Many-body effects on the surface tension of inert fluid-substrate interfaces

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A simple, often employed expression for the interfacial tension of inert fluid-substrate interfaces is improved using the Dzyaloshinskii-Lifshitz-Pitaevskii formalism. The expression is analyzed in terms of many-body effects, and better estimates for both surface tensions and wetting temperatures emerge. Numerical results are given for a variety of substrate-adsorbate systems.

I. INTRODUCTION

There has been striking recent progress in our understanding of wetting phenomena, initiated by the theoretical prediction[1,2] and nearly immediate experimental verification[3-7] of nonwetting of Cs by ^{4}He, and by subsequent discoveries of wetting transitions in this system as well as that of H$_2$ on Rb.[8] The theoretical ideas have more recently been applied to predict wetting transitions in helium isotopic mixtures[9] and in rare gas adsorption[10] on a variety of substrates. Their success can be attributed, as shown here, to a simple and physically reasonable way of approximating the ^{4}He-Cs surface tension, producing results that are in good agreement with the values calculated from more involved density-functional theories.[1] We begin by stating the assumptions that go into the theory of Refs. 1, 2, and 10. Subsequently, we derive improvements to the theory through a better treatment of dispersion forces equivalent to the inclusion of many-body effects.

In Refs. 1, 2, and 10, the inert-fluid (adsorbate)-substrate surface tension is assumed to be a sum of the adsorbate-vacuum surface tension, the substrate-vacuum surface tension, and a correction term. It is assumed that the presence of the adsorbate has no effect on the atomic arrangement of the substrate, assumed completely inert. In this case, the substrate-vacuum surface tension is well defined and is merely a constant in the substrate-adsorbate free energy. The correction term is calculated from the potential energy of individual atoms in the presence of the substrate. The potential produced by the substrate consists of an attractive van der Waals piece and a repulsive piece, which prevents the adsorbate atoms from getting close to the substrate. The potential energy of an atom at a distance z above the substrate is given by

$$V(z) = -\frac{C_3}{z^3} + \frac{C_9}{z^9}, \qquad (1)$$

where C_3 and C_9 are tabulated for various substrates and inert gas atoms in Ref. 11. C_3 can be calculated in terms of the substrate dielectric function $\epsilon_s(i\zeta)$ and the polarizability of the atom $\alpha(i\zeta)$, both evaluated at the imaginary frequency $i\zeta$. It is given by

$$C_3 = \frac{\hbar\omega_0(T)}{8\pi^2\rho(T)}, \qquad (2)$$

where $\rho(T)$ is the number density of the adsorbate atoms and the frequency ω_0 is given by

$$\omega_0(T) = \frac{4\pi\rho(T)}{2} \int_0^\infty \frac{\epsilon_s(i\zeta) - 1}{\epsilon_s(i\zeta) + 1} \alpha(i\zeta) d\zeta. \qquad (3)$$

The potential energy of substrate-adsorbate interaction, assuming additivity of atom-substrate interaction, and using a step function density profile for the adsorbate $\rho_a(z) = \rho(T)\theta(z - d_0)$, where z is the distance from the substrate, is seen to be[12]

$$\int_{d_0}^\infty \rho(T)V(z)dz = -\rho(T)\left(\frac{8C_3^4}{243C_9}\right)^{1/3}. \qquad (4)$$

The distance d_0 in the step function is the minimum of the potential that appears in Eq. (1). The final expression for the substrate-adsorbate surface tension σ_{sa} is then

$$\sigma_{sa} = \sigma_{svac} + \sigma_{avac} - \rho(T)\left(\frac{8C_3^4}{243C_9}\right)^{1/3}, \qquad (5)$$

in which σ_{svac} and σ_{avac} are the substrate-vacuum and adsorbate-vacuum surface tensions, respectively.

