RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 17 1 MAY 1993-I

Capillary condensation refrigerator

R. A. Guyer

Department of Physics and Astronomy, University of Massachusetts/Amherst, Amherst, Massachusetts 01003

(Received 17 December 1992)

In a system consisting of ^{3}He, ^{4}He, and a porous material, manipulation of the ^{4}He chemical potential leads to modification of the ^{4}He configurations. Changes in the ^{4}He configuration change the phase space available to the ^{3}He and the entropy of the ^{3}He changes accordingly. This system can be operated as a refrigerator by judicious choice of its parameters.

A generic adiabatic refrigerator is a physical system for which one has a control variable, x, whose value determines the accessability of some of the degrees of freedom of the system, often a set of excitations of the system. The refrigerator is operated by coupling the system to a temperature reservoir, at a "high" temperature, with x chosen so that the set of excitations is inaccessible. After coming into thermal equilibrium with the temperature reservior the system is isolated. From this moment onward the entropy is constant; further evolution of the system is adiabatic. Then, x is adjusted to make the set of excitations accessible. These excitations soak up part of the entropy residing in the other degrees of freedom of the system and the system as a whole cools.[1]

Perhaps the most exotic example of an adiabatic refrigerator is the Pomeranchuk refrigerator[2] in which the set of excitations is the spin degrees of freedom of ^{3}He fermions. When in the liquid state the Pauli principle operates to correlate almost all of the spins (to antialign the spins of particles of the same wave vector) and to make the spin degrees of freedom inaccessible. The liquid state is achieved by suitable choice of the pressure, $x=P$. Adjusting the pressure to cause the formation of a solid localizes the fermions on lattice sites and frees them of the demands of the Pauli principle. The spin degrees of freedom become accessible in the solid phase and soak up entropy from the liquid. (It was in such a refrigerator that the ^{3}He superfluid was discovered.) The purpose of this paper is to describe a refrigerator, involving the ^{3}He and ^{4}He fluids, that uses the capillary condensation process for ^{4}He in porous media for control of the accessability of the spin degrees of freedom of the ^{3}He.

We begin by reviewing the capillary condensation process for ^{4}He in a porous medium.[3,4] In order to be specific about quantitative aspects of this process we discuss it in terms of a particular porous material, Nuclepore.[5] The evolution of ^{4}He configurations through a complete capillary condensation hysteresis loop, brought about by change in the ^{4}He chemical potential, is described using the Priesach model.[6,7] We then discuss the behavior of ^{3}He in the presence of various ^{4}He configurations. When a small concentration of ^{3}He is added to the ^{4}He-Nuclepore system there are two possibilities for where it will reside. It may reside in the surface state,[8] available on the (free) surface of the ^{4}He fluid configuration, or it may reside in the bulk ^{4}He fluid that is in the "filled" pores of the ^{4}He configuration. We review the description of ^{3}He in the surface state and in bulk liquid. Finally we discuss use of the composite system, ^{3}He-^{4}He Nuclepore, as a refrigerator. A simple argument for the cooling process is presented. Then quantitative results from application of a refined form of this argument to the ^{3}He-^{4}He-Nuclepore system are presented. Substantial cooling is found.

Consider a Nuclepore filter (a filter material that comes in sheets $l \approx 10$ μm thick that have of order 10^8 pores/cm^2 of nominal radius $R \approx 1000$ Å), in an evacuated space that contains ^{4}He at temperature $T \approx 1$ K and chemical potential[9] (pressure) a few percent below the chemical potential, μ_{sat}, at saturated vapor pressure.[10] This dilute ^{4}He gas is in equilibrium with a ^{4}He film approximately 10 layers thick, covering all of the surface area of the filter. The film is held in place by the ^{4}He substrate van der Waal force. (The internal area of a filter is about 10 times its superficial area,[5] $2\pi R l \times 10^8 \approx 10$ cm^2; the two-dimensional tortuosity[4] is of order 10.) The surface tension of the ^{4}He would like to reduce the surface area of this thin film of fluid. The best opportunity for it to be successful is in the pores. The surface tension works to collapse the annular cylinder of fluid in the pores. The ^{4}He film thickness in a pore of radius R, $h(R)$, results from competition of the van der Waal force and the surface tension force. We have[4]

