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Critical supersaturation of ^{3}He-^{4}He liquid mixtures at low temperatures

Dora M. Jezek
Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires,
RA-1428 Buenos Aires, Argentina

Montserrat Guilleumas, Martí Pi, and Manuel Barranco
Departament d'Estructura i Constituents de la Matèria, Facultat de Física, Universitat de Barcelona,
E-08028 Barcelona, Spain

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We have investigated the phase separation in supersaturated ^{3}He-^{4}He liquid mixtures due to nucleation via thermal fluctuations below $\sim$ 200 mK and found a large discrepancy in the supersaturation value between recent experiments ($\sim$ 1%) and nucleation theory ($\sim$ 10%). We suggest that the rather small degree of supersaturation found experimentally is due to destabilization of vortices with cores rich in ^{3}He.

During the past 15 years, there has been a common belief[1] that supersaturated ^{3}He-^{4}He liquid mixtures at very low temperature (T) could be found in a metastable state for ^{3}He concentrations $x = \rho_3/(\rho_3 + \rho_4)$ well above the saturation value $x_s \sim 6.6\%$ at pressure $P \sim 0$.[2] That belief was motivated by an extrapolation to T=0, of the measured ^{3}He chemical potential excess $\Delta\mu_3$ along the coexistence line carried out by Seligmann *et al.*[3] This extrapolation yields $\partial\Delta\mu_3/\partial x \geq 0$ up to $x > 16\%$, opening the possibility that the system can be in a metastable state up to or even above that concentration.[4] Lifshitz, Polesskii and Khokhlov,[5] have studied nucleation in a capillarity model and have calculated the degree of supersaturation $\Delta x_{\rm cr} \equiv x - x_s$ obtaining a value around 15% and a crossing temperature T^* from thermal to quantum nucleation regimes of about 14 mK.

The first systematic study of phase separation from supersaturated ^{3}He-^{4}He liquid mixtures has recently been made,[6] with the result that at $P \sim 3 - 5$ bars, $\Delta x_{\rm cr} \sim 0.2 - 0.5\%$, and $T^* \sim 20$ mK. Other experiments at lower pressures (Ref. 7 as quoted in Ref. 8) yield $\Delta x_{\rm cr} \sim 1\%$. It is worth recalling that the Ohio State group had actually found metastable ^{3}He-^{4}He solutions up to $\Delta x_{\rm cr} \sim 0.3\%$.[2] The above nucleation calculations are clearly in sharp disagreement with these experimental results.

Let us first review nucleation (either thermal or quantal) of ^{3}He-rich droplets in the mixture within the capillarity model and within the improved density functional approach of Ref. 9 and show that it is hardly compatible with these experimental findings. Making use of the capillarity approximation, the potential energy of a ^{3}He-nucleus of radius R in a metastable supersaturated mixture near saturation ($x \sim x_s$) has the form[5,8]

$$\Delta U(R) = 4\pi\sigma R^2 - \frac{4\pi R^3}{3}\rho_3\Delta\mu_3\,, \tag{1}$$

where σ is the surface tension of the ^{3}He-^{4}He interface, ρ_3 is the particle density of pure ^{3}He inside the droplet at a given pressure, and $\Delta\mu_3$ is the difference between the chemical potential of ^{3}He in the metastable, dilute phase, and in pure ^{3}He at saturation. Minimizing the right-hand side of (1) with respect to R, the radius of the critical drop $R_c = 2\sigma/(\rho_3\Delta\mu_3)$ and the critical barrier $\Delta U(R_c) = 4\pi R_c^2\sigma/3$ are obtained. The probability per unit time and unit volume of thermally forming such a drop is $\Gamma = \Gamma_0 \exp[-\Delta U(R_c)/T]$. In order to observe nucleation, one must have $V\tau\Gamma \sim 1$, where V and τ are the experimental volume and time, respectively. Thus, $\Delta U(R_c) = T \ln(V\tau\Gamma_0)$. Typical values of the logarithm are about 80.[4,8,10] Taking $T \sim 100$ mK, it yields $\Delta U(R_c) \sim 8$ K.

