

Impact of Negative Line Tension on the Shape of Nanometer-Size Sessile Droplets

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The sign and value of the line tension has been measured from the size dependence of the contact angle of nanometer-size sessile fullerene (C_{60}) droplets on the planar SiO_2 interface, measured with atomic force microscopy (AFM). Analysis according to the modified Young's equation indicates a negative line tension, with a magnitude between -10^{-11} and -10^{-10} N/m, in good agreement with theoretical predictions. The experiments also indicate that droplets with contact area radii below 10 nm are in fact two-dimensional round terraces.

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Line tension, τ , [1] often plays a role in the interaction of very small aggregates with interfaces or bulk material. Its effects are ubiquitous, affecting nucleation [2–4], droplet formation [5–7], attachment of small particles to fluid interfaces [3,8], formation of foam films [9], and the organization within biomembranes [10,11]. Still, despite its importance, details on τ are highly controversial. There have been many theoretical studies [11–13], which meanwhile at least agree [14] that τ should have a value of about 10^{-11} J/m. There have also been numerous experimental studies [7,15–17], however, not even the magnitude of τ could to date be measured unambiguously. This is surprising since the definition of τ is straightforward, and its measurement appears routine. For instance, for a sessile droplet in equilibrium with its vapor phase, τ is the first order correction for the contact angle, Θ , with respect to the curvature of the three-phase contact line, κ ($\kappa = 1/r$, where r is the droplet contact line radius). This is expressed by the modified Young's equation

$$\cos\Theta = \cos\Theta_\infty - \frac{\tau}{\gamma_{LV}} \kappa \quad (1)$$

with γ_{LV} as the liquid-vapor interfacial energy and Θ_∞ as the contact angle of a macroscopic droplet ($\kappa = 0$). Equation (1) is the most common description of a line tension effect and may even be considered as a (practical) definition of line tension. Thus, it appears most desirable to also measure line tension in the relation described by Eq. (1). According to the theoretically estimated magnitude of τ , line tension only affects the contact angles of nanometer-size droplets. This is the main obstacle to experimental line tension studies. Up to now, all experimental investigations were performed with droplets that were orders of magnitude larger and the deduced line tension values varied in sign and covered a wide range from 10^{-6} to 10^{-12} J/m [17]. It has been suggested [14] (occasionally even by the authors of the studies themselves [16]) that these inconsistencies may have originated from measurement artifacts caused by substrate heterogeneities, both chemical [18] and topographical [19], or other artifacts were interpreted as line tension effects.

In this Letter, we will present for the first time an experimental line tension study with nanometer-size sessile droplets. We indeed observe a size-dependent variation of the contact angle, which can be attributed to a line tension value in agreement with the theoretical predictions. In addition, owing to the observed negative sign of τ , we conclude a minimum size for three-dimensional sessile droplets. The experimental data suggest that smaller aggregates might be two-dimensional discs, which is important for a better understanding of heterogeneous nucleation processes [2,6].

We investigated fullerene (C_{60}) aggregates with the shapes of sessile droplets adsorbed to planar surfaces. The fullerene droplets were prepared by spin-coating (3000 rpm, RT) molecularly smooth silica substrates [20,21] with toluene solutions of different concentrations (typically $<10^{-3}$ mol/l) of C_{60} (99.9 + %, Alfa Aesar) in toluene. The toluene (99.9 + %, Sigma-Aldrich) evaporates and the nonvolatile fullerenes precipitate at the silica surfaces. The fullerene concentration determines amount, size, and distribution of the deposited fullerene aggregates [22]. The surface aggregates were investigated by non-contact Atomic Force Microscopy (Multimode IV, Veeco Instruments, USA) with ultrasharp silicon tips with a tip radius of 2 nm (SSS-NCH model, Nanoworld AG, Switzerland). Great precautions were taken to minimize atmospheric contaminations (spin-coating in a dust free-flow hood and minimum time between substrate cleaning and fullerene deposition, as well as between deposition and imaging).

