

UC Irvine

UC Irvine Previously Published Works

Title

Phonon contribution to wetting phenomena: macroscopic theory

Permalink

<https://escholarship.org/uc/item/9ns9w8c8>

Journal

Physics Letters A, 234(3)

ISSN

0375-9601

Authors

Hawkins, DL
Maradudin, AA
Shchegrov, AV

Publication Date

1997-09-01

DOI

10.1016/s0375-9601(97)00610-5

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed



ELSEVIER

22 September 1997

PHYSICS LETTERS A

Physics Letters A 234 (1997) 225–228

Phonon contribution to wetting phenomena: macroscopic theory

D.L. Hawkins, A.A. Maradudin, A.V. Shchegrov

Department of Physics and Astronomy and Institute for Surface and Interface Science, University of California, Irvine, CA 92697, USA

Received 7 July 1997; accepted for publication 21 July 1997

Communicated by L.J. Sham

Abstract

We present a macroscopic treatment that clarifies the role of phonons in the wetting of a solid by an ideal liquid, such as liquid ^4He . We show that in the equation for the wetting temperature the phonon contribution cancels exactly. Therefore, a pure phonon mechanism always results in wetting, and other mechanisms determine whether wetting or non-wetting occurs. The importance of ripplon excitations for the wetting phenomenon is discussed. © 1997 Published by Elsevier Science B.V.

PACS: 68.45.Gd; 68.10.Cr; 67.40.Kh; 65.50.+m

Keywords: Surfaces and interfaces; Wetting; Phonons; Ripplons

In recent years, there has been a great deal of theoretical and experimental attention paid to the wetting of alkali metals (Cs and Rb) by liquid helium [1]. Since 1991 liquid helium has no longer been considered a universal wetting agent. In the case of liquid ^4He on Cs, wetting does not occur as long as $T < T_w$, where the measured value for the wetting temperature is $T_w \simeq 2$ K [2,3]. As mentioned in Ref. [1], at the present time this value “is far from being clearly understood”. In this work we approach the wetting phenomenon within the framework of continuum elasticity theory, and analyze the role of long wavelength vibrational excitations in this phenomenon.

To determine when wetting occurs, one has to examine the energy required for a drop of liquid to spread out over a solid surface. As the drop spreads, the areas of the solid–liquid and liquid–vapor interfaces increase, and the area of the solid–vapor interface decreases, resulting in a net change of energy per unit

area of

$$\Delta(T) = \sigma_{sl}(T) + \sigma_{lv}(T) - \sigma_{sv}(T), \quad (1)$$

where $\sigma_{sl}(T)$, $\sigma_{lv}(T)$, and $\sigma_{sv}(T)$ are the solid–liquid, liquid–vapor, and solid–vapor interfacial tensions, respectively. For $T > T_w$ this energy change is negative ($\Delta(T) < 0$), it is energetically favorable for the drop to spread out, and wetting occurs. For $T < T_w$ this energy change is positive ($\Delta(T) > 0$), the drop contracts, and does not wet the surface. The vanishing of $\Delta(T)$ determines the wetting temperature T_w ,

$$\Delta(T_w) = 0. \quad (2)$$

A comprehensive theoretical calculation of $\sigma_{sl}(T)$, $\sigma_{lv}(T)$, and $\sigma_{sv}(T)$ is a formidable problem. Therefore, one of the most difficult questions in the calculation of T_w is what physical processes give the dominant contributions to $\sigma_{sl}(T)$, $\sigma_{lv}(T)$, and $\sigma_{sv}(T)$. Available experimental measurements of $\sigma_{lv}(T)$ [4] and

$\sigma_{sv}(T) - \sigma_{sl}(T)$ [5] for ^4He on Cs should help theory to answer this question. In the current theoretical literature on the subject most of the effort is devoted to studying the spectrum of collective excitations associated with all three interfaces in order to calculate their contribution to $\sigma_{sl}(T)$, $\sigma_{lv}(T)$, and $\sigma_{sv}(T)$. Several microscopic approaches to determining these spectra have been developed, especially in dealing with excitations in liquid ^4He in contact with Vs and vapor. Nevertheless, satisfactory agreement with experimental data has not been achieved until now. We refer the reader to the work by Treiner [1] for an overview of the current situation in this field.

It is suggested by experimental data [4,5] that the low-temperature behavior of $\sigma_{sl}(T)$, $\sigma_{lv}(T)$, and $\sigma_{sv}(T)$ is governed by the low energy vibrational excitations associated with the corresponding interface: (i) phonons: excitations, for which the relation between their frequency ω and wavenumber k is $\omega = ck$, and (ii) ripplons: excitations, whose dispersion relation is $\omega = \beta k^{3/2}$. Phonons contribute to all three interfacial energies and their leading temperature-dependent contribution is proportional to T^3 . Ripplons were believed to exist only on the liquid-vapor interface and to give a contribution to $\sigma_{lv}(T)$, whose leading temperature-dependent term is proportional to $T^{7/3}$. However, recent experiments by Klier *et al.* [5] found a $T^{7/3}$ contribution to $\sigma_{sv}(T) - \sigma_{sl}(T)$, suggesting existence of ripplon-like excitations at the ^4He -Cs interface as well.

