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Comments and Addenda

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Extraction of the surface thickness of liquid argon near its triple point from the data of Shih and Uang

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Accurate calculations by Shih and Uang of the surface tension and surface energy of argon at 85 K are used to extract the interfacial thickness. The data indicate that 80% of the transition from liquid to vapor takes place in about 4.5 Å.

I. INTRODUCTION

Shih and Uang[1] have recently calculated the surface tension σ and the surface energy ϵ of liquid Ar at 85 K. They evaluate Kirkwood-Buff expressions for σ and ϵ with a linear, cubic, and Fermi function density profile, using the Barker-Fisher-Watts[2] (BFW) potential, and the Parson-Siska-Lee[3] (MSV III) potential, and approximating the pair-correlation function $g(r,z_1,z_2)$ in the interfacial region by the bulk liquid $g_l(r)$ determined experimentally by Yarnell *et al.*[4] The expressions for σ and ϵ involve two-body interactions only. (In Refs. 2, 3, and 5 of Ref. 1, the three-body contributions are estimated. Assuming a step-function density profile, the three-body terms are found to be about 30% of the two body result for σ and about 10% for ϵ.) The purpose of this note is to use the numerical results of Shih and Uang to estimate the surface thickness of liquid Ar at 85 K.

II. METHODS OF DETERMINING THE SURFACE THICKNESS

In Sec. 8 of Ref. 5 and in Ref. 6, methods are described for calculating the thickness[7] t of a liquid-vapor interface from theoretical curves for σ and ϵ as a function of t. The obvious method is to find where the theoretical $\sigma(t)$ and $\epsilon(t)$ curves intercept the experimental values. This requires accurate calculations of σ and ϵ. We will also use two methods[6] that compare experimental and theoretical values of dimensionless ratios. In the first method, the intercept of the theoretical ϵ/σ curve with the experimental ϵ/σ value gives t. In the second method, the experimental reciprocal length $n_l\bar{u}_l/\epsilon$ is compared with theoretical values of $\epsilon_\infty(t)/t\epsilon(t)$. Here n_l is the number density of the liquid, $\bar{u}_l$ is the average potential energy per atom in the liquid phase, and $\epsilon_\infty(t)$ is the asymptotic form of $\epsilon(t)$ attained when the interface thickness is much larger than the range of the interatomic potential. The ϵ_∞/ϵ method is based on the fact that $\epsilon_\infty(t)$ is proportional to $-n_l\bar{u}_l t$ when $g(r,z_1,z_2)$ is approximated by $g_l(r)$.[8] The physical interpretation of this result is that the (positive) surface energy is due to the loss of about $\frac{1}{2}$ of the potential energy per atom for every atom in the surface layer.[6]

III. RESULTS

In Table I we have listed the results for the 10–90 interface thickness, calculated from the ϵ and σ data of Shih and Uang. For the methods involving $\sigma(t)$ we have used the data for both the MSV III and BFW potentials. For those involving $\epsilon(t)$ we have given the results for the MSV III potential

TABLE I. 10–90 surface thickness t (in Å) of Ar at 85 K, calculated from the data of Shih and Uang.

		linear	cubic	Fermi function
$\epsilon_{expt}=\epsilon(t)$		5.18	5.10	4.63
$\sigma_{expt}=\sigma(t)$	MSVIII	4.73	4.70	4.37
	BFW	3.92	3.85	3.40
$(\epsilon/\sigma)_{expt}=(\epsilon/\sigma)(t)$	MSVIII	5.00	4.93	4.51
	BFW	4.62	4.54	4.14
ϵ_∞/ϵ method		6.08	6.25	5.45
Average		4.92	4.90	4.42

only, since the differences between the surface energies calculated from the two potentials are not large enough to be significant. The asymptotic value $\epsilon_\infty(t)=c_1 t$ was extracted from the Shih-Uang data by plotting $t\epsilon$ vs t^2 (the large-t behavior has been established in Sec. 5 of Ref. 5 to be $\epsilon \to c_1 t + c_2/t$). The experimental data used (for Ar at 85 K) was $n_l = 2.126\times10^{-2}$ Å^{-3} and $\epsilon = 34.9$ ergs/cm^2, $\sigma = 13.12$ ergs/cm^2 (Ref. 9); $\overline{u}_l = -0.981 \times 10^{-13}$ ergs/atom (Ref. 10).

IV. CONCLUSION

In Table I of Ref. 6 we have collected previous theoretical estimates of the surface thickness of liquid argon near its triple point. The values of t range from 3.4 to above 10 Å. The results we extract from the Shih-Uang data range from 3.4 to 6.25 Å. The average is 4.9 Å for the linear and cubic profiles, and 4.4 Å for the Fermi profile. If we restrict consideration to the most realistic profile, the Fermi function, we have the result

$$t = 4.4 \pm 1.0 \text{ Å}.$$

The Shih-Uang data thus indicates that 80% of the transition from liquid to vapor density in argon at 85 K takes place in about 1.3 atomic diameters. This conclusion is the same as that obtained from much cruder calculations in Ref. 6.

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[1] C. C. Shih and Y. H. Uang, Phys. Rev. A 17, 377 (1978). Professor Shih has kindly informed us that the limits of integration in Eq. (18) should be 1 to ∞ and not 0 to 1 (the correct formula was, however, used by them in the calculation of ϵ). With this correction, it can be shown that their Eq. (18) reduces to the much simpler expression given by Eq. (46) in J. Lekner and J. R. Henderson, J. Low Temp. Phys. 31, 763 (1978). See also Eq. (12) of Ref. 6.

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[5] J. Lekner and J. R. Henderson, Mol. Phys. 34, 333 (1977). The functions $E(r)$ and $T(r)$ defined by Eqs. (12) and (13) of Shih and Uang are related to our functions q_i and p_i as follows: $q_1+q_2=-\frac{1}{2}r^2E$, $p_1+p_2=\frac{1}{4}r^4T$.

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[7] In Ref. 6 eight possible definitions of surface thickness are discussed. It is found that a simple and satisfactory measure of the interface thickness is the distance over which $n(z)-n_v$ falls from 90% of n_l-n_v to 10% of n_l-n_v. This is referred to as the 10–90 thickness t. For the linear and cubic profiles used by Shih and Uang, t is, respectively, 0.8 and 0.6084 times the full profile width. For the Fermi-function profile $n(z)=n_v+(n_l-n_v)/(1+e^{z/\delta})$, $t=(2\ln 9)\,\delta \simeq 4.394\delta$.

[8] Shih and Uang use this approximation, and argue that it should be accurate when $n_l \gg n_v$.

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