The original theory given in Eq. (5) is crude, but strikingly accurate in its prediction of the wetting temperatures of light adsorbates. This is seen in its comparison in Ref. 1 with the results of a detailed density-functional theory calculation and in its accurate prediction of the wetting temperature of H$_2$ on Rb.[8] The present work provides a correction that is significant for denser rare gases. This theory is more sophisticated than the original one in that fluid-fluid interactions are better accounted for.

We point out that though the earlier work[1] does not explicitly note that Eq. (5) approximates the adsorbate-substrate surface tension, we see that this indeed is the case because Eq. (5), when used in the general wetting condition

$$\sigma_{sv} = \sigma_{sa} + \sigma_{av}, \qquad (6)$$

where σ_{av} and σ_{sv} are adsorbate-vapor and substrate-

<u>52</u>   11 471

vapor surface tensions, respectively, gives

$$2\sigma_{\text{av}} = \rho(T) \left(\frac{8C_3^4}{243C_9} \right)^{1/3}, \tag{7}$$

which is the specific wetting criterion obtained in that work. In obtaining Eq. (7), we have assumed that vapor is very dilute, so that the number density in vapor phase is approximately zero and have set $\sigma_{\text{avac}} \approx \sigma_{\text{av}}$. These assumptions were also made in Refs. 1, 2, and 10.

While the above method works well for a dilute adsorbate, it is clear that additivity of atom-substrate energy will not be a good approximation at higher densities. In Sec. II of this paper, we develop an improved method to calculate the dispersive (van der Waals) contribution to surface tension, using the Dzyaloshinskii-Lifshitz-Pitaevskii[13] (DLP) formalism, which does not assume additivity of atom-substrate interactions. The following section deals with the comparison of the results from the earlier and current approaches, with emphasis on elucidating the importance of many-body effects in the dispersive part of the surface energy and demonstrating that they lead to increases in wetting temperatures. Finally, we conclude by explicit calculation of these increases for Kr and Xe on LiF.

II. IMPROVED CALCULATION OF THE SURFACE TENSION

As before, we assume that the adsorbate-substrate surface tension is the sum of adsorbate-vacuum surface tension, the substrate-vacuum surface tension, and a correction term that has been divided into dispersive and nondispersive contributions denoted by σ^{disp} and $\sigma^{\text{non-disp}}$, respectively. We now discuss the calculation of dispersive part of surface energy assuming the density profile $\rho_a(z) = \rho(T)\theta(z - d_0)$ as before, but where the distance d_0 is yet to be determined. Let us assume that the substrate and adsorbate are characterized by dielectric functions $\epsilon_s(\omega)$ and $\epsilon_a(\omega)$, respectively. The dispersive part of the surface energy is the free energy $G(l = d_0)$ of the normal photon modes of the configuration shown in Fig. 1, where the adsorbate and substrate surfaces are separated by a vacuum of thickness l, minus the free energy $G(l = \infty)$ of the normal modes at infinite separation. This is given by[13]

$$\sigma^{\text{disp}} = \frac{k_B T}{8\pi} \sum_{n=0}^{\infty}{}' \left\{ \frac{2\zeta_n}{c} \right\}^2$$
$$\times \int_1^{\infty} p\,dp\,(\ln\{[1 - \Delta \exp(-2p\zeta_n d_0/c)]$$
$$\times [1 - \bar{\Delta} \exp(-2p\zeta_n d_0/c)]\}), \tag{8}$$

in which the prime means to use $1/2$ the value of the summand for the case $n = 0$, and where

$$\zeta_n = n(2\pi k_B T/\hbar), \tag{9}$$
$$\Delta = \frac{(s_1 - p)(s_2 - p)}{(s_1 + p)(s_2 + p)}, \quad \bar{\Delta} = \frac{(s_1 - p\epsilon_s)(s_2 - p\epsilon_a)}{(s_1 + p\epsilon_s)(s_2 + p\epsilon_a)},$$
$$s_1 = \sqrt{\epsilon_s - 1 + p^2}, \quad s_2 = \sqrt{\epsilon_a - 1 + p^2}.$$
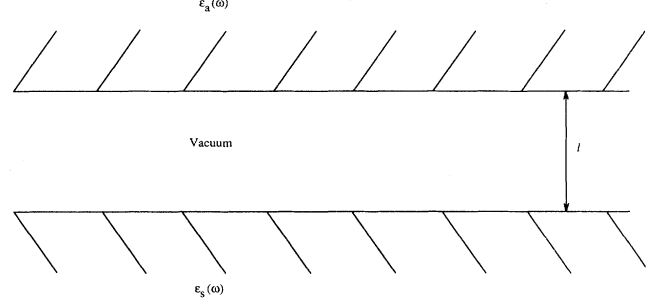

