

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

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We have investigated the phase separation in supersaturated ${}^3\text{He}$ - ${}^4\text{He}$ liquid mixtures due to nucleation via thermal fluctuations below ~ 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 ${}^3\text{He}$.

During the past 15 years, there has been a common belief¹ that supersaturated ${}^3\text{He}$ - ${}^4\text{He}$ liquid mixtures at very low temperature (T) could be found in a metastable state for ${}^3\text{He}$ 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 ${}^3\text{He}$ 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 $\Delta x_{\text{cr}} \equiv x - x_s$ 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 ${}^3\text{He}$ - ${}^4\text{He}$ liquid mixtures has recently been made,⁶ with the result that at $P \sim 3 - 5$ bars, $\Delta x_{\text{cr}} \sim 0.2 - 0.5\%$, and $T^* \sim 20$ mK. Other experiments at lower pressures (Ref. 7 as quoted in Ref. 8) yield $\Delta x_{\text{cr}} \sim 1\%$. It is worth recalling that the Ohio State group had actually found metastable ${}^3\text{He}$ - ${}^4\text{He}$ solutions up to $\Delta x_{\text{cr}} \sim 0.3\%$.² The above nucleation calculations are clearly in sharp disagreement with these experimental results.

Let us first review nucleation (either thermal or quantum) of ${}^3\text{He}$ -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 ${}^3\text{He}$ -nucleus of radius R in a metastable supersaturated mixture near saturation ($x \sim x_s$) has the form^{5,8}

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

where σ is the surface tension of the ${}^3\text{He}$ - ${}^4\text{He}$ interface, ρ_3 is the particle density of pure ${}^3\text{He}$ inside the droplet at a given pressure, and $\Delta\mu_3$ is the difference between the chemical potential of ${}^3\text{He}$ in the metastable, dilute phase, and in pure ${}^3\text{He}$ 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 \AA^{-2} (Ref. 11) and $\rho_3 \sim 0.016$ \AA^{-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

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

For $\Delta x \sim 0.004$, which is within the range of experimental values of,⁶ one gets $R_c \sim 230$ \AA 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 ${}^3\text{He}$ 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 $T^* = \Delta U(R_c)/(2S)$.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 Δx_{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 functional¹⁵ 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 $x_s(P=3 \text{ atm})$

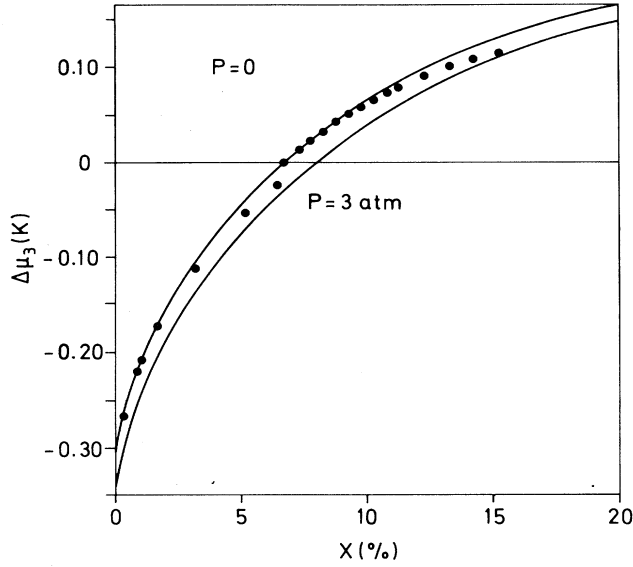


FIG. 1. ^3He chemical potential excess as a function of the ^3He concentration for $P = 0$ and 3 atm (solid lines). The dots have been extracted from Fig. 4 in Ref. [3].

