

## Thermodynamics of quantum fluids confined in zeolites at low temperature

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The thermal properties of quantum fluids at low temperature ( $T$ ) are determined by the spectrum of excitations which possess the lowest frequencies. In the case of a fluid such as helium or hydrogen, confined in a one-dimensional (1D) pore, these excitations are phonons, with wave vector parallel to the pore's axis. This paper describes the consequences of this fluid's confinement for the low- $T$  heat capacity and explores the crossover from 1D to higher dimensionality in terms of both temperature and cross-sectional dimension.

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A central theme of condensed matter physics is the consequences of reduced dimensionality. For example, a fundamental motivation for exploring very thin films has been the opportunity to study two-dimensional (2D) and quasi-2D matter, for which the ordered phases differ significantly from those of three-dimensional (3D) matter. The same motivation, *inter alia*, has stimulated research concerning the behavior of 1D and quasi-1D systems, such as gases adsorbed within nanotubes<sup>1</sup> and porous material with complex pore geometries.<sup>2</sup> The crossover from 1D to a higher dimensionality regime is a subject of current interest; in particular, observation of 1D excitations in superfluid <sup>3</sup>He and <sup>3</sup>He-<sup>4</sup>He mixtures adsorbed in alumina powder have been reported recently.<sup>3</sup> The present paper is concerned with a different quasi-1D system, a quantum fluid adsorbed within a porous material, such as a zeolite. We address the low- $T$  thermal properties in the approximation that the modes are described by continuum hydrodynamics.<sup>4</sup> This is the case when the cross-sectional dimension is very large compared to the atomic size of the fluid, in contrast to the nanotube case, for which the ratio of these lengths is of order five.

The systems we have in mind are helium and hydrogen. Helium is known to remain liquid at the lowest temperatures. While bulk hydrogen freezes below  $T=13.8$  K, the triple temperature is reduced in films<sup>5</sup> and ought to be zero in a strictly 1D system because of thermal fluctuations. In the case of hydrogen within a typical porous environment, one expects the solid to be particularly disfavored, relative to the liquid, due to the poor epitaxy likely to be present when crystallized within the pore. This contributes to the well-known depression of freezing points within pores.<sup>6</sup>

For an ideal inviscid fluid, the relevant linearized hydrodynamic equation gives rise to the scalar Helmholtz equation for density fluctuations  $\delta\rho(\mathbf{r},t) = \delta\rho(\mathbf{r})e^{i\omega t}$ :

$$(c_s^2 \nabla^2 + \omega^2) \delta\rho(\mathbf{r}) = 0. \quad (1)$$

Here  $\omega$  is the angular frequency and  $c_s$  is the speed of sound, which we assume to be uniform in spite of the possible compressional effects of the pore's adsorption potential. This represents the most significant approximation in our treatment; it is difficult to improve upon this approximation which is conventionally used in treating the hydrodynamics of films.

Since the closest approximation to an ideal inviscid fluid is superfluid helium, one may wonder about the applicability of alternative theoretical descriptions to the present hydrodynamic model. For example, a mean field treatment based on Bogoliubov's approach starting from the Gross-Pitaevskii equation in the given geometry, such as that applied in Ref. 7 would not be valid for helium at bulk density; in such a case, the strong He-He interaction is responsible for the high value of the sound velocity,  $c_s = 238 \text{ m s}^{-1}$ , which largely overrides the single-particle (sp) contributions to the Bogoliubov spectrum that are clearly visible in the dilute gas regime.<sup>7</sup>

In order to exhibit and explore explicit solutions of the problem here presented, we assume a cylindrical cross section of the pore; other, more general, shapes will be described in a future presentation. We note that the apparently naive substitution of the true pore's cross section by an equal area, circular one is known to yield remarkably reliable hydrodynamic spectra for other shapes.<sup>8</sup> In the cylindrical geometry, the eigenvalue problem (1) can be analytically solved for fluctuations of the form

$$\delta\rho(\mathbf{r}) = \frac{1}{\sqrt{2\pi L}} e^{i(kz + m\varphi)} J_m(kr) \quad (2)$$

describing free propagation parallel to the  $z$  direction, i.e., the pore's axis, with linear momentum  $k$ , with the usual azimuthal variation and with  $J_m(kr)$  being a Bessel function for radial motion. As in the membrane problem, the boundary condition that the normal component of the velocity vanishes at the wall for radius  $r=R$  gives rise to a discrete spectrum, namely

$$\omega^2 = c_s^2 (k^2 + k_{mn}^2). \quad (3)$$

Here the discretized wave numbers  $k_{mn}$  are given by the zeros  $\alpha_{mn} = k_{mn}R$  of the slope of the Bessel function  $J'_{mn}(\alpha)$ , in contrast to the membrane case, for which the function itself vanishes at the boundary. The lowest ( $mn$ ) values of these coefficients can be found, i.e., in Ref. 9.