Figures 1(a) and 1(b) show that fullerene surface aggregates with droplet contact line radii between ≈ 10 and ≈ 100 nm consistently have the shape of smooth spherical caps (aggregates with radii larger than ≈ 100 nm have irregular shapes [23]). The profile of the aggregates suggests that their shape results from the balance of interfacial and line energies. Figure 2(a) presents the contact angles, Θ , of the droplets as a function of the contact line radius, r , for various measurement series performed during the span of several months [24]. Θ was derived by approximating the measured droplet profiles with spherical caps and ex-

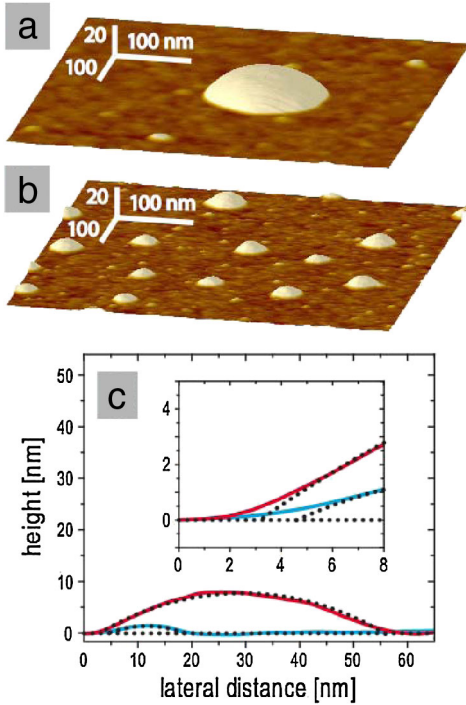


FIG. 1 (color online). Sessile droplets of fullerenes of different sizes, (a) and (b), at a planar silica-air interface. Profiles, (c), show the semispherical cap shape, as well as the decrease of contact angle with decreasing radii. The dashed lines show the idealized spherical droplet profiles from which the contact angles were derived. The smoothing of the measured contact line section (see inset) compared to the sharp contact line for the idealized cap profile is predominantly a tip size artifact.

trapolating the slope of the caps to the contact line [25]. Droplets with radii between ≈ 100 nm and ≈ 30 nm have a contact angle of around 30° . For droplets between ≈ 30 nm and ≈ 10 nm the contact angle decreases to ≈ 5 – 10° .

Figure 2(b) presents $\cos\Theta$ vs κ . The dashed, red line assumes a behavior according to the modified Young's equation [Eq. (1)] with $\cos\Theta_\infty = 0.86$ ($\approx 30^\circ$) and $\cos\Theta = 1$ for $\kappa > 0.10$ nm $^{-1}$. It fits the data reasonably well with the characteristic length scale $\tau/\gamma_{LV} \approx 1.4$ nm. For the explicit calculation of τ , it is assumed that $\gamma_{LV} = 0.05$ J/m 2 [26]. Thus, the data of Fig. 2(b) denote a negative line tension with $\tau = -(7.0 \pm 3.0) \times 10^{-11}$ J/m. The error is estimated based on feasible slopes in Fig. 2(b), without the uncertainty for γ_{LV} .

According to the Eq. (1), for negative τ , $\cos\Theta$ should be 1 at distinct curvature κ . Taking into account the errors, the data from Fig. 2(b) suggest this for κ larger than ≈ 0.1 nm $^{-1}$ ($r = 10$ nm). The data points with $\kappa > 0.1$ nm $^{-1}$ and $\Theta \approx 10^\circ$ might be considered outliers. On the other hand, the measured height of surface aggregates smaller than $r < 10$ nm ($\kappa > 0.1$ nm $^{-1}$) is only $\approx 0.7 \pm 0.2$ nm, the molecular size of C $_{60}$. Hence, they are two-dimensional disks (the seemingly no-zero contact angle results from the breakdown of the spherical cap approximation and the tip curvature, see discussion).

