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[20] This means that, e.g., the 3D, sc, nearest-neighbor Ising model has $T_R \neq 0$ only for the six principal planes. Compare with Ref. 1.

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[26] Gravity gives the vortex excitation a mass inversely proportional to the capillary length. Finite mass destroys RT in the strict sense. For crystals small compared to the capillary length this is irrelevant.

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Theory of the Surface Tension of Simple Liquids: Application to Liquid Metals

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This Letter presents an approximate closed-form solution to the density-functional theory for the surface tension and surface width of simple liquids. The results for both are in excellent agreement with experiments on Ar over wide range of temperature and density. The theory is extended via an ion density-functional formalism to simple metals. Good agreement is obtained for the surface tensions of ten liquid metals and for the surface width of liquid Hg.

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The thermodynamics and structure of liquid-vapor interfaces are subjects of intensive experimental and theoretical interest.[1] Although various theoretical methods have obtained very good agreement with experiment for the surface tension of liquid Ar,[1,2] it is commonly believed that the surface free energies of liquid metals are dominated by electronic effects and that, therefore, theoretical techniques which are successful in treating simple nonmetallic surfaces cannot be used for metals. The work of Evans and Kumaravadivel,[3] which extends the theory of Lang and Kohn[4] to liquid metals, does lead to agreement with the surface tension in several cases but the predicted widths for the transition profile are small compared with those of most other fluids.

In this Letter we present a simple and quite successful theory for the surface tension τ and width l of simple liquids, *both* metallic and nonmetallic. It involves a number of approximations which allow one to solve a density-functional theory in closed form and obtain simple expressions for τ and l. The results for both are in excellent agreement with experiment for liquid Ar over wide range of temperature and reproduce the scaling results of Fisk and Widom.[5] The results for the surface tensions of liquid metals are in good agreement with experiment, for all metals studied. The surface widths emerging from the calculations are of the order of one to two atomic layers in all cases and for Hg, the one metal for which an experimental width is available, are in excellent agreement with the results of Lu and Rice.[6]

The basis of our method is the following expression for the Helmholtz free energy of an inhomogeneous classical fluid[2] of density $n(\vec{r})$:

$$F[n(\vec{r})]=\int d^3r f(n(\vec{r}))+\tfrac{1}{4}k_BT\int d^3r\, d^3r'\, C(\vec{r}-\vec{r}\,';\bar{n})[n(\vec{r})-n(\vec{r}\,')]^2 . \tag{1}$$

Here $f(n(\vec{r}))$ is the free-energy density, T the absolute temperature, and $C(\vec{r},\bar{n})$ the direct correlation function at some intermediate density $\bar{n}$ $\{$for example, $\bar{n}\equiv\frac{1}{2}[n(\vec{r})+n(\vec{r}\,')]\}$. This is the classical analog of a treatment suggested by Hohenberg and Kohn[7] for the inhomogeneous electron gas. To apply (1) to the present case, we have expanded $n(z)$ in a Taylor series so that the last term in (1) can be expressed in terms of the density gradient dn/dz. The surface tension becomes

$$\tau=\int_{-\infty}^{\infty}dz[f(n(z))-\mu n+P]+\int K'(n(z))(dn/dz)^2dz, \tag{2}$$

where $K'(n)=\frac{1}{12}k_BT\int_0^{\infty}d^3r\, r^2C(r;\bar{n})$, P is the pressure, and μ is the chemical potential.

While there exist reasonably successful theories for the "grand potential" $\Omega=f(n)-\mu n+P$ near the equilibrium liquid density, extrapolation to the vapor phase is much more difficult especially for liquid metals, since it would require passing through an intermediate region where there is, presumably, a metal-nonmetal transition. We have, therefore, fitted $\Omega(n)$ to experiment by expanding it in the form $\Omega(n)=a_0-a_2n'^2+a_4n'^4$, where $n'\equiv n-\frac{1}{2}(n_l+n_v)$, n_l and n_v being the equilibrium densities of the liquid and vapor phase. By requiring that $\Omega(n)$ have a minimum at the observed liquid density and reproduce the measured liquid compressibility K_T, we obtain $a_2=K_T^{-1}/4n_l^2$, $a_4=K_T^{-1}/[2n_l^2(n_l-n_v)^2]$ and $a_0=a_2^2/4a_4$. Note that if $a_2\propto(T_c-T)$, where T_c is the liquid-gas critical temperature, this would be a standard Ginzburg-Landau expansion; by fitting a_2 and a_4 in the manner just described, we effectively produce an expansion which is adequate far outside the critical region. If K' is assumed to be a constant (evaluated at the density where the gradient is maximum), then (2) is minimized by a density of the form $n(z)=\frac{1}{2}(n_l+n_v)+\frac{1}{2}(n_l-n_v)\times\tanh(w^{-1}z)$, with

$$w=2\sqrt{2}\,n_l(K_TK')^{1/2} , \tag{3}$$

and the corresponding surface tension

$$\tau=\frac{1}{3\sqrt{2}}\frac{(n_l-n_v)^2}{n_l}\left(\frac{K'}{K_T}\right)^{1/2} . \tag{4}$$