Using the experimental values $\sigma = 0.017 \pm 0.002$ K Å^{-2} (Ref. 11) and $\rho_3 \sim 0.016$ Å^{-3}, and approximating $\Delta\mu_3 \sim \Delta x\partial(\Delta\mu_3)/\partial x \,|_{x_s}\!\sim 2.3\,\Delta x$ (K) (Ref. 12), one has

$$\Delta U(R_c) \sim 6.1 \times 10^{-2}/(\Delta x)^2 \text{ (K)}. \tag{2}$$

For $\Delta x \sim 0.004$, which is within the range of experimental values of,[6] one gets $R_c \sim 230$ Å and $\Delta U(R_c) \sim 3800$ K, being over two orders of magnitude larger than the value at which phase separation via nucleation of ^{3}He drops mediated by thermal fluctuations would become possible. It is quite obvious that a poor evaluation of $\Delta U(R_c)$ also leads to a wrong value of T^*, since it is obtained from $\Delta U(R_c)$ and the underbarrier action S [usually determined in the Wentzel-Kramers-Brillouin (WKB) approximation], since $T^* = \Delta U(R_c)/(2\,S)$.[13]

One might argue about the validity of the capillarity approximation, as well as the value of $\partial(\Delta\mu_3)/\partial x \,|_{x_s}$, which is crucial to obtain the barrier height. Let us first mention that the capillarity approximation is appropriate if the nucleation process takes place near the saturation curve,[14] as the present case seems to be in view of the smallness of $\Delta x_{\rm cr}$ encountered.[5,6] The reason is the large size of the critical drop, that makes curvature and compressional effects negligible.

To put our estimates of $\Delta U(R_c)$ and $\partial(\Delta\mu_3)/\partial x \,|_{x_s}$ on firmer grounds, we have resorted to a density functional[15] to obtain these quantities following the method of.[4] Figure 1 shows $\Delta\mu_3$ as a function of x for P=0 and 3 atm. The results obtained in Ref. 3, as an extrapolation of experimental measurements, are also displayed. The functional yields $x_s(P = 0) \sim 6.6\%$, and $x_s(P = 3$ atm)

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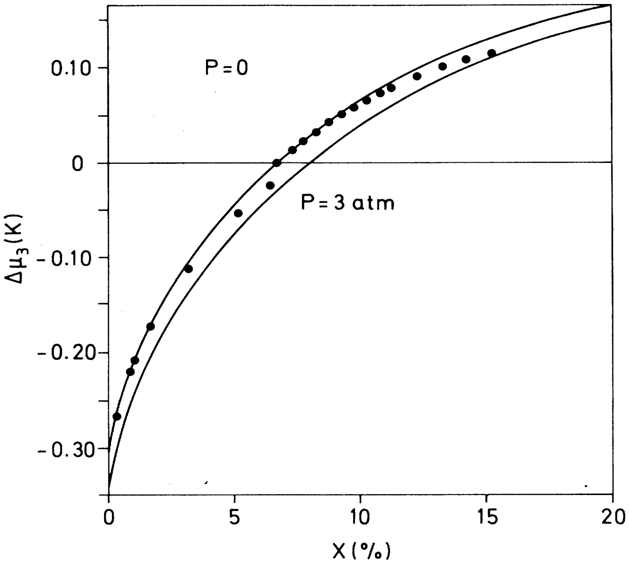

FIG. 1. ^{3}He chemical potential excess as a function of the ^{3}He concentration for $P = 0$ and 3 atm (solid lines). The dots have been extracted from Fig. 4 in Ref. [3].

$\sim 7.9\%$. The slopes at these values of x_s are 2.34 K and 2.13 K, respectively. We can appreciate a good agreement between our calculations and those of Ref. 3.