In view of the primary importance of low frequency, long wavelength excitations in wetting phenomena, we will try to describe these phenomena within the framework of continuum elasticity theory. Application of macroscopic theory is quite justified for low temperatures – for example, the classic $T^{7/3}$ contribution to $\sigma_{lv}(T)$ due to ripplons derived by Atkins [6], is entirely explained by the macroscopic theory. Liquid superfluid helium is excellent for modeling by an ideal, inviscid liquid, and its bulk properties will be characterized by its mass density ρ_0 and the speed of longitudinal sound c_0 . The solid (Cs) will be modeled by an isotropic elastic medium with the mass density ρ and the speeds of longitudinal and transverse sound c_l and c_t , respectively. The solid-vapor and liquid-vapor interfaces will be considered as stress-free surfaces. In this work we will concentrate on the phonon contribution to $\Delta(T)$ in Eq. (1). An attempt to include the

temperature-independent contribution to $\sigma_{sv}(T)$ from zero-point surface phonons was made by Cole *et al.* [7]. However, the contribution to the interface free energy due to the distortion of the spectrum of bulk excitations by the presence of the interface is of the same order as the contribution due to surface phonons, and one should not be separated from the other [8]. A consistent calculation of the phonon contributions $\sigma_{sl}^{\text{ph}}(T)$, $\sigma_{lv}^{\text{ph}}(T)$, and $\sigma_{sv}^{\text{ph}}(T)$ to the interfacial tensions $\sigma_{sl}(T)$, $\sigma_{lv}(T)$, and $\sigma_{sv}(T)$, takes into account the contributions from both interface phonons and bulk phonons. The calculation of $\sigma_{sv}^{\text{ph}}(T)$ was essentially done by Shchegrov [8], whose result for the stress-free surface of an isotropic solid is

$$\sigma_{sv}^{\text{ph}}(T) = -\frac{\hbar\omega_s^3}{96\pi c_s^2} + \left(\frac{k_B T}{\hbar}\right)^3 \frac{\hbar}{8\pi c_s^2} \zeta(3). \quad (3)$$

Here \hbar is Planck's constant, k_B is Boltzmann's constant, $\omega_s = (18\pi^2 n_s)^{1/3} [(2/c_t^2) + (1/c_l^2)]^{-1/3}$, where n_s is the number of atoms per unit volume of the solid, $c_s^2 = c_l^2 c_t^2 (c_l^2 - c_t^2) / (3c_l^4 - 3c_t^2 c_l^2 + 2c_t^4)$, and $\zeta(z)$ is the Riemann zeta function. The first, temperature-independent, term in Eq. (3) is due to the zero-point phonons. It is important to point out here that the absence of the speed c_R of a Rayleigh surface wave in Eq. (3) does not mean that its contribution is not taken into account.

The low-temperature behavior of $\sigma_{sl}^{\text{ph}}(T)$ was calculated by the present authors [9]. Surprisingly, it was found to contain additive contributions from the solid and the liquid, with its explicit form given by

$$\sigma_{sl}^{\text{ph}}(T) = \sigma_{sv}^{\text{ph}}(T) - \frac{\hbar\omega_0^3}{96\pi c_0^2} + \left(\frac{k_B T}{\hbar}\right)^3 \frac{\hbar}{8\pi c_0^2} \zeta(3), \quad (4)$$

where $\sigma_{sv}^{\text{ph}}(T)$ is defined by Eq. (3), and $\omega_0 = (18\pi^2 n_0)^{1/3} c_0$, where n_0 is the number of atoms per unit volume of the liquid. The contribution from the liquid to $\sigma_{sl}^{\text{ph}}(T)$ is given by the last two terms in Eq. (4) and is equal to the interface free energy per unit area for an ideal liquid bounded by a hard wall which, in turn, is equal to the negative of the "phonon" interface tension $\sigma_{lv}^{\text{ph}}(T)$ of the stress-free liquid-vapor interface [9],

$$\sigma_{lv}^{\text{ph}}(T) = \frac{\hbar\omega_0^3}{96\pi c_0^2} - \left(\frac{k_B T}{\hbar}\right)^3 \frac{\hbar}{8\pi c_0^2} \zeta(3). \quad (5)$$

The additivity of the contributions from the solid and the liquid in Eq. (4) is ascribed to the fact that the solid supports both longitudinal and transverse vibrations, whereas the liquid supports only longitudinal vibrations [9]. This decoupling does not occur in the case of two solids in contact [8]. The temperature dependences of $\sigma_{sv}^{\text{ph}}(T)$ and $\sigma_{sl}^{\text{ph}}(T)$ due to the phonons, and explicitly presented in Eqs. (3) and (4), indicate that the widely used assumption that σ_{sv} and σ_{sl} are fairly insensitive to temperature is not valid. The validity of this assumption was also cast into doubt by recent experimental results [5].