The coefficient K' in (3) and (4) is proportional to the fourth moment of the direct correlation C. We have approximated C as follows: $C(r;n)=C_{hc}(r;n)$ for $r<\sigma_{hs}$ and $-V(r;n)/k_BT$ for $r>\sigma_{hs}$, where $C_{hc}(r;n)$ is the direct correlation function for a fluid of hard spheres of diameter σ_{hs}, as evaluated in the Percus-Yevick approximation[8] and $V(r;n)$ is the pair potential of the liquid. The form assumed for the attractive tail correction is exact in the high-temperature and low-density limit; even at lower temperatures, it is in good accord with the results of machine calculations.[9] The hard-core diameter σ_{hs} was chosen as the smallest interatomic separation at which the pair potential equals $\frac{3}{2}k_BT$; other reasonable prescription led to similar results for τ and w.

Combining Eqs. (3) and (4) gives

$$w=12[n_l^2/(n_l-n_v)^2]\tau K_T , \tag{5}$$

independent of any approximations used for K'. Equation (5) can be viewed as a phenomenological relation from which w can be calculated given the measured values of K_T, n_l, n_v, and τ.

We remark that Eq. (4) has the same form as that of Fisk and Widom,[5] first derived from scaling arguments. By introducing critical exponents with $t=|(T-T_c)/T_c|$ where T_c is the critical temperature, namely $(n_l-n_v)\sim t^{\beta}$, $K_T\sim t^{-\gamma}$, $\tau\sim t^{\mu}$ and $w\sim t^{-\nu}$, we obtain the Widom exponent relations $\mu+\nu=2\beta+\gamma$ and $K'\sim t^{\gamma-2\nu}$ from Eqs. (5) and (3).

We have calculated the gradient coefficient K' for the case of liquid argon by assuming a Lennard-Jones pair potential $\{V(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]\}$ with $\epsilon=119.8\,^{\circ}\mathrm{K}$ and $\sigma=3.405$ Å, using numerical integration. K' is weakly density and temperature dependent and varies by less than a few percent over the temperature and density range considered. At each temperature K' is evaluated at half the liquid density with n_l, n_v, and K_T taken from experiment.[10] The result for surface tension is compared with Monte Carlo results in Fig. 1. The agreement between theory and Monte Carlo[11-13] results is very good but there is a systematic deviation from the surface tension of liquid argon.[14] This is a reflection of the inade-

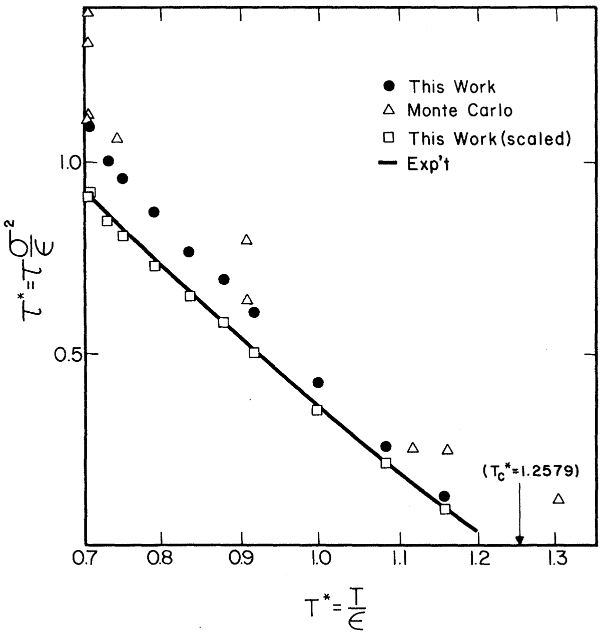

FIG. 1. Surface tension of liquid Ar vs temperature. Triangles: Monte-Carlo results from Refs. 11, 12, 13, and 15. Full circles: present work with Eq. (5) and $\epsilon = 119.8$ K, $\sigma = 3.405$ Å. Squares: present work scaled to experiment at one point to correct for three-body forces. Full curve: experiment (Ref. 14).

quacy[13, 15] of the Lennard-Jones potential in describing the surface properties of argon and is most likely due to three-body forces. We have accounted for these in an approximate way by rescaling K' and hence τ by a constant factor of 0.83 over the temperature and density range considered. The agreement with experiment is then excellent. This scaling factor is in agreement with perturbation calculations[13] of the effects of three-body forces which suggest a correction factor to τ of 0.8.