$$\mu_4 - \mu_{\text{sat}} = -\frac{\alpha}{h^3} - \frac{\sigma}{\rho(R-h)} , \tag{1}$$

where ρ is the density of bulk liquid ^{4}He, $\alpha \approx 30$ K-layer,[3] and $\sigma \approx 0.4$ erg/cm^2 is the surface tension.

As the ^{4}He chemical potential is raised toward μ_{sat} the ^{4}He film thickens. At $\mu_4 = \mu_F$ (the point of absolute instability[3] as illustrated in Fig. 3 of Ref. 4), the surface tension force overcomes the van der Waal force and succeeds in collapsing the annular cylinder; ^{4}He fills the pore. This is the rudimentary pore filling or capillary condensation event.[11] The pores in Nuclepore have a spectrum of radii[12] that is spread around the average radius by about 20%. For a pore of radius R there is a critical chemical potential $\mu_F(R)$ at which the pore fills and for the system as a whole there is a set of these chemical potentials. Thus as the ^{4}He chemical potential is raised toward μ_{sat} there is a sequence of pore fillings that leads to the distinctive feature in a volume (mass) isotherm that is shown in Fig. 1. In this figure we show the volume of the pore space filled with fluid, normed to the total volume of the pore space, as a function of μ_4. The mass

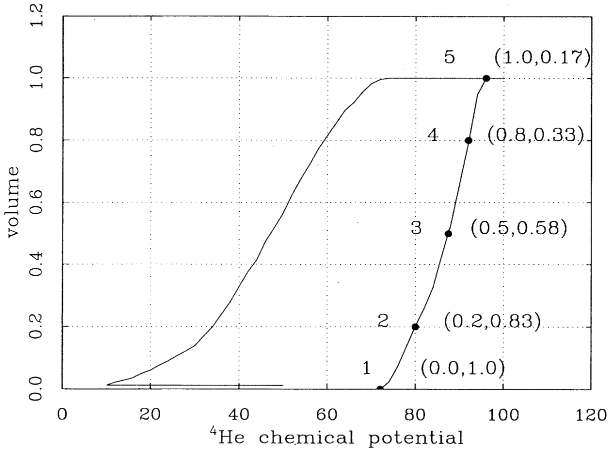

FIG. 1. Volume vs ^{4}He chemical potential. The volume of ^{4}He fluid in the pores is plotted as a function of the ^{4}He chemical potential as it is cycled from 72 to 100 to 10 to 50. Pore filling occurs during the 72→100 part of this cycle. The ^{4}He fluid configurations at 5 points in the cycle, the filled circles, are shown as $(\mathcal{V},\mathcal{S})$ pairs. (The calculations that lead to this hysteresis loop are from Ref. 13. The ^{4}He chemical potential is in arbitrary units.)

isotherm is a hysteresis loop. It is found from realistic modeling[13] of the ^{4}He-Nuclepore system using Eq. (1), a model of the pore emptying event and a Priesach-Mayergoyz model[6,7] of the capillary condensation process. As μ_4 is increased pore filling occurs for the first time beyond point 1 on the hysteresis loop. (see Fig. 1). It is complete at point 5 on the loop, just before $\mu_4=\mu_{\text{sat}}$. (The second part of the hysteresis loop, the upper-left part, is generated upon decreasing μ_4 after complete pore filling and is determined by the model of the pore emptying event. For present purposes we are concerned with the filling part of the loop, points 1–5.) As the chemical potential is increased to cause the increased filled pore volume, points 1–5, the surface area of the ^{4}He fluid configuration decreases. At point 1 the fluid configuration has surface area of order 10 cm^2; at point 5 the surface area of the fluid configuration is the superficial area only, about 1 cm^2; all of the interior surface has disappeared. The volume-surface pairs at the 5 marked points along the pore filling part of the hysteresis loop are shown on the figure as $(\mathcal{V},\mathcal{S})$ pairs, V and S normed by the total pore volume and the total surface area (the superficial surface and the surface in the pores) respectively; see Eqs. (4) below.