Figure 2 shows ΔU as a function of x for $P = 0$ and 3 atm. It is worth noticing that $\Delta U \sim 8$ K for $x \sim 0.15$ at P=0. This result is consistent with the positiveness of $\partial(\Delta\mu_3)/\partial x$ up to $x \sim 0.16$ found in Ref. 3, and up to ~ 0.3 found in Ref. 4, indicating that, if phase separation by ^{3}He drop nucleation took place, the degree of supersaturation would be $\Delta x_{\rm cr} \sim 9\%$. The corresponding radius of the critical nucleus is $R_c \sim 15$ Å (see Fig. 3). However, if $\Delta x_{\rm cr} \sim 0.4\%$, then $x = x_s + \Delta x_{\rm cr} \sim 7\%$, $R_c \sim 250$ Å, and $\Delta U \sim 4500$ K out of scale in Fig. 2. That would have been the result obtained in the capillarity approximation if we had used there the same value of σ (see Ref. 11).

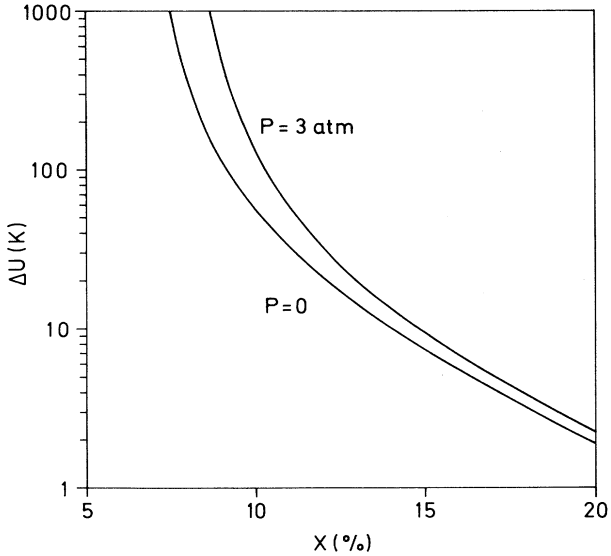

FIG. 2. Nucleation barrier of ^{3}He-rich drops as a function of the ^{3}He concentration for $P = 0$ and 3 atm.

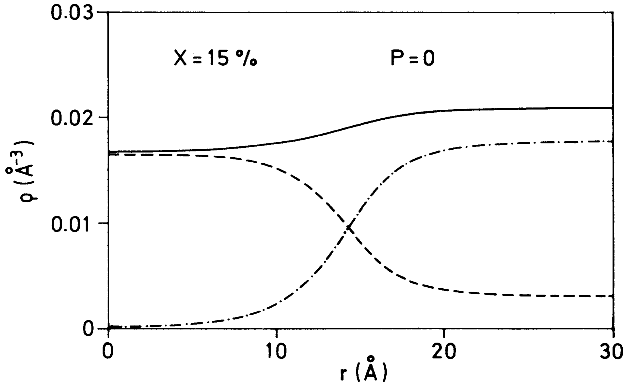

FIG. 3. Critical-drop density profile corresponding to the situation $P = 0$, $x = 15\%$. Solid line, total density. Dashed-dotted line, ^{4}He density. Dashed line, ^{3}He density.

A possible way to solve these difficulties is to consider the existence of vortices in the mixture,[16] since ^{4}He is superfluid under the given conditions. Let us assume the hollow core model for the ^{4}He vortex, i.e., the ^{4}He density is zero within the core and equal to the bulk value ρ_4 elsewhere. As x increases, the ^{3}He atoms located at the surface of the vortex[17] migrate to the interior of the hollow core. If ρ_3 is the ^{3}He particle density inside the vortex core, then for $x \gtrsim x_s$ the energy per unit length of a vortex of radius a and circulation n can be written as

$$E_v = 2\pi\sigma a - \pi a^2 \rho_3 \, \Delta\mu_3 + \pi n^2 \frac{\hbar^2}{m_4} \rho_4 \ln\left(\frac{a_\infty}{a}\right) , \qquad (3)$$

where m_4 is the atomic mass of ^{4}He and a_∞ is a large enough radius. Minimizing E_v with respect to a, we get the radius of the stable vortex. If $a_0 \equiv n^2\hbar^2\rho_4/(2\sigma m_4)$ and $\mu_c \equiv \sigma^2 m_4/(2n^2\hbar^2\rho_3\rho_4)$, one has

$$a = 2a_0 \frac{\mu_c}{\Delta\mu_3}\left[1 \pm \sqrt{1 - \frac{\Delta\mu_3}{\mu_c}}\right] . \qquad (4)$$

