Phonon-Roton Excitations in Liquid ^{4}He at Negative Pressures

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We present neutron scattering measurements of the phonon-roton excitations of superfluid ^{4}He held at negative pressures from zero to -5 bar. The liquid was stretched to negative pressures by immersing it in the porous medium MCM-41. In the wave vector range $0.35 \leq Q \leq 1.55$ Å^{-1} and temperature $T = 0.4$ K investigated, the phonon and maxon energies decrease systematically below bulk values as the negative pressure is increased. The energies are consistent with extrapolation of positive pressure values from which the negative internal pressure can be estimated. The maximum negative pressure realized is consistent with surface tension arguments and the MCM-41 pore diameter of 47 Å.

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We report the first measurements of the phonon-roton excitations of superfluid ^{4}He under negative pressure. Fluids under tension are of interest to reveal intrinsic liquid binding and thermodynamic properties [1–6]. Water, a strongly bound liquid, can be stretched to internal pressures of -1400 bar before becoming mechanically unstable [7]. Sound propagation in water has been measured to -1000 bar [8]. Liquid ^{4}He is much less strongly bound. The maximum negative pressure that liquid ^{4}He can sustain, denoted the "spinodal" pressure, is predicted [9,10] to be $p_c = -9.42$ bar at $T = 0$ K. At p_c the compressibility, κ, becomes infinite and the sound velocity $c \sim (\rho\kappa)^{-1/2}$ goes to zero. Near p_c, the condensate fraction is predicted [11] to increase to nearly 30% compared with the zero pressure value [12] of $n_0 = (7.25 \pm 0.75)\%$. In a series of dynamic stressing experiments using sound waves [2,5,13], negative pressures near the spinodal pressure in liquid ^{4}He have now been reached. Because of its lighter mass and greater zero point energy, liquid ^{3}He is even less tightly bound with a spinodal pressure of $p_c \simeq -3$ bar [5,14,15].

Fluids at negative pressure are also of interest to explore the liquid/gas transition [1,16,17]. At negative pressures, fluids are metastable. The transition to the stable gas phase begins with gas bubble formation in the liquid, denoted cavitation. If the bubble can reach a critical size, it can grow without limit and the phase transition to the vapor phase takes place. If the bubble does not reach the critical size, it collapses under the surface tension between the liquid and the vapor, and the metastable liquid remains. Gas bubbles can initiate on impurities, denoted heterogeneous nucleation. In this event, the intrinsic stability limit of the liquid (p_c) cannot be reached. Liquid helium has played a unique role in the study of cavitation [2,5,13], since it can be made extremely pure and heterogeneous nucleation of bubbles can be prevented. Bubbles can also nucleate in crevices and edges of rough surfaces. To remove this source of heterogeneous nucleation, negative pressures are created away from walls using sound waves as noted above.

A second important finding reported here is that negative pressures of up to -5 bar can be set up in liquid ^{4}He in the porous medium MCM-41 (in the presence of surfaces). The metastable (negative pressure) state can be maintained indefinitely (hours). This is presumably because the liquid ^{4}He is pure, and because the MCM-41 walls are smooth. Also, Apaja and Krotscheck [18,19] have predicted the existence of negative pressures in liquid ^{4}He at specific fillings of small pore material.

In this neutron scattering measurement, carried out on the IN6 spectrometer at ILL, Grenoble, France, with an incident neutron wavelength of 5.92 Å, we filled 47 Å pore diameter MCM-41 with superfluid ^{4}He at $T = 0.4$ K until it was approximately 92% full. At this filling, the liquid fills the entire pores but at a density below the bulk value. The liquid is stretched and under tension by attraction to the MCM-41 walls with a negative internal pressure. The pressure is raised to zero by adding more liquid. We measured the phonon-roton energies of the confined helium [20] as a function of filling of the pores until the bulk values [21] were observed at full filling. The sound velocity was obtained by extrapolation. Comparing our observed maxon energies with the extrapolation of the maxon energy from positive to negative pressures gives the most reliable values of the internal pressure. These negative pressures are consistent with those obtained from the sound velocity and from surface tension arguments. Measured values of the mode energies will assist prediction of thermodynamic properties of liquid ^{4}He at negative pressures [3]. The present technique also opens the path to reaching larger negative pressures using smaller pore diameter media.