Let us now turn to the question of the behavior of ^{3}He that is added to the ^{4}He-Nuclepore system. A single ^{3}He atom in the presence of ^{4}He with a *free* surface[14] has the lowest energy in the surface state,[8] a state at -5.0 K well localized in the surface of the ^{4}He. In this state the ^{3}He atom translates parallel to the surface.[13] As more ^{3}He atoms are added to a ^{4}He fluid configuration, at fixed surface area S, their density increases as does their Fermi energy. For the moment suppose we are at low enough temperature that the ^{3}He on the surface are degenerate. The entropy per particle of the ^{3}He in the surface state is $S_S/N_S \propto k_B(k_BT/\epsilon_{F,S})$, where $\epsilon_{F,S}$, the Fermi energy of N_S ^{3}He particles in the surface state is proportional to N_S/S.

There are states available to a ^{3}He atom in bulk ^{4}He liquid[8] at -2.8 K. At $\bar{N}_3$ such that

$$-5.0+\frac{\pi\hbar^2}{m}\frac{\bar{N}_3}{S_S}=-2.8\,, \tag{2}$$

^{3}He will enter the bulk liquid ^{4}He for the first time. As the number of ^{3}He atoms is increased beyond $\bar{N}_3$ most of them will go into the bulk ^{4}He liquid. If this liquid is vast the ^{3}He will be nondegenerate with entropy per particle $S_B/N_B \propto k_B \ln N_3\lambda_T^3/V$, where λ_T is the thermal de Broglie wavelength. It is the entropy difference between ^{3}He on the surface and in the bulk that we use for cooling. At *fixed number* of ^{3}He we shift particles between surface state and bulk fluid by manipulating the capillary condensation process.

Consider a system consisting of ^{3}He, ^{4}He, and Nuclepore. The ^{4}He chemical potential is initially chosen so that no pores are filled $V\propto\mathcal{V}=0$, $\mathcal{S}=1$. The number of ^{3}He and the initial temperature are chosen so that the ^{3}He is degenerate, e.g., $T_i\approx 100$ mK, $N_3\approx 0.1$ monolayers. The entropy of the system is

$$\frac{S_S}{N_0k_B}\approx \mathcal{S}T_i^*\,. \tag{3}$$

In writing this equation we use variables that measure energy, number, volume, and surface area in terms of standards set by the structure of the physical system: $\epsilon_0=\pi\hbar^2/ma^2$, $\rho=$ bulk liquid density $=a^{-3}$, $N_0=$ (total surface area of porous material) $/a^2\equiv S_T/a^2$, $V_T=$ total volume of the pore space;

$$\begin{aligned} T^*&=\frac{k_BT}{\epsilon_0}\,,\\ \mathcal{N}&=\frac{N_3}{N_0}\,,\\ \mathcal{V}&=\frac{\text{fluid volume}}{V_T}\,,\\ \mathcal{S}&=\frac{\text{fluid surface}}{S_T}\,. \end{aligned} \tag{4}$$

(In these units the Fermi energy of the ^{3}He on the surface is $\mathcal{N}_S/\mathcal{S}$, where $\mathcal{N}_S$ is the number of ^{3}Ne on the surface in units of N_0. Thus the total entropy of the ^{3}He on the surface is independent of their number and proportional to $\mathcal{S}$.) Now with $\mathcal{N}$*fixed* isolate the system and raise the chemical potential of the ^{4}He toward μ_{sat} so that all of the pores are filled with ^{4}He liquid. If we naively assume that all of the ^{3}He go into the bulk liquid, because $\mathcal{S}\to 0$, and that they are nondegenerate there, the system has entropy at temperature T_f given by

$$\frac{S_B}{N_0k_B}\approx \mathcal{N}\ln\left[\frac{\mathcal{N}}{g\mathcal{V}T_f^{*3/2}}\right]\,, \tag{5}$$

where $g=V_T/aS_T$. Equating the two entropies we find

$$T_f^* = \left[\frac{\mathcal{N}}{g\mathcal{V}} \right]^{2/3} \exp\left[-\frac{2}{3} T_i^* \frac{\mathcal{S}}{\mathcal{N}} \right] . \tag{6}$$