The plus sign corresponds to a maximum of E_v with $a = a_>$, and the minus sign to the stable minimum with $a = a_<$. a_0 is the equilibrium radius for $\Delta\mu_3 = 0$, i.e., for $x = x_s$. This simple expression shows that for $\Delta\mu_3 > \mu_c$ the vortex is no longer stable. Taking $n = 1$, $\rho_4 = 0.020$ Å^{-3}, and $\hbar^2/m_4 \sim 12$K Å^2, one gets $a_0 = 7.1$ Å and $\mu_c = 0.038$ K. Thus, for $\Delta\mu_3 = 0.038$ K the mixture will necessarily undergo phase separation. Using our linear approximation, this corresponds to $\Delta x_{\rm cr} \sim 1.6\%$ at P=0, which is considerably smaller than the quantity obtained from ^{3}He drop nucleation.

That value constitutes an upper limit of the actual $\Delta x_{\rm cr}$, as we have not taken into account that the stable vortex may destabilize by quantum or thermal fluctuations. The barrier to be overcome, per vortex unit length, is the difference $E_v(a_>) - E_v(a_<)$, and may be written as function of $y \equiv \Delta\mu_3/\mu_c$,

$$\Delta U(y) = \frac{4\pi a_0 \sigma}{y}\sqrt{1-y} + 2\pi a_0 \sigma \ln\left(\frac{1-\sqrt{1-y}}{1+\sqrt{1-y}}\right) . \tag{5}$$

Then, $\Delta U(y) = 0$ for $y = 1$ and diverges at the saturation value x_s, for which $y = 0$. Now let L_v be the vortex length per unit volume in the experimental sample. The probability per unit time and unit vortex length of thermally forming a critical vortex of length L_c is $\Gamma = \Gamma_0^v \exp(-L_c \Delta U/T)$. Consequently, to observe such a fluctuation one must have $L_c\,\Delta U = T\,\ln(L_v V \tau \Gamma_0^v)$. Taking $L_c \sim 10\ a_0$ and $T = 0.1$ K, we get $\Delta x_{\rm cr} \sim 1.3 - 1.4\,\%$ for values of the logarithm between 80 and 40. We are then led to conclude that barrier crossing is not a very favorable process.

We have also considered the possible growth of a ^{3}He-rich drop on a stable vortex of radius a. The previous calculations indicate that $a << R$, in which case it is easy to check that the associated barrier ΔU for this process is the one given by (1) plus a corrective term $\Delta U_{\rm cor}$:

$$\Delta U_{\rm cor} = \left\{ -4\pi a\sigma + 2\pi a^2 \rho_3 \Delta\mu_3 + 2\pi \frac{\rho_4 \hbar^2}{m_4} n^2 \left[1 - \frac{1}{2}\left(\frac{a}{R}\right)^2 + \ln\left(\frac{a}{2R}\right)\right]\right\} R. \tag{6}$$

This correction is negative, and for $\Delta x_{\rm cr} \sim 0.4\%$ and P=0 we get $R_c \sim 210$ Å and $\Delta U(R_c) = 2200$ K, which is still too large a value.

In conclusion, we have shown that a plausible way to explain the small degree of supersaturation found in ^{3}He-^{4}He liquid mixtures is to consider the destabilization of vortex lines filled with ^{3}He. A precise evaluation of $\Delta x_{\rm cr}$ is a very demanding task, involving a detailed calculation of the structure of these vortices for $x \geq 6.6\%$ and different pressures. Moreover, it is worth mentioning that in order to describe vortex structure, any density functional has to be a galilean invariant, and none of the current density functionals for ^{3}He-^{4}He mixtures fulfills this requirement.

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[12] We have computed $\partial(\Delta\mu_3)/\partial x\ |_{x_s}$ from Fig. 4 of Ref. 3, obtaining 2.3 K instead of the value quoted in Ref. 5 ($\sim$ 0.3 K) which came also from the same reference. In our opinion, this gross error invalidates the numerical calculations of Lifshitz *et al.*

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