The MCM-41 sample was synthesized at the "Laboratoire de Materiaux Mineraux," Mulhouse, France.

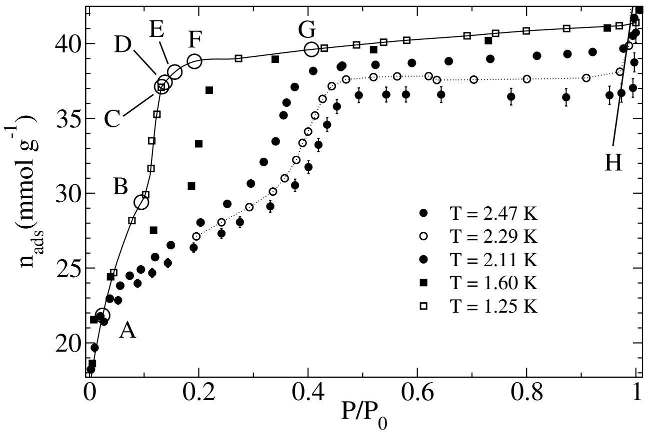

FIG. 1. Adsorption isotherms of ^{4}He in 47 Å pore diameter MCM-41. Shown is the vapor pressure, P, above the ^{4}He in the MCM-41 relative to the vapor pressure of bulk ^{4}He , P_0, versus filling (amount adsorbed per g of MCM-41, n_{ads}). The fillings A to H that were used in the neutron scattering experiment are marked on the isotherm at $T = 1.25$ K.

Using standard characterization methods, they obtained a mean pore diameter of 47 Å, with a distribution around the mean of 3 Å, and a Brunauer, Emmet, and Teller surface area of 931 m^2/g.

We conducted ^{4}He adsorption isotherm measurements at temperatures between $T = 1.25$ and 2.47 K. Shown in Fig. 1 is the amount of ^{4}He adsorbed per gram of MCM-41 at constant temperature T versus the vapor pressure above the sample, P/P_0. Here $P_0(T)$ is the saturated vapor pressure of the bulk liquid. The adsorption isotherms are interpreted as follows. For fillings up to $n_{ads} \leq 25$ mmol/g, the helium entering the pores is tightly bound to the pore walls (probably in solid layers) leading to a low vapor pressure, $P/P_0 \leq 0.1$. At fillings in the range $25 \leq n_{ads} \leq 30$ mmol/g, the ^{4}He forms liquid layers (on the solid layers), which are less tightly bound (for example, $P/P_0 \simeq 0.4$ at $n_{ads} = 30$ mmol/g and $T = 2.47$ K). Liquid layers are indicated because in the neutron data discussed below, we observe "ripplons" propagating on the free liquid/vapor surface at $n_{ads} \simeq 30$ mmol/g (filling B shown in Figs. 1 and 2). For fillings $30 \leq n_{ads} \leq 37$ mmol/g, the ^{4}He enters as liquid by "capillary condensation" in which whole pores are filled. At $n_{ads} \simeq 37$ mmol/g, the pores are largely full but with liquid at density less than bulk density (the liquid has a negative internal pressure). This negative internal pressure in the liquid is supported by the liquid-vapor surface tension, $\gamma \sim 3.5 \times 10^{-4}$ J/m^2, and a curved meniscus in the pores separating the liquid and the vapor. The anticipated maximum negative pressure that can be sustained by the liquid in the pores is $p \simeq -2\gamma/R$ where R is the radius of the liquid in the pores (of the meniscus) ($R \simeq 15$ Å, $p \simeq -4.7$ bar).