The argument of the exponential is by assumption small compared to 1, the ^{3}He on the surface at T_i is degenerate, so the final temperature is determined by the factor in front of the exponential. We take $\mathcal{V}=1$ and $\mathcal{N}\approx 0.1$. Thus the final temperature is determined primarily by the geometrical factor g, a measure of the change in phase space available to the ^{3}He upon leaving the surface and going into the bulk. For Nuclepore $g \approx R/2a \approx 150$ and $T_f \approx 20$ mK. (The entropy made available by the bulk ^{4}He is much more than just the ln2 due to freeing up the spin degree of freedom that we remarked on above.) An essential ingredient to the operation of the cooling process described here is the reduction in available surface that accompanies the opening up of the volume. It is the porous media that lets us accomplish this.

The idea suggested by this simple argument is supported by careful calculations of the entropy evolution for the ^{3}He-^{4}He-Nuclepore system. For the five ^{4}He fluid configurations shown on the hysteresis loop in Fig. 1 we follow the entropy as the temperature varies by a factor of 20, from $T^*=0.20$ to $T^*=0.01$, from 20 mK $\leq T \leq 400$ mK. We choose $\mathcal{N}=0.2$, an amount of ^{3}He such that when the full surface is available, $\mathcal{S}=1$, the concentration on the surface is 0.20. As T varies, for the $(\mathcal{V},\mathcal{S})$ of a particular ^{4}He configuration, the number of ^{3}He atoms on the surface and in the bulk liquid vary to maintain chemical potential equilibrium. At each $(\mathcal{V},\mathcal{S},T)$ we find $(\mathcal{N}_B=\mathcal{N}-\mathcal{N}_S,\mathcal{N}_S)$. The entropy is taken as the sum of these two independent components, a bulk component and a surface component. As matters of principle are involved here we use a simple model of the ^{3}He system. The ^{3}He on the surface is taken to be a two-dimensional ideal Fermi gas with bare mass. Similarly the ^{3}He in the bulk is taken to be a three-dimensional ideal Fermi gas with bare mass. (No Fermi-liquid effects nor modification of the surface tension with concentration were considered. These neglected effects produce small changes in the resulting curves.)

Let us begin by looking at Fig. 2 in which we show the number of ^{3}He on the surface, $\mathcal{N}_S=N_S/N_0$, as a function of T^* (it is the log base 10 of T^* that is plotted on the x axis), for the five ^{4}He fluid configurations shown in Fig. 1. For curve 1, corresponding to point 1 on Fig. 1, there is no bulk fluid in the ^{4}He configuration, $\mathcal{N}_S=1$ at all T. When bulk ^{4}He liquid is present, as at points 2–5, the ^{3}He population in this liquid is largest at high temperatures. The lowest-energy state available to the ^{3}He is on the surface and it is to this state that the ^{3}He goes as T is lowered. When the amount of surface is reduced, $2\rightarrow3\rightarrow4\rightarrow5$, the ^{3}He is slower to take advantage of this possibility. The most extreme case is the ^{4}He configuration corresponding to 5. A modest amount of surface is available in this ^{4}He configuration and at $T\rightarrow0$ approximately equal amounts of ^{3}He reside on the surface and in the bulk liquid. (These scenarios are by no means a best case. Porous materials other than Nuclepore offer the possibility of reducing $\mathcal{S}$ as $\mathcal{V}\rightarrow1$ by much more than Nuclepore.)

