Layer– and bulk roton excitations of $^4$He in porous media

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We examine the energetics of bulk and layer–roton excitations of $^4$He in various porous media such as aerogel, Geltech, or Vycor, in order to find out what conclusions can be drawn from experiments on the energetics about the physisorption mechanism. The energy of the layer–roton minimum depends sensitively on the substrate strength, thus providing a mechanism for a direct measurement of this quantity. On the other hand, bulk-like roton excitations are largely independent of the interaction between the medium and the helium atoms, but the dependence of their energy on the degree of filling reflects the internal structure of the matrix and can reveal features of $^4$He at negative pressures. While bulk-like rotons are very similar to their true bulk counterparts, the layer modes are not in close relation to two–dimensional rotons and should be regarded as a third, completely independent kind of excitation.

I. INTRODUCTION

Collective excitations of superfluid helium confined in various porous media have been studied by neutron scattering since early 90’s, and by now a wealth of information about helium in aerogel, Vycor and Geltech has been collected [1]-[10]. Aerogel is an open gel structure formed by silica strands (SiO$_2$). Typical pore sizes range from few Å to few hundred Å, without any characteristic pore size. Vycor is a porous glass, where pores form channels of about 70 Å diameter. Geltech resembles aerogel, except that the nominal pore size is 25 Å [9].

Liquid $^4$He is adsorbed in these matrices in the form of atomic layers, the first layer is expected to be solid; on a more strongly binding substrate, such as graphite, one expects two solid layers. Energies and lifetimes of phonon–roton excitations for confined $^4$He are nearly equal to their bulk superfluid $^4$He values [11], but differences appear at partial fillings. The appearance of ripplons is tied to the existence of a free liquid surface; neutron scattering experiments show clearly their presence in adsorbed films [10, 12, 13] with few layers of helium.

An exclusive feature of adsorbed films is the appearance of “layer modes”. The existence of such excitations has been proposed in the seventies [14, 15] from theoretical calculations of the excitations of two–dimensional $^4$He and comparison with specific heat data. Direct experimental evidence for the existence of collective excitations below the roton minimum has first been presented by Lauter and collaborators [12, 16], identification of these excitations with longitudinally polarized phonons that propagate in the liquid layer adjacent to the substrate has been provided by microscopic calculations of the excitations of films [17, 18].

In an experimental situation, the topology gives rise to non–uniform filling of the pores. But from the theoretical point of view different materials are characterized solely by their substrate potentials, because as long as the wavelength of the excitation in concern is much shorter than any porosity length-scale, the topology of the confining matrix is immaterial. We therefore examined solely by their substrate potentials, because as long as the wavelength of the excitation in concern is much shorter than any porosity length-scale, the topology of the confining matrix is immaterial. We therefore examined the energetics of the layer–roton as a function of the substrate–potential strength which determines, in turn, the areal density in the first liquid layer. For that purpose, we have carried out a number of calculations of the structure of helium films as a function of potential strength. The microscopic theory behind these calculations is described in Ref. [19]. Our model assumes the usual 3-9 potential

$$ U_3(z) = \frac{4C_3^3}{27D^2} \left( \frac{1}{z^9} - \frac{C_3}{z^3} \right); \quad (1) $$

we have varied the potential strength $D$ from 8 K to 50 K and the range $C_3$ from 1000 K Å$^3$ to 2500 KÅ$^3$. In all cases, we have considered rather thick films of an areal density of 0.45 Å$^{-2}$. Fig. 1 shows density profiles for these potential strengths close to the substrate; the density profiles are practically independent of the potential range $C_3$.  

![FIG. 1: The density profiles of the first three layers are shown as a function of the depth $D$ of the substrate potential. The substrate is at $z = 0$.](image-url)
II. THEORY OF EXCITATIONS

To introduce excitations to the system one applies a small, time–dependent perturbation that momentarily drives the quantum liquid out of its ground state. Generalizing the Feynman–Cohen wave function ²⁴, we write the excited state in the form

$$\Psi(t) = e^{-iE_{\text{ext}}/\hbar} e^{\delta U(t)} |\Psi_0\rangle$$

where $|\Psi_0\rangle$ is the exact or an optimized variational ground state, and the excitation operator is

$$\delta U(t) = \sum_i \delta u_1(r_i; t) + \sum_{i<j} \delta u_2(r_i, r_j; t) + \ldots$$