For increasing fillings $37 \leq n_{ads} \leq 40$ mmol/g (at $T = 1.25$ K), the added ^{4}He increases the liquid density in the pores. Full pores at bulk liquid density is reached when $P/P_0 = 1$. Our chief interest is the fillings in the range

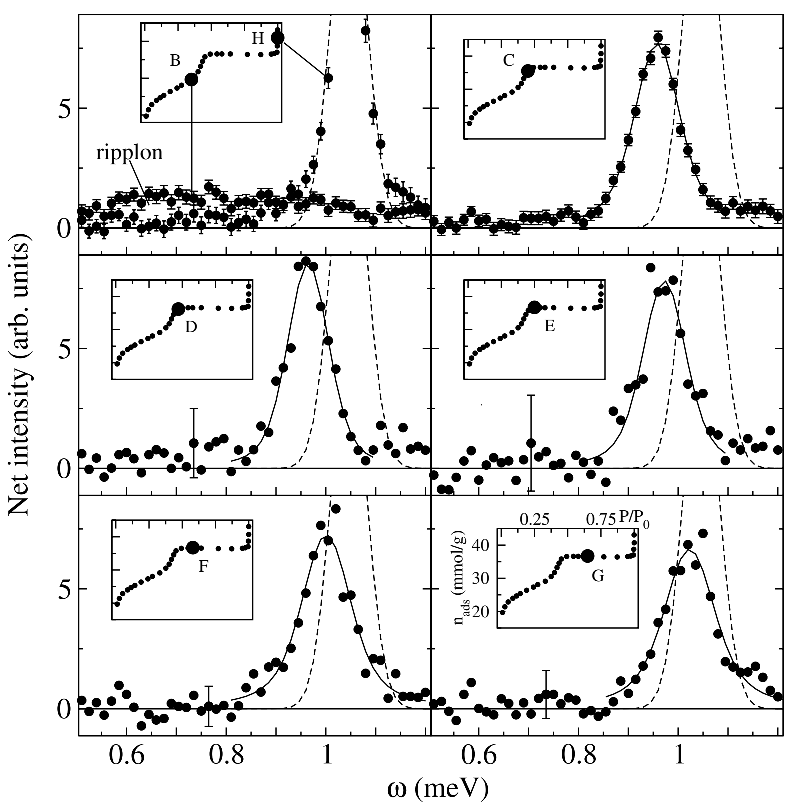

FIG. 2. Net inelastic neutron scattering intensity [proportional to $S(\mathbf{Q}, \omega)$] at wave vector $Q = 1.50$ Å^{-1} versus energy transfer ω from ^{4}He in MCM-41 at $T = 0.4$ K. The insets show the filling on the adsorption isotherm at $T = 2.47$ K. Error for data at filling D to G is shown on a single point only for clarity. At filling B, there are liquid layers only on the media walls, and we observe "ripplons" propagating on the liquid film surface (solid circles). At filling H, the pores are full with superfluid at bulk density, there is zero negative pressure, and we observe a phonon-roton mode propagating in the superfluid (open circles) with bulk liquid energy, $\omega_Q = 1.046 \pm 0.001$ meV. At filling C and estimated negative pressure -5.5 bar, the mode energy ($\omega_Q = 0.958 \pm 0.001$ meV) lies below the bulk value. The net intensity for the other fillings from D to G (decreasing negative pressure) are also shown. The mode energy increases toward the bulk value with increased fillings through C, D, E, F, and G as the negative pressure decreases.

$37 \leq n_{ads} \leq 40$ mmol/g where the pressure in the liquid increases from approximately -5 bar ($\rho \simeq 0.020$ Å^{-3}) to zero pressure (bulk density, $\rho_0 = 0.0218$ Å^{-3}).

