscopic probes of the cluster dynamics.

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