

ADDITIONS AND CORRECTIONS

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R. Garcia,* K. Osborne, and E. Subashi: Validity of the “Sharp-Kink Approximation” for Water and Other Fluids

Page 8114. Our paper¹ contains two typographical errors, and also some serious mistakes in the equations as presented in the Introduction, which we explain below.

The resistivity of the water used in our experiments was 18.2 M Ω -cm, not “8 M Ω ” as incorrectly indicated. Also, eq 8 of our paper should state $D = 2C/3z_{\min}^3 = 8\pi C/9\tilde{V}$.

The principal consequence of the mistakes in the equations as presented in the Introduction is that we must take $V = V_s$ in eq 6 of our paper. Since in all of our subsequent calculations we approximated $V = V_s$ anyway, this does not affect any of the results and comparisons made in the paper. Nevertheless, the difference in the meaning of the equations is important.

In place of eq 2 of our paper, we should have stated that the gas–solid surface tension σ_{gs} should equal the minimum Ω_m of the surface contribution to the grand canonical free energy functional $\Omega[\rho(z)]$

$$\sigma_{gs} = \Omega_m \quad (1)$$

so that eq 3 of our paper should have been

$$\cos \theta = \frac{\Omega_m - \sigma_{ls}}{\sigma_{lg}} \quad (2)$$

To arrive at eq 6 of our paper, we then substitute eqs 2.6 and 2.11 from ref 9a,² obtaining in the special case $l = d_w = z_{\min}$

$$\sigma_{gs} = \Omega(l = z_{\min}) = \sigma_{ls} + \sigma_{lg} + (\Delta\rho) \int_0^\infty \rho_l t(z) dz - \Delta\rho \int_{d_w=z_{\min}}^\infty V_s(z) dz \quad (3)$$

where $\Delta\rho = \rho_l - \rho_g$ is the difference between liquid and gas densities, V_s is the attractive potential of the substrate, and $\rho_l t$ is the attractive potential of the liquid. In this equation, d_w is the minimum distance of approach to the substrate in the sharp-kink approximation, which in our paper we take to coincide with the minimum of the potential z_{\min} (a valid approximation as long as the well depth D is sufficiently deep). By setting $\Omega_m = \Omega(l = d_w = z_{\min})$, we are then in effect assuming that there is, at most, a negligibly thick adsorption layer on the substrate next to the droplet.

We then simplify this by substituting eq 2.9 from ref 9a²

$$-2\sigma_{lg} = (\Delta\rho)^2 \int_0^\infty t(z) dz \approx \Delta\rho \rho_l \int_0^\infty t(z) dz \quad (4)$$

where, in the last step, the density of the gas relative to the liquid is neglected. Substituting, we obtain

$$\sigma_{gs} = \Omega(l = z_{\min}) = \sigma_{ls} - \sigma_{lg} - \Delta\rho \int_{z_{\min}}^\infty V_s(z) dz \quad (5)$$

Then, if we substitute this into eq 2 above, we obtain

$$\cos \theta = -1 - \frac{\Delta\rho}{\sigma_{lg}} \int_{z_{\min}}^\infty V_s(z) dz \quad (6)$$

As stated at the outset, this would be the same as eq 6, which is the central equation of our paper, except that the potential V which appears in the equation should only be the bare substrate potential ($V = V_s$). By similar steps, the same equation may be obtained using eq 2.4 for $\Omega(l)$ in ref 12b if we set the parameter $\delta = 2$.³

Our derivation of eq 6 in our paper is not completely general, since we assumed that the adsorption layer next to the droplet is of negligible thickness ($l - z_{\min} \approx 0$). Profs. L. Schimmele and S. Dietrich, however, recently suggested⁴ that the case where a non-negligible adsorption layer of thickness $l > d_w$ appears on the substrate is also worth considering, since it would be relevant to investigation of second-order wetting transitions.⁴ In this case, substituting eqs 2.6, 2.9, and 2.11 from ref 9a, and making no approximations other than the sharp-kink approximation, we would obtain in terms of the equilibrium thickness l (i.e., coverage $l - d_w$)

$$\cos \theta = -1 - \frac{\Delta\rho}{\sigma_{lg}} \int_l^\infty V_s(z) dz - \frac{\Delta\rho^2}{\sigma_{lg}} \int_0^{l-d_w} t(z) dz + \frac{\Delta\rho}{\sigma_{lg}} \rho_g \int_{l-d_w}^\infty t(z) dz \quad (7)$$

The first of these two corrections gives the increase in the free energy of the adsorbed film due to the formation of increasingly bulk-like solid–liquid and liquid–vapor interfaces as the film grows. The second correction is the decrease in the free energy due to the proximity of the gas phase atoms, which is expected to be negligible so long as $\rho_g \ll \rho_l$.

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References and Notes

- Garcia, R.; Osborne, K.; Subashi, E. *J. Phys. Chem. B* **2008**, *112*, 8114.
- Dietrich, S.; Schick, M. *Phys. Rev. B* **1986**, *33*, 4952 (ref 9a in original paper).
- Cheng, E.; Cole, M. W.; Saam, W. F.; Treiner, J. *Phys. Rev. B* **1992**, *46*, 13967 (ref 12b in original paper).
- Schimmele, L.; Dietrich, S. Private communication.

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