The net inelastic neutron scattering intensity from ^{4}He in the pores at wave vector transfer $Q = 1.50$ Å^{-1} is shown in Fig. 2 as a function of filling. The net intensity is proportional to the dynamic structure factor, $S(Q, \omega)$. With only solid ^{4}He layers on the MCM-41 walls, we observe no net scattering intensity from the ^{4}He in the energy range $0.35 \leq \omega \leq 1.4$ meV investigated (not shown). The fillings B to H used in the neutron scattering experiment are shown in Fig. 2 placed on the adsorption isotherm at $T = 2.47$ K for clarity. At filling B, with liquid layers on the walls, we observe a broad inelastic response. This is scattering from ripplons on the free liquid surface as reported previously [22]. Ripplons are observed in superfluid ^{4}He on flat surfaces [23]. At filling C, full filling of the pores with low-density liquid, we no longer observe ripplons since the free liquid surface has disappeared. Rather at filling C we observe well-defined phonon-roton excitations propagating in the liquid in the pores. The estimated negative pressure at filling C is -5.5 bar, and the mode has an energy $\omega_Q = 0.958 \pm 0.001$ meV. As the filling is increased (negative pressure reduced) in the sequence C, D, E, F, G, we see that the mode energy increases. At filling G, for example, the mode energy is $\omega_Q \simeq 1.02$ meV. At filling H, the liquid in the pores is at bulk density and the present energy, $\omega_Q = 1.046 \pm 0.001$ meV, recovers the bulk value $\omega_Q = 1.042 \pm 0.006$ meV [21] within error.

Figure 3 shows the observed phonon-roton energy dispersion curve for wave vectors $0.35 \leq Q \leq 1.55$ Å^{-1} as a function of filling. At full filling (H) our observed energies lie on the bulk superfluid dispersion curve [21] given by the solid line. The phonon-roton energies have been measured in porous media of varying pore size (see Ref. [24]), e.g., 25 Å [25], 32 Å [22], and 70 Å [26]. In each case the energies at full filling are the same as those in the bulk, independent of the pore size. As the filling is decreased (sequence G to C), we see that the mode energies fall below the bulk values. The decrease is largest at the maxon wave vector, $Q = 1.1$ Å^{-1}. Specifically, we show the mode energy at the maxon wave vector in Fig. 4. The dashed line shows a cubic fit to the maxon energy observed at positive pressures [27–30], extrapolated to negative pressures. We have placed our observed maxon energies on this fit to estimate the density and negative pressure at each filling. This suggests that the largest negative pressure in liquid (at filling C) is -5.5 bar with a density of $\rho = 0.020$ Å^{-3}, as noted above. Density functional [3,31] and Monte Carlo [32] values are also shown in Fig. 4.

The sound velocity, c, in superfluid ^{4}He at low temperature can be described accurately as a function of pressure using simple expressions [31,33] which agree well [3], e.g., [33] $c = [b(p - p_c)]^\nu$ where p_c is the spinodal pressure and $\nu = 1/3$ (except close to p_c where ν becomes a critical exponent [34], $\nu = 1/4$). We may invert this expression to obtain the pressure as a function of c as $p = p_c[1 - (c/c_0)^{1/\nu}]$ where c_0 is the velocity at zero presssure, $c_0 = 238.25$ m/s. We can estimate c from the phonon energies ω_Q shown in Fig. 3 assuming linear

