

Rapid Communication

Theoretical Analysis of Neutron Scattering Spectra of ^4He Films on Graphite

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We compare microscopic calculations of the dynamic structure function of helium films adsorbed to a graphite substrate with neutron scattering data. Starting from a generalized Feynman theory of collective excitations, we include successively, three-phonon interactions, self-energy corrections, and experimental broadening and thereby improve the agreement between theoretical predictions and experiments. The inclusion of three-phonon vertices allows high-lying excited states to decay into lesser energetic ones and thus leads to a natural linewidth. It is shown that the theoretical linewidth of the excitations is typically smaller than the experimental resolution, and that much structure of the spectrum in the neutron scattering data is obscured under a broad plateau between the ripplon and the phonon excitations. This analysis leaves little doubt of the existence of layer-phonons and that the observed shoulder in the dynamic structure function, near the roton minimum, is actually a 2D roton propagating in the inner-most liquid layer.

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1. INTRODUCTION

The dynamic structure function, $S(k, \omega)$, provides useful information about the strength, lifetime, and dispersion of dynamical excitations of quan-

tum fluids. Inelastic neutron scattering experiments performed at the Institute Laue-Langevin's (ILL) neutron scattering facility, on atomically thin liquid ^4He films, have measured a dynamic structure function that is rich in structure and complexity.¹⁻³ To gain a full understanding of the experimental $S(k, \omega)$ for this system requires precise theoretical guidance. Quantitative calculations for the *ground-state* properties of liquid ^4He for various simple geometries like the uniform liquid in two and three dimensions,^{4,5} adsorbed films,^{6,7} or clusters⁸⁻¹⁰ using either simulation techniques or integral equation methods are now a very routine matter. From no input other than the microscopic Hamiltonian, virtually perfect agreement has been obtained between theoretical results and available experimental information such as the energetics, structure, and distribution functions. The situation is somewhat different for excited states, where a comparably good understanding has been obtained only for the lowest excitation of the bulk, three-dimensional liquid.^{11,12}

Many studies of *non-uniform* helium were restricted to the so-called Feynman approximation.^{13,14,10} The Feynman approximation needs, for its implementation, only information of the one- and two-body ground-state densities. These densities can be obtained from simulation techniques; the only difficulty arises from statistical uncertainties which can be very significant. In fact, even in the Feynman approximation, the calculation of surface excitations by simulation techniques becomes forbiddingly timeconsuming.¹⁰

The Feynman approximation provides for many effects a physically plausible and consistent picture of excitation mechanisms and energies, in particular it is exact in the long-wavelength limit. It is also well known that the theory has several quantitative and qualitative shortcomings; the most visible is the over-estimate of the energy of the roton minimum by about a factor of two. Somewhat more subtle, but equally important, is the omission of multi-phonon effects which contribute a broad continuum of excitations above the phonon/roton spectrum.¹⁵

2. THEORETICAL BACKGROUND

For the purpose of studying strongly interacting quantum liquids, the method of variational wave functions has proven to be most effective. The only phenomenological input to the theory is the microscopic Hamiltonian

$$H = \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 + U_{\text{sub}}(\mathbf{r}_i) \right] + \sum_{i < j} V(|\mathbf{r}_i - \mathbf{r}_j|), \quad (1)$$

where $V(|\mathbf{r}_i - \mathbf{r}_j|)$ is the ^4He - ^4He interaction, and $U_{\text{sub}}(\mathbf{r})$ is an external potential. The theory starts with the *Jastrow-Feenberg ansatz* for the ground-

state wave function of the form

$$\Psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N) = \exp \frac{1}{2} \left[\sum_i u_1(\mathbf{r}_i) + \sum_{i < j} u_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i < j < k} u_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) \right]. \quad (2)$$