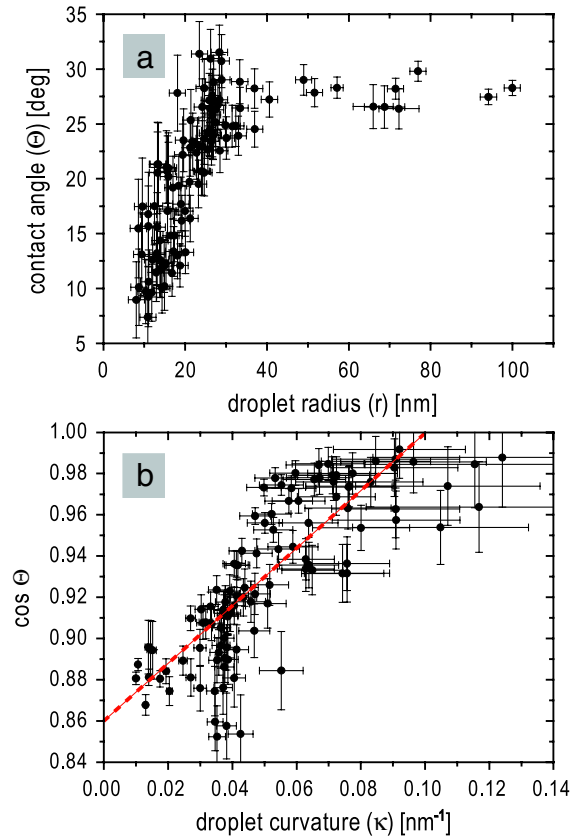


FIG. 2 (color online). Droplet contact angles (Θ) vs radii (r) of the three-phase contact line, (a), and cosine of the contact angle vs droplet curvature (κ) (b). The slope of the dashed, red line corresponds to the characteristic length scale $\tau/\gamma_{LV} \approx 1.4$ nm.

The data suggest the morphological sequence of Fig. 3. Very small aggregates with radii $r < 5$ – 10 nm are two-dimensional, round terraces. Larger aggregates with radii up to ≈ 30 nm are three-dimensional droplets with a pronounced size dependence of their contact angles. For radii larger than ≈ 30 nm, the contact angles are virtually size independent because the line tension term, $\tau/\gamma_{LV}\kappa$, is negligible above that size.

The experimental data and their interpretation raise several questions, in particular, concerning possible experimental artifacts and the applicability of modified Young's equation. The AFM measurements were performed in

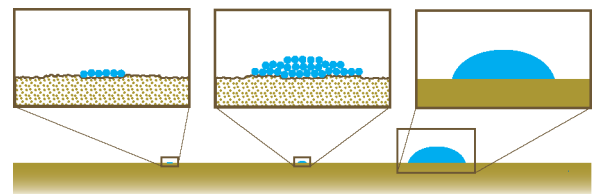


FIG. 3 (color online). Shapes of fullerene aggregates on the silica surface as function of their volume, ranging from small two-dimensional discs (left), to droplets with size-dependent contact angles (middle), to larger droplets with a virtually constant contact angle (right).

amplitude-modulated mode (AM-AFM) with a vertically oscillating cantilever. Experimental [27,28] and theoretical [27,29] studies show that AM-AFM can provide stable, high-resolution images while minimizing the deformation of the sample. The tip is most of the time in the attractive force field at some nm distance from the sample and there is only intermediate, if any, direct contact between tip and sample, with a strong repulsive force. The surface topology is measured by scanning with a constant reduction of the cantilever amplitude ($\approx 25\%$ compared to the free air amplitude, driven at a frequency slightly higher than the free air resonance frequency). The reduction of the amplitude is the result of the distant-dependent forces acting on the tip during the cantilever oscillation. The relation between oscillatory behavior and typically acting force fields is not trivial [27,29]. In spite of this, it is safe to assume that the method approximately probes an equipotential interaction surface, which reflects line tension contributions. For the subtle relation between the choice of the Gibbs dividing interface and the resulting effective line tension, see Schimmele *et al.* [12]. Measurements of the same sample area with varying AFM parameter settings were performed to repudiate imaging-induced, irreversible deformation of the samples. Imaging parameters were optimized to maintain a signal phase lag of less than 1° , minimizing the energy dissipation and, in turn, deformation.

Tip convolution effects were tested by measurement with tips with a larger radius (NCR tips, 10 nm radius, Nanoworld AG). There was a slight decrease in Θ at large κ for the 10 nm tips. Overall, however, a similar line tension effect was observed for both tip radii. For the noncontact mode, the influence of the tip geometry on the measured surface topology is not well known. An educated guess can be drawn, however, from tip radius effects in the contact mode. For small aggregates, this is shown in Fig. 4 with a 2 nm tip in scale with a two-dimensional terrace of C_{60} with a radius of 9 molecules each 0.7 nm in diameter. The measured terrace diameter appears 2–3 nm ($\approx 30\%$ – 40%) larger than the real one and with smoothed edges instead of a step. With our analysis procedure assuming a spherical cap based on the measured height and diameter, such terraces appear to have a contact angle of about 10° , similar to the measured 2D domains.

