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LETTERS TO THE EDITOR

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NOTES

Can trimers influence the free surface density profile of liquid ${}^4\text{He}$ at zero temperature?

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One of the attractions of studying the free surface of liquid ${}^4\text{He}$ in its ground state is that one has a great decrease in the density profile $\rho(z)$ perpendicular to a planar surface in the (x,y) plane in going from bulk quantal liquid to bulk quantal vapor. This allows, at least in principle, a study of the role of trimers in this quantal interface. The possibility of relevance of such trimers in the ground state of bulk liquid ${}^4\text{He}$ was discussed in this Journal¹⁻³ in early work. Independently and very recently, Bulgac⁴ has set out a rather general study of dilute quantum droplets of which his “bosolet” results are qualitatively relevant to describe the low-density vapor in the ground state of the free surface density profile $\rho(z)$ of ${}^4\text{He}$.

Two of us have already focused earlier on the free surface healing length, l say, of ${}^4\text{He}$ at $T=0$, using a simple density functional theory.⁵ This allowed the surface tension σ of liquid ${}^4\text{He}$ at $T=0$ to be written approximately in terms of (i) the gradient $\nabla\rho$ of the particle density $\rho(z)$ introduced above and (ii) the local term in the correlation energy density denoted by $\epsilon_c(\rho(z))$ below. Decomposing the constant pressure p through the liquid–vapor interface into two parts,

$$p = p(\rho(z)) + p_{dg}(z) \quad (1)$$

with $p_{dg}(z)$ being due to the density gradient, in Ref. 5 we wrote the surface tension σ in the equivalent forms

$$\begin{aligned} \sigma &= 2 \int dz p_{dg}(z) \\ &= 2 \int dz [p - \mu\rho(z) + \epsilon_c(\rho(z))], \end{aligned} \quad (2)$$

with μ the (constant) chemical potential of the inhomogeneous fluid. The first equality in Eq. (2) shows that the range of the integration goes only over the healing length of the interface. We followed then the earlier classical fluid treatment of Bhatia and March⁶ to expand the second equality in Eq. (2) around the bulk liquid density, and using the thermodynamic result

$$\kappa^{-1} = \rho^2 \frac{d^2 \epsilon_c(\rho)}{d\rho^2}, \quad (3)$$

one is led to the form for the surface tension in terms of the healing length l as

$$\sigma \approx l\kappa^{-1}, \quad (4)$$

where κ is the compressibility of the bulk liquid ${}^4\text{He}$. The classical analog of Eq. (4) goes back at least to Cahn and Hilliard⁷ and its relevance to experiment was established especially by the study of Egelstaff and Widom.⁸

As pointed out in Ref. 5, one can estimate the length l by inserting experimental values of the surface tension and the compressibility from the bulk ${}^4\text{He}$, and we found $l \approx 0.15 \text{ \AA}$, which is of the same order of classical liquids such as Ar or Kr near freezing.

However, in Ref. 5 we cautioned, by reference to vacancy formation in solid ${}^4\text{He}$,⁹ against pressing too far the analogies between defect (and perhaps also surface) properties of quantal and classical systems. Thus, in classical crystals such as condensed heavier rare gases, e.g., Kr,¹⁰ the vacancy formation energy scales as $E_V \approx B\Omega$ where $B = \kappa^{-1}$ is the isothermal bulk modulus while Ω is the atomic volume. For ${}^4\text{He}$ the product $B\Omega$ is $\approx 70 \text{ K}$ whereas in the cubic phases of ${}^4\text{He}$ E_V was estimated by independent arguments as $\approx 10 \text{ K}$.

We now turn to the recent experimental approaches to the study of dimers and trimers of helium in free space.^{11,12} In Ref. 11 Grisenti *et al.* have conclusively demonstrated, using a diffraction transmission grating technique, the existence of a helium dimer with a “bond length” of $\approx 50 \text{ \AA}$, and as a consequence a very tiny binding energy. The He trimer in free space has also been identified experimentally.¹² We note here that when a boson dimer, such as for ${}^4\text{He}$ atoms, is either weakly bound or just “unbound,” such conditions from ground-state properties of three-boson systems¹³ are favorable for trimer formation.

This situation has been pressed for quantum droplets in the work of Bulgac,⁴ who proposes a transition to a trimer state in a dilute boson droplet. Even if the existence of ⁴He trimers in bulk liquid ⁴He is by no means established as yet, in the low density regime of the profile $\rho(z)$ through the free surface of liquid ⁴He at $T=0$ we must expect on both theoretical¹³ and experimental¹¹ grounds the existence of trimers when the still inhomogeneous density becomes sufficiently small. As a consequence, there should be a substantial density gradient associated with going from the quantal vapor of monomers to the lower density of trimers. This, we suggest, is one reason why the classical liquids analogy (say with Ar or Kr near freezing) may fail quantitatively, as was suspected in Ref. 5.

Of course, experimentally it seems extremely unlikely that one can avoid the obviously difficult experiment of measuring directly the profile $\rho(z)$ by scattering of either electromagnetic or matter waves from inhomogeneous fluid ⁴He. Such experiments have been carried out successfully at the surface of a liquid metal such as Hg by Pershan and co-workers,¹⁴ but now one would have to carry out measurements at the lowest feasible temperatures. One also recognizes that, if the idea of a phase transition to a “pure trimer” state is correct in a dilute boson droplet at $T=0$, at finite though very low T there will be a mixture of n -mers with n from 1 through 3, the relative concentration depending on the (very small) binding energies of the n -mers.

Our final comment takes us back to the dilute quantum droplet discussion of Bulgac.⁴ In his model there exist a large number of the so-called Efimov states¹³ of the three-boson system. However, in contrast, with appropriate interactions in ⁴He quantal vapor at $T=0$, it seems highly probable from existing quantitative studies that only a single Efimov state exists.¹¹

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