We now turn to Fig. 3 where we show the total entropy of the system for the five ^{4}He configurations from Fig. 1 as a function of temperature. We see in the evolution of the entropy reflection of the qualitative features seen in Fig. 2. When the ^{3}He is on the surface the entropy is relatively low and roughly proportional to the temperature. When there is substantial ^{3}He in the bulk liquid there is a marked increase in the entropy of the system because the ^{3}He in the bulk liquid is nondegenerate (or nearly so).

Operation of this system as a refrigerator could begin at point 1 at $T\approx0.1$ K, at $\log(T^*)=-1$ on the scale used in Figs. 2 and 3, on the curve with closed circles in

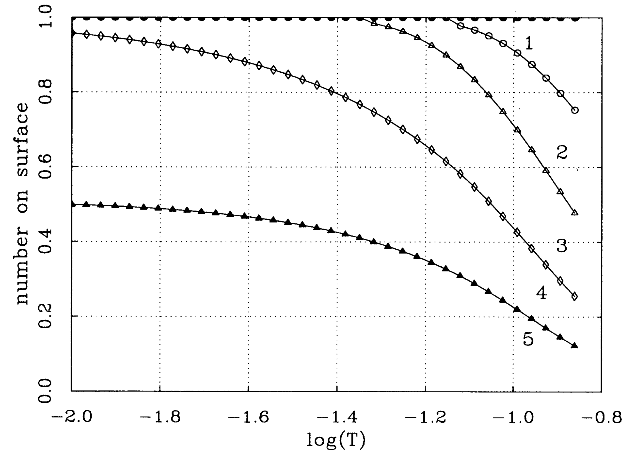

FIG. 2. $\mathcal{N}_S$ vs T^*. The number of ^{3}He atoms on the surface is plotted as a function of temperature for the five fluid configuration indicated in Fig. 1. The curve numbers are in agreement with those used in Fig. 1. The x axis is log base 10 of the scaled temperature from Eq. (4); the values of $\mathcal{N}_S$ are scaled by N_0, as in Eq. (4), and equal to 1 when all of the ^{3}He are on the surface.

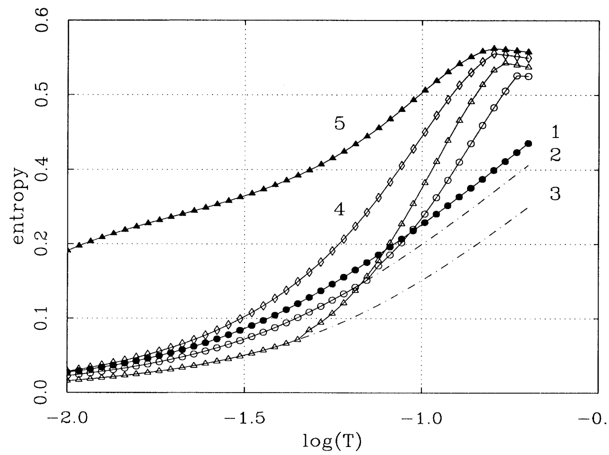

FIG. 3. Entropy vs T^*. The entropy of the system, normed as in Eq. (4), is plotted as a function of T^* (as in Fig. 2 the x axis is log base 10). The curve numbers and symbols are in agreement with those used in Figs. 1 and 2. The dash-dotted lines associated with curves 2 and 3 are the entropy of the system for the case where all of the ^{3}He is confined to the surface.

these figures. Upon isolating the system the ^{4}He chemical potential is raised to bring the system at constant entropy to point 5. (This step might be carried out for example using a bellows and superleak to "flood" the pore space with ^{4}He. It requires doing the work necessary to change the ^{4}He configuration. This work is done by the mechanical system that moves the ^{4}He, e.g., the bellows, and is not a part of the energy budget involved in determining the cooling provided by the refrigerator.) From the filled triangle curve corresponding to the ^{4}He configuration of point 5 we see that the temperature drops by approximately an order of magnitude, to $\log(T^*) = -2$. This drop in temperature is less than that of the naive approximation above but nonetheless substantial. (We have not included the entropy of the substrate, in this example Nuclepore, in following the entropy of the system. We imagine use of this refrigerator at temperatures of order 100 mK with substrates that carry at most a phonon entropy, an entropy typically of order $10^{-9} k_B$ per particle at 100 mK, that can be neglected.)