An essential part for the approach is the optimization of the many-body correlations by solving the Euler equations

$$\frac{\delta E}{\delta u_n(\mathbf{r}_1, \dots, \mathbf{r}_n)} = 0 \quad (n = 1, 2, 3), \quad (3)$$

where E is the energy expectation value of the Hamiltonian (1) with respect to the wavefunction (2). The energy itself is evaluated using the hypernetted chain (HNC) hierarchy of approximations.¹⁶ The only “adjustable parameters” are the restriction to triplet correlations in the wavefunction (2) and the numerical effort one is willing to spend in the computation of the relevant “elementary” diagrams. For the price of these “adjustable parameters”, statistical fluctuations imminent to Monte Carlo evaluations are virtually eliminated. While the approximate (HNC) ground state is no longer a *rigorous* upper bound to the *true* ground state, we have found^{7,17} that the agreement of our HNC calculations with exact simulations is, for literally every quantity available for comparison, satisfactory for all practical purposes.

The model considered here is a system of ^4He particles adsorbed to an attractive substrate which is translationally invariant in the $x - y$ plane, *i.e.* $U_{\text{sub}}(\mathbf{r}) = U_{\text{sub}}(z)$. The systems under consideration are characterized by the surface coverage

$$n = \int_0^\infty dz \rho_1(z) \quad (4)$$

where $\rho_1(\mathbf{r}) = \rho_1(z)$ is the density profile of the ^4He host system. This density profile is, along with the energetics, structure, and distribution functions, obtained through the optimization of the ground state (2). Technical details of this procedure are provided in Ref. 7 (see also Ref. 18).

Excited states can be treated within precisely the same framework by placing the system in a weak, time-dependent external field $U_{\text{ext}}(\mathbf{r}; t)$ and making the correlation functions appearing in the wave function (2) *time-dependent*. Separating out the time-independent ground-state correlations, we write the wave function of the excited states in the form

$$|\Psi(t)\rangle = \frac{e^{-iE_0 t/\hbar} e^{\frac{1}{2}\delta U(t)} |\Psi_0\rangle}{[\langle \Psi_0 | e^{\delta U(t)} | \Psi_0 \rangle]^{1/2}}, \quad (5)$$

where $|\Psi_0\rangle$ is the ground-state wavefunction, E_0 is its energy, and

$$\delta U = \sum_i \delta u_1(\mathbf{r}_i; t) + \sum_{i < j} \delta u_2(\mathbf{r}_i, \mathbf{r}_j; t) + \dots, \quad (6)$$

is the complex *excitation operator*. The variational principle (3) is generalized to an *action principle*^{19,20}

$$\delta \int dt \left\langle \Psi(t) \left| H - i\hbar \frac{\partial}{\partial t} \right| \Psi(t) \right\rangle = 0, \quad (7)$$

where the $\delta u_i(\mathbf{r}_1, \dots, \mathbf{r}_i; t)$ are taken as the independent functions. As long as we are interested in small perturbations, it is legitimate to evaluate the action integral (7) to second order, which leads to a set of linear equations of motion.²¹ The Feynman approximation results when the excitation operator (6) is restricted to the one-body term $\delta u_1(\mathbf{r}; t)$. Of course, it is plausible that this approximation is invalid when the wavelength of the excitations becomes comparable to the average particle distance. What remains is essentially the technical problem of evaluating the action integral (7) and accurately solving the resulting equations of motion for a sufficiently flexible excitation operator (6). A very complete evaluation, including time-dependent pair correlations $\delta u_2(\mathbf{r}_i, \mathbf{r}_j; t)$ has been done by Saarela¹¹ who found a value of 9.7 K for the roton minimum in the bulk liquid, in quite satisfactory agreement with the experimental value¹⁵ of 8.5 K. Furthermore, Saarela's calculated dispersion relation is in satisfactory agreement with experiment at momentum values above $k = 2\text{\AA}^{-2}$. One can conclude two things from this: First, this approach describes the physics of the phonon-roton spectrum correctly. Secondly, there is no need for including three-body (or higher) time-dependent fluctuations.