The modes satisfy Bose statistics, in which case the specific heat (in units of Boltzmann's constant  $k_B$  and with  $N$  the number of atoms in the pore) may be written as

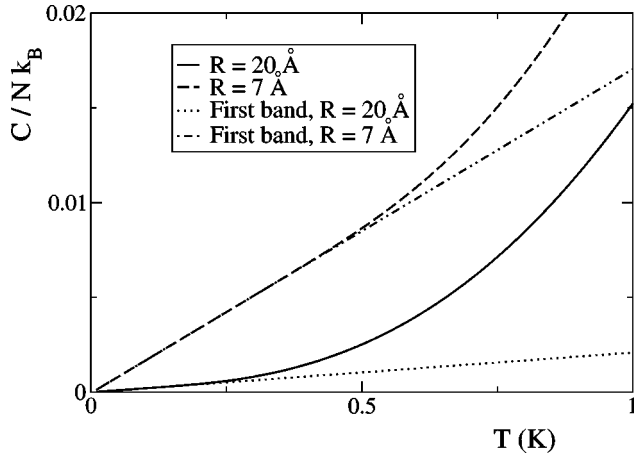


FIG. 1. Specific heat as a function of  $T$  for liquid helium in cylindrical pores of radii  $R=7$  Å and  $R=20$  Å, together with the 1D contributions from the respective ground state bands ( $mn$ ) = (00).

$$\frac{C}{Nk_B} = \frac{k_B T}{\pi n_1 \hbar c_s} \sum_{mn} \int_0^{x_M} dx \frac{x^3}{\sqrt{x^2 - x_{mn}^2}} n(x) [1 + n(x)] \quad (4)$$

with  $x = \hbar \omega / k_B T$  and  $x_M$  a cutoff that we choose according to [cf. Eq. (3)]

$$\omega_M^2 = c_s^2 (k_M^2 + k_{mn}^2) \quad (5)$$

for a maximum wave vector  $k_M = 1$  Å<sup>-1</sup>, corresponding to the maxon excitation in the dispersion relation of helium. Here  $n(x) = 1/(e^x - 1)$  is the population of excitations with reduced energy  $x$ . Expression (4) displays the divergences of the 1D density of states at the dimensionless band-head energies  $x_{mn}$ . Moreover,  $n_1 = \rho_0 \pi R^2$  is the number of particles per unit length of the pore,  $\rho_0$  being the saturation density of the liquid. At the very lowest temperatures, only the (0,0) mode is excited, in which case the heat capacity can be evaluated analytically if  $x_M$  is very large; in this regime,  $C/Nk_B$  is proportional to  $T$ , indicating the 1D character of the system, i.e.,

$$\frac{C}{Nk_B} = \frac{\pi}{3n_1 \hbar c_s} k_B T. \quad (6)$$

This dependence may be compared to the analogous 2D and 3D heat capacities, respectively proportional to  $(k_B T / \hbar c_s)^2 / n_2$  and  $(k_B T / \hbar c_s)^3 / n_3$ ,  $n_2$ ,  $n_3$  being the corresponding number densities.

The calculations presented here correspond to the bulk density of liquid helium at zero temperature,  $\rho_0 = 0.0219$  Å<sup>-3</sup>, for which we have  $\hbar c_s = 18.18 k_B$  K Å. In Fig. 1 we present the specific heat per particle for liquid helium in two different pores with radii  $R=7$  and  $20$  Å, together with the respective contribution from the ground state band. Note that the smallest pore exhibits the largest specific heat at low  $T$ , corresponding to the reduced linear density  $n_1$  in the prefactor. In fact, the square of the radius here scales the heat capacity. In addition, this small pore

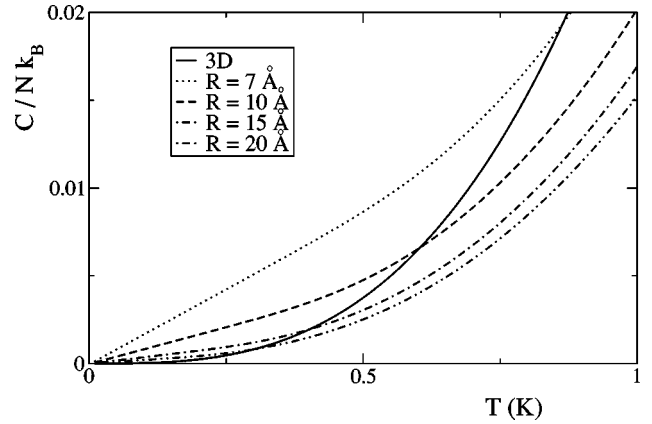


FIG. 2. Specific heat of bulk helium and of helium in cylindrical pores of several radii.

presents the most extended range of 1D behavior. The data indicate that the total heat capacity exceeds by 10% that of the lowest band at temperatures around 0.7 K for  $R=7$  Å and 0.25 K for  $R=20$  Å.