Combining Eqs. (3), (4), and (5) in Eq. (1) we obtain a remarkable property of the phonons – their contribution $\Delta^{\text{ph}}(T)$ to the energy change $\Delta(T)$ cancels exactly,

$$\Delta^{\text{ph}}(T) \equiv 0, \quad (6)$$

if the solid–vapor and liquid–vapor interfaces are stress-free. Moreover, careful analysis of the results of Refs. [8,9] leads to the conclusion that Eq. (6) holds not only for the low-temperature phonon contributions given in Eqs. (3) and (4), but for any T .

Thus, in the model system of a drop of an ideal liquid in contact with vapor across a stress-free interface, lying on a solid whose interface with vapor is stress-free, wetting always occurs, because the only contribution to the thermodynamic functions of this system is due to the phonons. But since $\Delta^{\text{ph}}(T) \equiv 0$, this wetting mechanism is marginal. This means that in a real system the phonon excitations do not determine whether wetting ($\Delta(T) < 0$) or non-wetting ($\Delta(T) > 0$) occurs, but other excitations do. Among the most important of these are surface capillary waves (ripples) at the liquid–vapor interface. These excitations appear after we take into account the surface tension boundary condition on the liquid–vapor interface for the scalar velocity potential in the liquid instead of the free surface boundary condition.

Djafari-Rouhani and Dobrzynski [10] in their calculations of the surface specific heat of a liquid found the term which adds to the contribution due to the stress-free surface after the surface tension boundary condition was taken into account. Their result for the surface specific heat immediately yields the temperature-dependent term $\delta\sigma_{lv}(T)$, which must be added to $\sigma_{lv}^{\text{ph}}(T)$,

$$\begin{aligned} \delta\sigma_{lv}(T) = & \delta\sigma_{lv}(0) - \frac{4\hbar}{\pi} \left(\frac{\rho_0}{\sigma_{lv}(0)} \right)^{2/3} \left(\frac{k_B T}{\hbar} \right)^{7/3} \\ & \times \Gamma(7/3)\zeta(7/3) - \left(\frac{k_B T}{\hbar} \right)^3 \frac{\hbar}{6\pi c_0^2} \zeta(3), \end{aligned} \quad (7)$$

but not the zero-point contribution $\delta\sigma_{lv}(0)$. We note that the $T^{7/3}$ term contains the surface tension of the liquid at absolute zero $\sigma_{lv}(0)$. This quantity is an important characteristic of the liquid, and is known for liquid ^4He [4]. The function $\Gamma(z)$ in Eq. (7) is the gamma-function. The temperature-dependent terms in Eq. (7) can be interpreted as follows. The $T^{7/3}$ term is due to ripplon excitations, while the T^2 term appears due to the distortion of the phonon spectrum of the system with a stress-free liquid surface by the surface tension boundary condition.

In understanding the phonon role in $\Delta(T)$, we have achieved the major goal of this study. We next see what wetting temperature we would obtain if the only excitations determining the thermodynamic properties of the system are phonons in all three media and ripples on the liquid–vapor interface. This idealistic calculation is presented for illustrative reasons only. For a real system we have to take into account other terms in $\Delta(T)$, one of the most important of which takes into account the adsorption properties of the substrate. Nevertheless, for weakly adsorbing substrates, like cesium, the contribution to $\Delta(T)$ from ripples at the liquid–vapor interface may become the most significant one. Since the phonon contribution vanishes, we have

$$\Delta(T) = \delta\sigma_{lv}(T). \quad (8)$$

We obtain the zero-point term $\delta\sigma_{lv}(0)$ in Eq. (7) by subtracting the phonon contribution $\sigma_{lv}^{\text{ph}}(0)$ given by Eq. (5) from the actual surface tension $\sigma_{lv}(0)$. The value of $\sigma_{lv}(0)$ is tabulated for liquid ^4He [4] together with its mass density ρ_0 and speed of longitudinal sound c_0 [10]. The result for $\Delta(T)$ then takes the form

$$\begin{aligned} \Delta(T) = & \sigma_{lv}(0) - \frac{\hbar\omega_0^3}{96\pi c_0^2} \\ & - \frac{4\hbar}{\pi} \left(\frac{\rho_0}{\sigma_{lv}(0)} \right)^{2/3} \left(\frac{k_B T}{\hbar} \right)^{7/3} \Gamma(7/3)\zeta(7/3) \\ & - \left(\frac{k_B T}{\hbar} \right)^3 \frac{\hbar}{6\pi c_0^2} \zeta(3). \end{aligned} \quad (9)$$