FIG. 1. Sketch of the adsorbate characterized by dielectric function $\epsilon_a(\omega)$ separated a distance l from the substrate, which is characterized by dielectric function $\epsilon_s(\omega)$. The dispersive part of the surface tension is the free energy of photon normal modes, when $l = d_0$ minus the free energy when $l = \infty$.

In the limit that $d_0 \ll \lambda_0$, where λ_0 is a length scale typically of order 100 Å,[14] determined from the absorption spectra of the adsorbate and substrate, the above expression simplifies to[13,14]

$$\sigma^{\text{disp}} = -\frac{\hbar \omega_1(T)}{16\pi^2 d_0^2} \equiv -\frac{C_3' \rho(T)}{2d_0^2}, \tag{10}$$

where

$$\omega_1(T) = \int_0^{\infty} \frac{[\epsilon_a(i\zeta) - 1][\epsilon_s(i\zeta) - 1]}{[\epsilon_a(i\zeta) + 1][\epsilon_s(i\zeta) + 1]}d\zeta. \tag{11}$$

Since d_0 is typically less than 10 Å, the approximation holds. Equation (10) defines C_3' in terms of ω_1.

The nondispersive part of the surface energy comes from the repulsive interaction at distances of the order of a few atomic layers closer to the substrate adsorbate interface. Since this interaction is very short ranged, we assume it to be the integrated atom-substrate interaction to get

$$\sigma^{\text{non-disp}} = \frac{\rho(T)C_9}{8d_0^8}. \tag{12}$$

We choose d_0 so that, in the dilute limit, we get the result obtained earlier. This value of d_0, given by

$$d_0 = \left(\frac{243C_9}{16C_3'} \right)^{1/6}, \tag{13}$$

leads to the expression

$$\sigma_{\text{sa}} = \sigma_{\text{svac}} + \sigma_{\text{avac}} - \rho(T) \left(\frac{8C_3'^4}{243C_9} \right)^{1/3}, \tag{14}$$

for the adsorbate-substrate surface tension, and a new wetting criterion,

$$2\sigma_{\text{av}} = \rho(T) \left(\frac{8C_3'^4}{243C_9} \right)^{1/3}, \tag{15}$$

emerges, replacing Eq. (7).

The dispersive part of the surface tension is always less than zero, because ω_1 is always greater than 0, as $\epsilon(i\zeta) > 1$ for all $\zeta > 0$ for all media. Consequently, the surface tension is determined by the competition between the repulsive and attractive parts, as was the case in the earlier approach.

III. MANY-BODY EFFECTS ON THE SURFACE TENSION

The simple model for surface tension given in Eq. (5) ignores many-body effects as it is obtained by integration of atom-substrate interactions. However, the current approach, leading to Eq. (14), contains many-body effects that can be examined in interesting detail. These many-body effects originate primarily from the dispersive part of surface tension, which is due to long-ranged interactions, in contrast to the nondispersive part, which is due to interactions essentially confined to within a few atomic spacings of the interface.

Comparing ω_1 and ω_0, we see that there are two differences: (a) the factor $\epsilon_a - 1$ that appears in the numerator of the integrand for ω_1 has been replaced by $4\pi\rho\alpha$ in ω_0 and (b) the factor $\epsilon_a + 1$ that appears in the denominator of the integrand for ω_1 has been replaced by 2 in ω_0.