Although the trend of these curves suggests a power law, full 3D behavior (i.e.,  $C \approx T^3$ ) is not attained within this very low temperature range; fits of the specific heat to power laws yield exponents 1.4 for the smallest pore and 1.96 for the largest, showing an increased presence of 2D phonons in this case. This reflects the sequence of filling the 1D bands labeled by azimuthal and radial quantum numbers  $m$  and  $n$ , respectively; the angular ( $m$ ) spectrum being more compressed than the transverse ( $n$ ) one, the first bands to be thermally excited are those associated to motion on a cylindrical surface at a given average radius. The 1D regime thus crosses over to 2D, rather than 3D, at the low temperatures considered here. Only at very large  $T$ —i.e., much above  $T_\lambda$  for liquid helium, which invalidates the present approach—the system approaches the expected 3D limit; in fact, we restrict our displayed results to the lowest temperatures, keeping in mind that already in the vicinity of  $T=1$  K, the roton contribution to the thermal properties of bulk helium is non-negligible.

Our calculations also demonstrate that the pore's heat capacity exceeds the bulk's at temperatures where the phonon thermal wavelength

$$\lambda_{\text{ph}}(T) = \frac{2\pi \hbar c_s}{k_B T} \quad (7)$$

is larger than the pore's radius. This can be visualized in Fig. 2 where we plot the 3D heat capacity for bulk helium given by

$$\frac{C}{Nk_B} = \frac{2\pi^2}{5(\hbar c_s)^3} (k_B T)^3, \quad (8)$$

which cannot be distinguished from the numerically integrated expression allowing for a finite momentum cutoff  $k_M = 1$  Å<sup>-1</sup> in 3D, together with the pore's specific heat (4) for various radii. From the data we infer that the 3D and finite radius curves cross at temperatures of approximately

0.85, 0.6, 0.42, and 0.3 K, for radii equal to 7, 10, 15, and 20 Å, respectively. At these temperatures, the phonon wavelengths ( $\lambda$ ) remain one order of magnitude higher than the pore's diameter; however, the derived thermal wavelengths and imposed radii agree within a factor of 3 if one considers that the propagation along the 1D channels takes place with the 1D sound velocity  $c_1 = c_s / \sqrt{3}$ .

Our study demonstrates the possibly surprising fact that the heat capacity of the quantum fluid confined in a very small capillary exceeds both those of the bulk material and the pore background. This fact reflects the reduced dimensionality through the high density of states at low energy and in the neighborhood of the bandheads [cf. Eq. (4)]. While clearly this is the case within the present hydrodynamic approximation, it is interesting to observe that such behavior is expected even for fluids within nanotubes, the finest known regular porous media.<sup>10</sup> This is a consequence of the long-wavelength modes present in very long pores. If the pores were to have finite lengths, instead, the linear heat capacity would become exponentially small below the temperature corresponding to the gap in the spectrum associated with the long-wavelength cutoff. We note one further point in this context. The modes might be argued to possess high velocities when confined in such a small space. While this can occur due to compression by the adsorption potential, it should not be the case near the threshold for fluid uptake in the given region of space, since there the system is “soft” mechanically and thermodynamically. An extreme example of this behavior is the nature of the axial phase within nanotubes, which is a very low density fluid at its formation

threshold.<sup>11</sup> Thus this class of problem presents a number of surprising features which remain to be investigated experimentally.

*Note added.* Recently, we became aware of a report by Wada and co-workers<sup>12</sup> of the vapor pressure and heat capacity of <sup>4</sup>He adsorbed in 1D pores. In this work, it is shown that the heat capacity data are compatible with the presence of 2D phonons belonging to a first inert layer for helium 3D densities below a critical monolayer coverage, plus 1D phonons corresponding to the fluid in the second layer when the density exceeds that threshold, all the way up to bulk saturation at about 50% above monolayer coverage. The radius of the adsorption shell in this experiment is 5.5 Å and temperatures vary up to 0.5 K. For such a radius and temperature range, the results in Fig. 1 indicate that within the present model, the 1D phonon heat capacity should prevail, without any contribution from higher bands of angular motion, in agreement with the experimental output. Moreover, the authors in Ref. 12 employ their data to derive, out of Eq. (6), values of the sound velocity for the 1D coverages which correspond to their reported 3D ones. These sound velocities lie above 100 m/s for the reported density range, also in agreement with our parameter input for the present calculations.

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