3. LIQUID FILM EXCITATIONS

While the Feynman approximation has the above-mentioned difficulties, it provides a framework for discussion, and defines a useful basis for the further calculations. Defining

$$\psi(\mathbf{r}) = \sqrt{\rho_1(\mathbf{r})} \delta u_1(\mathbf{r}) e^{i\omega t}, \quad (8)$$

the variation of the action integral (7) leads to the generalized eigenvalue problem

$$H_1 \psi_n(\mathbf{r}) = \hbar \omega_n \int d^3 r' S(\mathbf{r}, \mathbf{r}') \psi_n(\mathbf{r}') \quad (9)$$

with the coordinate-space representation of the static structure function

$$S(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') + \sqrt{\rho_1(\mathbf{r}) \rho_1(\mathbf{r}')} [g(\mathbf{r}, \mathbf{r}') - 1] \quad (10)$$

where $g(\mathbf{r}, \mathbf{r}')$ is the pair distribution function, and H_1 is the kinetic energy operator

$$H_1 = -\frac{\hbar^2}{2m} \frac{1}{\sqrt{\rho_1(\mathbf{r})}} \nabla \rho_1(\mathbf{r}) \nabla \frac{1}{\sqrt{\rho_1(\mathbf{r})}}. \quad (11)$$

We shall assume for the eigenstates the normalization $(\psi_m | H_1 | \psi_n) = \hbar\omega_m \delta_{mn}$. In view of the generalizations to be discussed below, it is useful to represent the dynamic response function $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ in the Feynman basis, $\{\psi_n(\mathbf{r})\}$, defined by Eq. (9), *i.e.*

$$\chi_{mn}(\omega) = \int d^3r d^3r' \frac{\psi^{(m)}(\mathbf{r})}{\sqrt{\rho_1(\mathbf{r})}} \chi(\mathbf{r}, \mathbf{r}'; \omega) \frac{\psi^{(n)}(\mathbf{r}')}{\sqrt{\rho_1(\mathbf{r}')}}. \quad (12)$$

If all excitations are assumed to be of the Feynman form we find the obvious form

$$\chi_{mn}^F(\omega) = 2 \frac{\hbar\omega_n}{(\hbar\omega)^2 - (\hbar\omega_n)^2 + i\eta} \delta_{mn}. \quad (13)$$

(We apply superscripts such as F to indicate the approximation under consideration whenever our result is specific to that approximation.)

Scattering experiments are performed at grazing angles relative to the basal planes of the graphite substrate; we therefore consider only momenta parallel to the surface. Thus, we define the *parallel* dynamic structure function in momentum space as

$$\begin{aligned} S(q_{\parallel}; \omega) &= -\frac{1}{\pi} \Im m \chi(q_{\parallel}; \omega) \\ &= -\frac{1}{\pi} \Im m \int dz dz' d^2r_{\parallel} e^{i\mathbf{q}_{\parallel} \cdot \mathbf{r}_{\parallel}} \sqrt{\rho_1(\mathbf{r})} \chi(\mathbf{r}, \mathbf{r}'; \omega) \sqrt{\rho_1(\mathbf{r}')}, \end{aligned} \quad (14)$$

and static structure function in the parallel direction

$$S(q_{\parallel}) = \frac{1}{n} \sum_{\omega} S(q_{\parallel}; \omega). \quad (15)$$

It is trivial that the $S^F(q_{\parallel})$ calculated for the Feynman response function (13) is identical to the $S_0(q_{\parallel})$ obtained directly from the ground-state calculation through

$$S_0(q_{\parallel}) = 1 + \frac{1}{n} \int dz dz' d^2r_{\parallel} \rho_1(z) \rho_1(z') [g(\mathbf{r}, \mathbf{r}') - 1] e^{i\mathbf{q}_{\parallel} \cdot \mathbf{r}_{\parallel}}. \quad (16)$$

and that the ω -weighted sumrule

$$\frac{\hbar^2 q_{\parallel}^2}{2m} = \frac{1}{n} \sum_{\omega} \hbar\omega S^F(q_{\parallel}; \omega) \quad (17)$$

is also satisfied within the same approximation. This is important because it ensures that the accuracy obtained in our ground-state calculations is maintained within the dynamic theory, and that the overall weight of the excitations at given momentum is correct.