What could you cool with the capillary condensation refrigerator? The capacity of this refrigerator as we have described it is very modest. If one could soak up a full k_B of entropy for every ^{3}He in the system one would still be limited by the small number of ^{3}He atoms. At $\mathcal{N} \approx 0.2$ there are of order 10^{16} atoms on a 1-cm^2 sheet of Nuclepore. Thus it would be best to use this refrigerator to cool itself or other surface systems. There are currently a number of interesting phenomena being sought in ^{3}He films at low temperature. Perhaps the most exciting is the possibility of the superfluidity of polarized two-dimensional ^{3}He.[15] In this regard notice that one could use the half of the capillary condensation hysteresis loop we have ignored to facilitate polarization of a ^{3}He film. One would polarize dilute, cold ^{3}He in the bulk ^{4}He liquid and then turn it into a dense, polarized two-dimensional fluid by reducing μ_4 and forcing pore emptying. There are porous media other than Nuclepore that may offer advantage, e.g., they may have more favorable surface-to-volume ratios or broader and more easily manipulated hysteresis loops.

We believe that the discussion here demonstrates the efficacy of a novel refrigeration scheme.

---

[1] D. S. Betts, *Refrigeration and Thermometry Below One Kelvin* (Sussex Univ. Press, Sussex, United Kingdom, 1976).

[2] O. Lounasmaa, *Experimental Principles and Methods Below 1 Kelvin* (Academic, New York, 1984), Chap. 4.

[3] W. F. Saam and M. W. Cole, Phys. Rev. B **11**, 1086 (1975).

[4] S. Cohen, R. A. Guyer, and J. Machta, Phys. Rev. B **33**, 4664 (1986).

[5] J. M. Valles, D. T. Smith, and R. B. Hallock, Phys. Rev. Lett. **54**, 1528 (1985), see also Ref. 12.

[6] F. Priesach, Z. Phys. **94**, 277 (1935).

[7] I. D. Mayergoyz, J. Appl. Phys. **57**, 3808 (1985).

[8] D. O. Edwards and W. F. Saam, in *Progress in Low Temperature Physics,* edited by D. F. Brewer (North-Holland, New York, 1978), Vol. 7A.

[9] At high temperatures, $T > 1$ K, one controls the ^{4}He chemical potential by controlling the unsaturated vapor pressure. Thus unsaturated vapor pressure and chemical potential are regarded as synonymous. At very low temperature one must control the total amount of ^{4}He in the sample chamber. This must be done through a superleak to prevent a change in the amount of ^{3}He in the system.

[10] J. G. Dash, *Films on Solid Surfaces* (Academic, New York, 1975).

[11] The emptying part of the hysteresis loop comes about because of an instability of the filled pore configurations that can be supported by the meniscus at the ends of a pore. The pore radii at the ends are often different from the interior pore radii. Details of the model of this geometrical feature show up in the appearance of the loop.

[12] A detailed description of the Nuclepore geometry, gleaned from study of the capillary condensation hysteresis loop is found in K. M. Godshalk, Ph.D. thesis, University of Massachusetts, 1990.

[13] R. A. Guyer (unpublished).

[14] Treiner and colleagues, e.g., N. Pavloff and J. Treiner, J. Low Temp. Phys. **83**, 331 (1991), have suggested that on some weakly binding substrates one might expect a second surface state near the substrate. The symmetry of the free-standing film supports this expectation. For simplicity we restrict our discussion to consideration of substrates for which only the free surface has a surface state. As of this writing empirical evidence is that this is *all* substrates.

[15] A. Chubukov and M. Kagan (unpublished).