Approximation (a) ignores the polarization of the adsorbate medium, which can be dealt with by using the Claussius-Mossoti relation to get $\epsilon_a - 1$ in terms of the polarizability of a single atom. Approximation (b) holds if $\epsilon_a - 1 \ll 1$, for all $\zeta > 0$. We now show that these approximations amount to ignoring substrate-mediated interactions between adatoms. According to the Claussius-Mossoti relation, the atomic polarizability is related to the dielectric function by

$$\frac{\epsilon_a(i\zeta) - 1}{\epsilon_a(i\zeta) + 2} = \frac{4\pi\rho(T)}{3}\alpha(i\zeta). \qquad (16)$$

Using the above expression, we write

$$\frac{\epsilon_a(i\zeta) - 1}{\epsilon_a(i\zeta) + 1} = \frac{\kappa(i\zeta)}{2[1 + \kappa(i\zeta)/6]}, \qquad (17)$$

where $\kappa(i\zeta)$ is an expansion parameter defined as $\kappa(i\zeta) \equiv 4\pi\rho(T)\alpha(i\zeta)$. This enables us to develop a series for $(\epsilon_a - 1)/(\epsilon_a + 1)$, in terms of $\kappa(i\zeta)$, which when used in Eq. (11), we get

$$\omega_1 = \omega_0 - \frac{1}{12}\int_0^\infty \frac{\epsilon_s(i\zeta) - 1}{\epsilon_s(i\zeta) + 1}\kappa^2(i\zeta)d\zeta$$

$$+ O\left(\int_0^\infty \frac{\epsilon_s(i\zeta) - 1}{\epsilon_s(i\zeta) + 1}\kappa^3(i\zeta)d\zeta\right) + \cdots. \qquad (18)$$

ω_0 turns out to be the leading term in the expansion parameter. The term that is second order in the expansion parameter can be written as

$$\frac{1}{12}\int_0^\infty \frac{\epsilon_s(i\zeta) - 1}{\epsilon_s(i\zeta) + 1}\kappa^2(i\zeta)d\zeta = \frac{4\pi^3\rho^2(T)}{9}C_{s1}, \qquad (19)$$

where C_{s1} is a coefficient that appears in the McLachlan theory[15] of substrate-mediated interactions between adatoms. The higher order terms likewise arise from three or more body interactions involving adatoms and the substrate. The expansion is similar to one done by Cheng and Cole[16] to make a connection between the DLP and Frenkel-Halsey-Hill theories for multilayer film adsorption.

It can further be seen from Eq. (17) that $(\epsilon_a - 1)/(\epsilon_a + 1)$ is less than $\kappa(i\zeta)/2$, so that the integrand in Eq. (3) is always greater than the integrand in Eq. (11), which implies that ω_1 is always smaller than ω_0. In order to see the importance of the many-body effects, we calculate the ratio ω_0/ω_1. Table I shows this ratio for inert fluids adsorbed on commonly used substrates at their triple points. We remark that at temperatures above the triple point, the density decreases and the many-body effects are of lesser importance.

In performing the calculations for Table I, we use Eq. (16) for the adsorbate dielectric function, where the polarizability has the simple one-resonance form,

$$\alpha(i\zeta) = \frac{\alpha_0}{1 + \zeta^2/\omega_n^2}. \qquad (20)$$

For the substrates, we similarly use the standard one-resonance form,

$$\epsilon_s(i\zeta) = 1 + \frac{\omega_\rho^2}{\zeta^2 + \omega_n^2}, \qquad (21)$$

in which $\omega_n = 0$ for metals. All the data for ω_n and ω_p were taken from Sabisky and Anderson.[18] The quantity α_0 was taken from Cheng and Cole.[16] From Table I, we see that many-body effects are less than 1% for ^{4}He, 2%–3% for Ne, 5%–6% for Ar, 6%–9% for Kr, and 8%–10% for Xe.