$\sim 7.9\%$. 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 ^3He drop nucleation took place, the degree of supersaturation would be $\Delta x_{\text{cr}} \sim 9\%$. The corresponding radius of the critical nucleus is $R_c \sim 15$ Å (see Fig. 3). However, if $\Delta x_{\text{cr}} \sim 0.4\%$, then $x = x_s + \Delta x_{\text{cr}} \sim 7\%$,

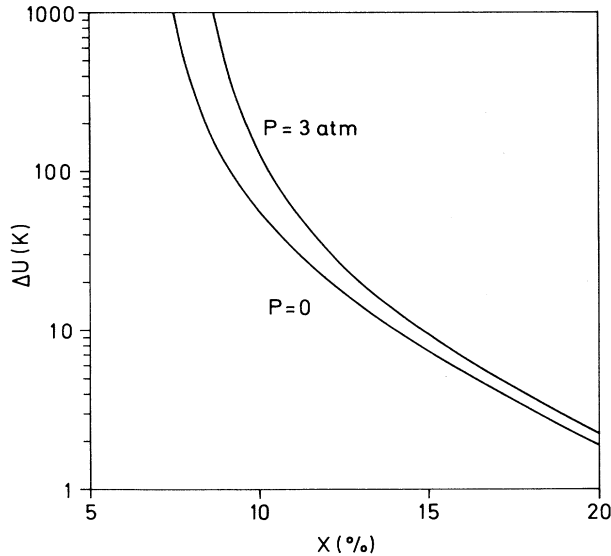


FIG. 2. Nucleation barrier of ^3He -rich drops as a function of the ^3He concentration for $P = 0$ and 3 atm.

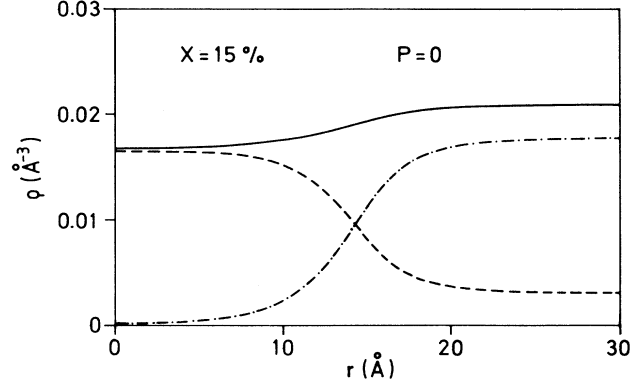


FIG. 3. Critical-drop density profile corresponding to the situation $P = 0$, $x = 15\%$. Solid line, total density. Dashed-dotted line, ^4He density. Dashed line, ^3He density.

$R_c \sim 250$ 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).

A possible way to solve these difficulties is to consider the existence of vortices in the mixture,¹⁶ since ^4He is superfluid under the given conditions. Let us assume the hollow core model for the ^4He vortex, i.e., the ^4He density is zero within the core and equal to the bulk value ρ_4 elsewhere. As x increases, the ^3He atoms located at the surface of the vortex¹⁷ migrate to the interior of the hollow core. If ρ_3 is the ^3He particle density inside the vortex core, then for $x > x_s$ the energy per unit length of a vortex of radius a and circulation n can be written as

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

where m_4 is the atomic mass of ^4He 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

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

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 Å², 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 $\Delta x_{\text{cr}} \sim 1.6\%$ at $P = 0$, which is considerably smaller than the quantity obtained from ^3He drop nucleation.

That value constitutes an upper limit of the actual Δx_{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 $y \equiv \Delta\mu_3/\mu_c$,

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

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 $\Delta x_{cr} \sim 1.3 - 1.4\%$ 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 ${}^3\text{He}$ -rich drop on a stable vortex of radius a . The previous calculations indicate that $a \ll R$, 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 ΔU_{cor} :

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

This correction is negative, and for $\Delta x_{cr} \sim 0.4\%$ and $P=0$ we get $R_c \sim 210 \text{ \AA}$ 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 ${}^3\text{He}$ - ${}^4\text{He}$ liquid mixtures is to consider the destabilization of vortex lines filled with ${}^3\text{He}$. A precise evaluation of Δx_{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 ${}^3\text{He}$ - ${}^4\text{He}$ mixtures fulfill this requirement.

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