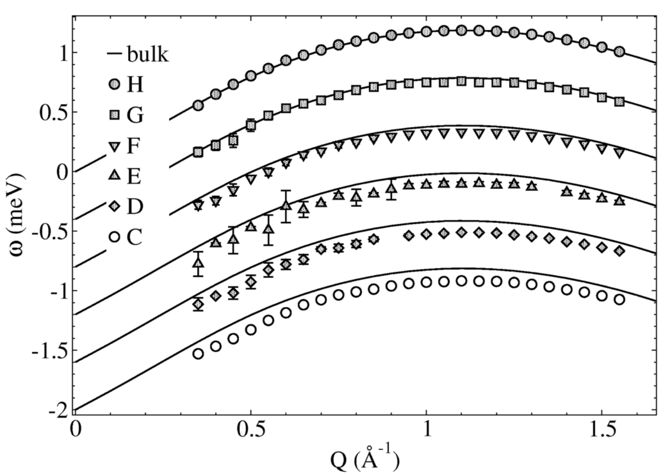

FIG. 3. The phonon-roton energy dispersion curve of liquid ^{4}He in MCM-41 at fillings C to H (at pressures -5.5 bar to zero) compared with the bulk liquid (zero pressure) curve (solid line) [21]. Data sets are displaced by 0.4 meV one from the other for clarity.

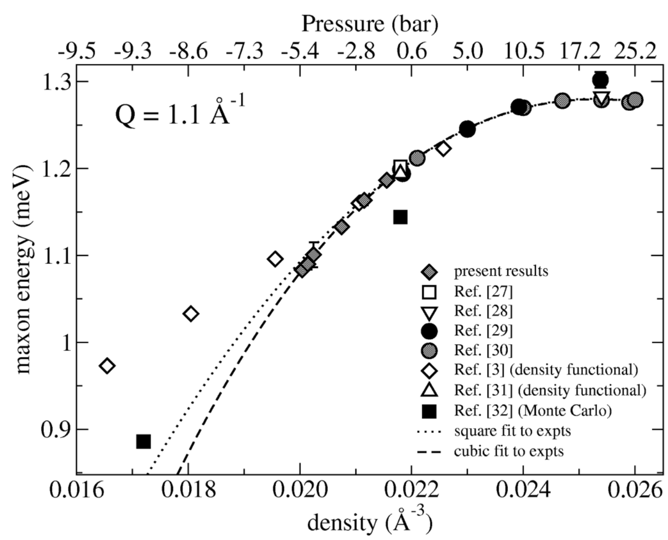

FIG. 4. The maxon energy as a function of density. Observed values at positive pressure are from Refs. [27–30]. The dashed and dotted lines are cubic and square function fits to the observed values at positive pressure. The diamonds are the present maxon energies observed at negative pressures, which are not known. The present maxon energies are placed on the cubic extrapolation to provide an estimate of the negative pressures. The maximum negative pressure indicated is -5.5 bar which is consistent with independent estimates of the negative pressure from the sound velocity and from the surface tension. The calculated values at zero and negative pressures are from Refs. [3,31,32].

dispersion, $\omega_Q = c\,Q$ up to $Q = 0.5$ Å^{-1}. With velocities adjusted to reproduce c_0 at filling H, this gives $c = 195$ m/s and a pressure $p = -4.3$ bar at filling C. We believe this is an overestimate of c at filling C since there is upward dispersion and this upward dispersion increases significantly at negative pressures. For example, the dispersion curves calculated in Ref. [32] show large upward dispersion near p_c. Similarly, calculations of mechanical stability in solids show that c can go to zero while the phonon energies ω_Q remain finite. Thus, c actually decreases more as the filling is decreased than predicted by $\omega_Q = c\,Q$, and $p = -4.3$ bar is an upper bound to liquid pressure, but a reliable one. We believe that the most reliable pressure is obtained here from simple extrapolation of the maxon energy giving a negative pressure at filling C of -5.5 bar.

In conclusion, we have measured the phonon-roton energies of liquid ^{4}He at negative pressures and temperature $T = 0.4$ K in the wave vector range $0.35 \leq Q \leq 1.65$ Å^{-1}. The energies observed at negative pressures are consistent with a straightforward extrapolation of previously observed values at positive pressures from which the negative pressure can be estimated. The sound velocity, c, can be estimated from the phonon energies assuming linear dispersion. The negative pressures are achieved by immersing the ^{4}He in MCM-41. The negative pressures reached are consistent with surface tension and pore diameter arguments. Higher negative pressures can presumably be reached using smaller pore diameter smooth-walled porous media.

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