The derivation of workable schemes to solve the time-dependent two-body equation is considerably more complicated than for the generalized Feynman formula (9). In particular, a rather elaborate diagrammatic analysis of the three- and four-body densities is involved. At the same time, we must keep the numerical feasibility of the theory in mind. In this work, we have decided to implement the theory at the level of the correlated basis functions (CBF) theory of Jackson²² and Chang and Campbell²³ which yields, in the bulk system, a roton minimum of about 14K, but is considerably easier to implement than Saarela's more advanced version of the same theory. Omitting technical details, we assert that the CBF response function is, in the basis of the Feynman states, of the form^{23,21,24}

$$\chi_{mn}^{\text{CBF}}(\omega) = G_{mn}(\omega) + G_{mn}(-\omega) \quad (18)$$

where $G_{mn}(\omega)$ is the CBF Green's function

$$[G_{mn}(\omega)]^{-1} = \hbar(\omega - \omega_m)\delta_{mn} + \frac{1}{2} \sum_{st} \frac{V_{st}^{(m)} V_{st}^{(n)}}{\hbar(\omega_s + \omega_t - \omega + i\eta)} \quad (19)$$

$$\equiv \hbar(\omega - \omega_m)\delta_{mn} - \Sigma_{mn}(\omega). \quad (20)$$

The $V_{st}^{(n)}$ are three-phonon vertices; their analytic form is irrelevant for our purposes; the interested reader may find expressions for this vertex function in Ref. 21.

A number of comments apply:

- The Feynman approximation for the dynamic response function (13) is recovered when the self-energy correction $\Sigma_{mn}(\omega)$ is omitted.
- The summation over intermediate states in the self-energy term (19) is to be understood as a principal value integral for sufficiently high lying excitations. Thus, the theory provides naturally a linewidth.
- The self-energy correction yields *no* change to the sumrules (15) and (17), in particular

$$S^{\text{CBF}}(q_{\parallel}) = -\frac{1}{\pi n} \sum_{\omega} \Im m \chi^{\text{CBF}}(q_{\parallel}; \omega) = S_0(q_{\parallel}). \quad (21)$$

The theorem (21) has been proven for the bulk liquid by Jackson;²⁵ the proof for a non-uniform geometry is somewhat more involved²⁴ but follows essentially the same lines.

- The self-energy form (19) suggests an obvious improvement by including a self-consistent spectrum, rather than the Feynman spectrum, into the energy denominator of (19). This new form, which is tantamount to including higher-order self-energy corrections, guarantees that the sumrules are still exactly satisfied. We refer to it as the *dressed* CBF response function.

4. RESULTS AND DISCUSSION

Using (18) and (19) for the response function we have calculated the dynamic structure function in the CBF and dressed CBF approximations. Theoretically, we have gone an important step beyond Ref. 21 where we have calculated only the lowest mode. For comparison, we have chosen a coverage $n = 0.240\text{\AA}^{-2}$ since experimental data are available for the very similar coverage of $n = 0.239\text{\AA}^{-2}$. This coverage corresponds to three filled, and one partly filled atomic layers of ^4He . Our results are shown in Fig. 1. It is clear from the figure that the major change occurring from going from the CBF to the dressed CBF approximations is an overall shift to lower energies, while the relative mode strengths remains largely unaltered. With the exception of the lowest mode (whose linewidth is artificially enhanced to improve its visibility) the theoretical linewidths are our calculated ones. These linewidths tend to be appreciably finer than the experimental ones; the latter being determined mainly by the resolution of the detectors. Using an experimental resolution of $0.5K$ we have convoluted the theoretical dressed CBF $S(k, \omega)$ with a gaussian. Having done so, the agreement between theory and experiment is sufficiently good to allow us to draw the following conclusions:

- A number of excitations which are well-defined theoretically, are obscured in the neutron scattering data under the broad plateau between the low-energy ripplon and the bulk-like phonon excitations. These modes, which are clear in the unconvoluted theoretical $S(k, \omega)$, have been predicted for many years,^{26,14,7} but never supported experimentally until this work. In theoretical work these are termed layer phonons. The theory shows that layer phonons propagate, to a large extent, in the individual liquid layers comprising the film.
- Near a momentum attributed with the roton minimum the lowest-lying excitation, corresponding to the low-energy shoulder in the theoretical figures, is actually a 2D roton that propagates in the liquid layer that is adjacent to the solid substrate. We use this observation to conclude that the similarly observed experimental shoulder, is of the

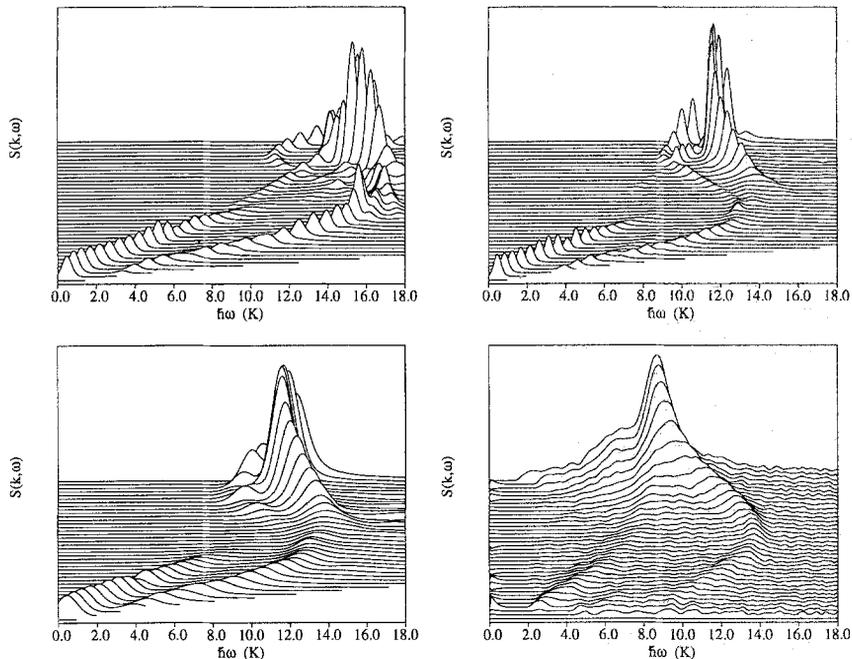


Fig. 1. Theoretical and experimental $S(k, \omega)$ for a film with a liquid helium coverage of $n = 0.024 \text{ \AA}^{-2}$. The CBF $S(k, \omega)$ in the top-left frame shows the full set of modes predicted by the theory. The dressed CBF approximation, top-right frame, shifts the layered-phonon and bulk-like modes to lower energies but leaves the surface mode unchanged. The dressed CBF $S(k, \omega)$ is convoluted with a gaussian having width $0.5 k$, equal to the experimental resolution, in the bottom-left frame. This result shows striking similarity with the experimental $S(k, \omega)$ in the bottom-right frame, measured at $T = 0.65 \text{ K}$.

same nature. This behavior is still true in the full-cell experiments (bulk amounts of Helium added to graphite containing cell) and for our thickest films studied theoretically. In that case (not shown here), the 2D roton is less intense than the bulk roton by many orders of magnitude, but remains having a slightly lower energy than the bulk mode. The theory and experiment are in complete accord, once again.

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