The time–dependent excitation functions $\delta u_n(r_1, \ldots, r_n; t)$ are determined by an action principle

$$\delta \int_{t_0}^{t_1} dt \left( \Psi(t) \left| H - i\hbar \frac{\partial}{\partial t} + U_{\text{ext}}(t) \right| \Psi(t) \right) = 0,$$

where $U_{\text{ext}}(t)$ is the weak external potential driving the excitations. The truncation of the sequence of fluctuating correlations $\delta u_n$ in Eq. (4) defines the level of approximation in which we treat the excitations. One recovers the Feynman theory of excitations ²⁴ for non–uniform systems ²² by setting $\delta u_2(r_1, \ldots, r_n; t) = 0$ for $n \geq 2$. The two–body term $\delta u_2(r_1, r_2; t)$ describes the time–dependence of the short–ranged correlations. It is plausible that this term is relevant when the wavelength of an excitation becomes comparable to the interparticle distance. Consequently, the excitation spectrum can be quite well understood ²³ ²⁴ ²⁵ by retaining only the time–dependent one– and two–body terms in the excitation operator ²⁴. The simplest non–trivial implementation of the theory leads to a density–density response function of the form ²⁷

$$\chi(r, r', \omega) = \sqrt{\rho(r)} \sum_{st} \phi^{(s)}(r) \left[ G_{st}(\omega) + G_{st}(-\omega) \right] \phi^{(t)}(r') \sqrt{\rho(r')}$$

where the $\phi^{(s)}(r)$ are Feynman excitation functions, and

$$G_{st}(\omega) = [\hbar(\omega - \omega_s + i\epsilon) \delta_{st} + \Sigma_{st}(\omega)]^{-1}$$

the phonon propagator. The fluctuating pair correlations give rise to the dynamic self energy correction ²⁷,

$$\Sigma_{st}(\omega) = \frac{1}{2} \sum_{mn} V_{mn}^{(s)} V_{mn}^{(t)} \frac{\hbar}{\hbar(\omega_m + \omega_n - \omega)}.$$
FIG. 2: The figure shows the map of the dynamic structure function $S(k, \omega)$ for a $^{4}$He film for the potential strength $D = 32$ K. The two layer–rotons, the bulk roton, and the ripplon are indicated by arrows.

FIG. 3: The transition densities of the three lowest excitation are shown for $D = 32$ K and $C_3 = 1500$ KÅ$^3$, normalized to the same maximum value. For comparison, the density profile of the film is shown as a gray–shaded area.

FIG. 4: The figure shows the energy of the roton in two dimensions, (long–dashed line) and the energy of the layer roton in a film (solid line) as a function of areal density. The areal densities of the layers were obtained by integrating the density up to the first minimum, the upper horizontal axis shows the corresponding values of the well-depth $D$. Also shown is the energy of a two–dimensional roton obtained with shadow wave functions [26] at the density of 0.0421Å$^{-2}$. The short–dashed horizontal lines show experimental values of the roton energy on aerogel [6, 10] (7.39 and 7.14 K), Vyccor [7, 8] (7.23 K), and Gelttech [9] (6.71 K), their energies are marked on the right margin.

in Fig. 1 to the first minimum. This is evidently not very well defined for the weakly bound systems, but it is not legitimate either for the case of strong binding where the first layer is well defined. In fact, the integrated density for the strongest substrate is 0.08 Å$^{-2}$, which is well beyond the solidification density of the purely two–dimensional system. Evidently, the zero–point motion in $z$ direction can effectively suppress the phase transition. We make therefore three conclusions: (i) The position of the layer roton minimum is indeed a sensitive measure for the strength of the substrate potential, (ii) purely two–dimensional models are manifestly inadequate for their understanding, and, hence, (iii) purely two–dimensional models are also questionable for interpreting thermodynamic data of adsorbed films.

IV. BULK EXCITATIONS

With one exception [6], the bulk roton energy in porous media have been reported to be practically identical to that in the bulk liquid, Ref. [6] reports a slight increase of the roton energy in aerogel at partial filling. A roton energy above the one of the bulk liquid can be explained by assuming that the density of the helium liquid in the medium is below that of the bulk liquid. This can, in turn, be qualitatively explained by the cost in energy to form a surface.

To be quantitative, we have performed calculations of
the energetics and structure of $^4$He in a gap between attractive silica walls \[15\] and obtained the energy of the bulk roton (c.f. Fig. 2) as a function of filling. Fig. 5 shows, as a typical example, the roton energetics in a gap of 25 Å width. The independent parameter is the areal density $n$, the corresponding three–dimensional density was obtained by averaging the density profile over the full volume. It is seen that the equilibrium density is well below the bulk value. In other words, the roton energy in a confined liquid should correspond to the one of a liquid that would, without confinement, have a negative pressure. The energy increase of the roton minimum found in this model is about 0.5 K, which is consistent with the experiments of Ref. \[6\].

To verify this interpretation of the data, it would be very useful to have comparable measurements for porous media with a more uniform distribution of pore sizes. In particular, comparably small pores should allow to densities that are even below the bulk spinodal density \[27\], thus facilitating experiments on $^4$He in density areas that were up to now inaccessible.

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