We next substitute the values $\rho_0 = 0.145 \text{ g/cm}^3$, $c_0 = 2.38 \times 10^4 \text{ cm/sec}$, $\sigma_{lv}(0) = 0.2567 \text{ K}\text{\AA}^{-2}$ (we measure the energy in the temperature units), and $\omega_0 = 3.74 \times 10^{12} \text{ sec}^{-1}$ for liquid ^4He to obtain

$$\Delta(T) = 2.308 \times 10^{-2} - 0.4913 \times 10^{-2} T^{7/3} - 0.0193 \times 10^{-2} T^3, \quad (10)$$

expressed in units of $\text{K}\text{\AA}^{-2}$ for the temperature T measured in kelvins. Eq. (2) for the wetting temperature then yields

$$T_w \simeq 1.9 \text{ K}. \quad (11)$$

We observe that this result, following only from introducing the surface tension boundary condition for the liquid helium–vapor interface, is very close to the wetting temperature of Cs, $T_w \simeq 2 \text{ K}$ [2,3]. This may seem surprising since the contribution from the solid in $\Delta(T)$ given in Eq. (10) is absent because of the cancellation we discussed above. We are inclined to believe, however, that this remarkable coincidence could be explained by the fact that due to the ultra-weak adsorption of ^4He by Cs the real system (liquid ^4He on Cs) is quite close to the model assumed in this work. Namely, the results of [9] were obtained under the assumption that the properties of the liquid and solid are the same throughout these media, up to their interface. This assumption does not hold in the case of significant adsorption.

In the present study we have looked at the wetting problem from the standpoint of the macroscopic theory. This theory provides us with a deeper understanding of the role of long wavelength vibrational excitations in the wetting phenomenon deeper than would be provided by a more complete, but also more obscure, microscopic theory. If the solid–vapor and liquid–vapor interfaces are stress-free, the liquid is ideal and inviscid, and the solid can be modeled by an elastically isotropic medium, then only phonon excitations exist in the system. We demonstrated that the contribution from these excitations cancels exactly in the equation for the wetting temperature T_w . This remarkable property of phonons means that it is other excitations, appearing after taking into account any

deviations of the system from this ideal model, that determine whether wetting or non-wetting occurs. We showed that taking into account only the contribution from the ripples to $\sigma_{lv}(T)$ predicts wetting for $T > T_w$, and non-wetting for $T < T_w$, with the wetting temperature $T_w \simeq 1.9 \text{ K}$. This result is very close to the temperature of wetting Cs by liquid ^4He – most likely, due to the resemblance between the real system and our model. The contribution from ripples associated with the liquid–vapor interface, certainly, is not sufficient for the calculation of the wetting temperature for different solids. This calculation requires the knowledge of the contributions from the adsorption potential of the solid and of the excitations at the solid–liquid interface, which may include ripplon-like ones [5]. The theoretical study of these contributions will be a subject of future research.

We thank Professor P. Taborek and Professor J. Rutledge for stimulating discussions. This work was supported in part by NSF Grant No. DMR 93–19404.

References

- [1] J. Treiner, in: Proc. of 21st Int. Conf. on Low Temp. Phys., Czech. J. Phys. 46, suppl. S6 (1996) 2957, and references therein.
- [2] P.J. Nacher and J. Dupont-Roc, Phys. Rev. Lett. 67 (1991) 2966.
- [3] P. Taborek and J.E. Rutledge, Phys. Rev. Lett. 68 (1992) 2184; 69 (1992) 937; 71 (1993) 263.
- [4] M. Iino, M. Suzuki and A.J. Ikushima, J. Low. Temp. Phys. 61 (1985) 155; A.J. Ikushima, M. Iino and M. Suzuki, Can. J. Phys. 65 (1987) 1505.
- [5] J. Klier, P. Stefanyi and A.F.G. Wyatt, Phys. Rev. Lett. 75 (1995) 3709; J. Klier and A.F.G. Wyatt, in: Proc. of 21st Int. Conf. on Low Temp. Phys., Czech. J. Phys. 46, suppl. S1 (1996), 439.
- [6] K.R. Atkins, Can. J. Phys. 31 (1953) 1165.
- [7] M.W. Cole, M.R. Swift and F. Toigo, Phys. Rev. Lett. 69 (1992) 2682.
- [8] A.V. Shchegrov, Phys. Rev. B 53 (1996) 13753.
- [9] D. Hawkins, A.A. Maradudin and A.V. Shchegrov, Solid State Commun. 103 (1997) 381.
- [10] B. Djafari-Rouhani and L. Dobrzynski, J. Physique 43 (1982) 523.