For completeness, we now estimate the magnitude of the substrate-mediated interaction between adsorbate atoms due to nondispersive forces. As a concrete example, we consider Xe adsorbed on Au. The adatoms in the first layer are polarized, due to charge overlap with the substrate, and the resulting dipole moment is given by $\mu = -\delta\phi/(4\pi N)$, where $\delta\phi$, the change in the work function of Au, was measured as[17] 0.52 V for Xe with coverage $N = 0.059$ Å^{-2} (ML). The magnitude of the dipole-dipole interaction per atom between adsorbate atoms induced by the substrate is given by $1/2\int_d^\infty \frac{\mu^2}{r^3}N2\pi r dr$, where $d = N^{-1/2}$ is 4.12 Å. The magnitude of this substrate induced interaction is calculated to be 1.4 meV,

TABLE I. The ratio ω_0/ω_1 for inert fluids at their triple points on some commonly used substrates.

Substrate/Fluid	^{4}He	Ne	Ar	Kr	Xe
Na	1.0091	1.030	1.067	1.085	1.103
MgO	1.0077	1.025	1.053	1.067	1.083
Si	1.0081	1.026	1.056	1.071	1.088
LiF	1.0076	1.024	1.052	1.066	1.081
Al$_2$O$_3$	1.0078	1.025	1.054	1.068	1.082

whereas the magnitude of the repulsive interaction of Xe, with Au given by C_9/d_0^9, is calculated to be 103 meV. The many-body effects, due to nondispersive forces, therefore, are estimated to give rise to a 1% correction to the surface tension, which is considerably smaller than the 10% correction arising from the dispersive forces for Xe.

Finally, for classical inert fluids (Ar, Kr, and Xe), if T'_w and T_w are, respectively, the wetting temperatures with and without including many-body effects, use of the old and new wetting criteria, leads to

$$\frac{\sigma_{\rm av}(T_w)\rho(T'_w)}{\sigma_{\rm av}(T'_w)\rho(T_w)} = \left(\frac{C_3(T_w)}{C'_3(T'_w)}\right)^{4/3}. \tag{22}$$

The surface tension and the density appearing in Eq. (22) can be written in the form[19]

$$\sigma_{\rm av}(T_w)(\sigma_{\rm av}(T'_w)) = \sigma^0 t_w^{2\nu}(t'^{2|\nu}_w), \tag{23}$$
$$\rho(T_w)(\rho(T'_w)) = \rho^0 t_w^{\beta}(t'^\beta_w),$$

where $t_w(t'_w) = [T_c - T_w(T'_w)]/T_c$, T_c is the critical temperature of the inert fluid, $2\nu \approx 1.14$ (Ref. 20) is the critical exponent for the surface tension, and $\beta \approx 0.35$ (Ref. 20) is the critical exponent for the density. σ^0 and ρ^0 are constants that are tabulated for various classical fluids in Ref. 17. It has been shown[19] that the density and the surface tension are well described by the expressions given in Eq. (23), over the temperature range extending from T_c to the triple point. Using Eq. (23) in Eq. (22) we obtain

$$\frac{t_w}{t'_w} = \left(\frac{\omega_0(T_w)}{\omega_1(T'_w)}\right)^{4/3(2\nu+\beta/3)}, \tag{24}$$

from which one can calculate the wetting temperature, including many-body effects. Since ω_0 is always greater than ω_1, t_w will be greater than t'_w, which implies that wetting temperatures are increased when many-body effects are included compared to the wetting temperatures obtained earlier.[10]

IV. SUMMARY AND DISCUSSION

By evaluating the magnitude of many-body effects in surface tension, we have shown that they are small for the lighter inert fluids, but can be more important in the heavier ones, with up to a 10% change in ω_0, and hence C_3, found for Xe. For substrates for which the wetting temperatures are close to triple point, the many-body effects give rise to a substantial increase in wetting temperatures. For example, using Eq. (24), we find that the wetting temperature of Xe on LiF is increased by 7 K, compared to its value of 170 K predicted by Cheng et al.,[10] while the wetting temperature of Kr is increased by 4.5 K for the same substrate compared to the earlier prediction[10] of 120 K.

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