Recently the 10%-90% width of the surface profile of liquid Ar has been measured by Beaglehole[16] at 90 °K and 120 °K to be 7.9 ± 0.5 Å and 15.2 ± 1 Å. From Eq. (5) we get a 10%-90% width of $2w_{10-90} \sim 2.2 n_l^2 (n_l - n_v)^{-2} \cdot 12 \tau K_T$ which gives 7.45 Å and 11.85 Å at 90 °K and 120 °K, using experimental values of K_T and τ.[10, 14] This is very good agreement especially considering the uncertainties in the interpretation of the experimental data.[16]

To apply our theory to liquid metals near melting, we invoke the adiabatic approximation,[17] which allows us to reduce the two-component electron-ion plasma, via many-body perturbation theory, to a system of classical ions interacting with an effective density-dependent ion-ion potential. We have computed $V(r;n)$ according to the standard prescription,[17] using an empty-core pseudopotential[18] and including exchange-correlation corrections via the Hubbard form[19] of the irreducible polarization kernel. Unlike Ar, the effective pair potentials of liquid metals are strongly density dependent.[20] We have, therefore, evaluated the gradient coefficient K' at $n = \frac{1}{2}(n_l + n_v) \sim \frac{1}{2} n_l$, at which the gradient of the profile is maximum, so that the gradient contribution to the free energy should be dominated by this density.

The results for τ are listed in Table I. In all cases but that of Li theory and experiment agree to within 30%, even though the experimental τ's themselves vary by more than an order of magnitude. We emphasize that there are *no* adjustable parameters in the theory. The pseudopotential parameters are all taken from the literature[20] and are based on various other experiments, and n_l and K_T are experimental[21] numbers. The Table suggests that we have systematically underestimated K' somewhat. Most likely either (i) the attractive part of the pair potential is too weak, on account of insufficiently accurate exchange-correlation corrections, or (ii) our method of computing the tail correction to $C(r;n)$ gives too small a positive contribution to K' (an explicit solution of the Percus-Yevick equation[2] probably would lead to a stronger attractive tail and hence a larger K'). Furthermore, the Li result would no doubt be improved by taking into account nonlocal or three-body effects; we have made no attempts at any such adjustment. We have found it crucial, however, to calculate $C(r, n)$ at $n = \frac{1}{2} n_l$. If it is evaluated at the full liquid density, τ is usually too low; in contrast to Ar, the altered (density-dependent) screening and correspondingly deeper potential well for pseudoatoms near the surface is evidently of prime importance in determining τ for liquid metals.

The width of the surface profile of Hg has been measured recently by Lu and Rice[6] at room temperature ($T = 298$ °K) to be $2w = 5.6 \pm 0.5$ Å, much wider than the prediction of Allen and Rice[22] of 2.5 Å using a theory based on the jellium model. Our Eq. (5) gives $2w = 4.54$ Å at 238 °K with use of the values $\tau = 498$ dyn/cm, $K_T = 3.8 \times 10^{-12}$ cm^2/dyn and $n_l = 0.041$ Å^{-3}.[21] If τ, K_T, n_l, and n_v were available experimentally at 298 °K, where w is expected to be larger, even better agreement is likely.

The success of the present theory for simple liquid metals suggests that many-body perturbation theory is adequately convergent for liquid-

TABLE I. Comparison of the theoretical τ's with experiments. There are no adjustable parameters in the theory.

	Temperature (K)	K_T[a] (10^{-12} cm^2/dyn)	R_{ec}[b] (a_0)	K'/a_0^5 (10^8 K)	τ_{expt}[c] [τ_{theor}][c] (a.u.)	w[d] (a_0)
Li^+	452	9.3	1.40	0.0867	398 [242]	5.11
Na^+	371	18.6	1.69	0.228	191 [151.6]	6.39
Na^+	452	21.0	1.69	0.242	··· [143.8][e]	
K^+	337	38.2	2.226	0.579	115 [88]	7.63
Rb^+	312	49.3	2.4	0.792	85 [74]	8.28
Cs^+	302	68.8	2.62	1.02	70 [57]	8.91
Mg^{+2}	924	4.0	1.38	0.154	559 [436]	3.96
Zn^{+2}	693	2.5	1.27	0.0805	782 [612]	3.47
Cd^{+2}	594	3.2	1.405	0.139	570 [504]	3.66
Al^{+3}	914	2.42	1.117	0.12	914 [666]	3.66
Pb^{+4}	600	3.49	1.48	0.362	468 [563]	4.46

[a] From Ref. 21.

[b] Empty-core radius in atomic units, from Ref. 20.

[c] From Eq. (4).

[d] With use of Eq. (3).

[e] With $(d\tau/dT)_{\mathrm{expt}} = -0.1$ dyn/cm·K and $(d\tau/dT)_{\mathrm{theor}} = -0.09$ dyn/cm·K.

metal surfaces. Since our calculated (and the experimental) surface widths are reasonably large (1–2 atomic layers), the liquid surface is apparently a much weaker perturbation on the electron gas than is the much sharper solid surface. Indeed, Allen and Rice[22] find that the electron gas will leak out of this "smeared jellium" to a much lesser extent than in the solid, thus justifying the use of perturbation theory. In reality, three-body forces undoubtedly play a role in liquid metals near the surface, just as in liquid Ar. But since reasonable results are obtained at second order, the present theory may be useful in estimating the widths of metallic surfaces, as well as for other problems, such as the interfacial tensions of phase-separated liquid alloys.

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