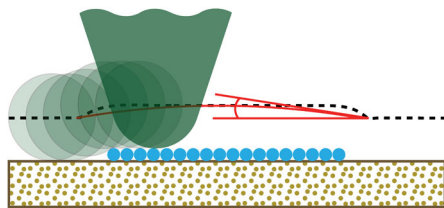


FIG. 4 (color online). Tip with about 2 nm radius scanning over a two-dimensional C_{60} domain ($r \approx 6$ nm). In contact, the tip measures the dashed, black height profile, which has a radius of about 8 nm. The analysis assuming the (solid, red) spherical cap with the measured diameter and apex height results in a contact angle of $\approx 10^\circ$.

A comparison of the measurement errors for different droplet sizes reveals that the measured contact angles of the very small, 2D, aggregates appear larger than they are in reality. For the large sessile droplets, the measured values will agree quite well with the real topology. Thus, the data from Figs. 2(a) and 2(b) might in fact underestimate the line tension. For instance, if $\cos\Theta = 1$ at $\kappa = 0.05 \text{ nm}^{-1}$ ($r = 20$ nm), then $\tau/\gamma_{LV} \approx 2.8$ nm, resulting in $\tau \approx 1.4 \times 10^{-10} \text{ J/m}$. Another point at issue is the value for γ_{LV} , which directly affects the calculated τ . In fact, the characteristic length scale τ/γ_{LV} is a better measure. It is less substance specific because both, τ and γ_{LV} originate from the same interactions. The characteristic length scale τ/γ_{LV} should be in the range of a few molecular sizes [14], which well agrees with the results.

Θ as well as τ are a continuum concept, which may be invalid for very small aggregates with molecular dimensions. However, even flat C_{60} aggregates with a radius of about 10 nm already consist of hundreds of molecules, thus a continuum interpretation of the data appears suitable.

The usage of the modified Young's equation is vindicated by the spherical cap shape of the aggregates, indicating their formation is determined by interfacial and line tension forces. It is important though, to know whether the droplets represent the advancing, receding or equilibrium situation. The spreading kinetics might be size-dependent and thus lead to an effect reminiscent of line tension. In the presented case, the droplets appear to be near or at equilibrium because they remain stable and withhold their shape over long times of weeks, as well as C_{60} exhibiting the mobility of a 2D ideal gas on SiO_2 surfaces [30]. An even stronger support for an equilibrium situation results from surface aggregates of C_{60} on atomically smooth graphite (HOPG) prepared under the same conditions. Contrary to the three-dimensional sessile droplets on silica surfaces, C_{60} forms two-dimensional domains or films (see supplementary material) on the graphite surfaces. Obviously, C_{60} molecules are sufficiently mobile to adjust to the given surface conditions and form the energetically most favorable, equilibrium aggregates.

According to the modified Young's equation a negative sign of τ leads to droplet disintegration for $\Theta = 0$. Thus, small two-dimensional terraces of C_{60} on silica seem inconsistent with the negative τ derived from the general data behavior and the data points for $\kappa > 0.1 \text{ nm}^{-1}$ could be neglected. However, τ is merely a theoretical concept and can be considered only as the first order correction to Young's equation. A general modification to Young's equation reads as

$$\cos\Theta = \cos\Theta_\infty - \frac{1}{\gamma_{LV}}[\tau\kappa + \chi\kappa^2 + \dots]. \quad (2)$$

A positive second-order correction, $\chi\kappa^2$, could stabilize two-dimensional aggregates even if $\tau < 0$, (χ is for τ what the Tolman correction term [31,32] is for γ). In fact, a scenario based on Monte Carlo simulations indicated the heterogeneous nucleation of crystallites is preceded by a

two-dimensional wetting layer, stabilized by a line tension with a second-order curvature correction [2].

In conclusion, a meticulously performed AFM-study shows that C_{60} deposited onto smooth silica surfaces forms small surface aggregates with the shape of nice spherical caps in the size regime between 100 and 10 nm, and probably two-dimensional terraces for smaller aggregates. The smooth, spherical cap profiles indicate that they can be treated like sessile droplets whose shape is determined by the balancing of interfacial energies and line tension effects. Accordingly, the experimental data were analyzed with the modified Young equation, which takes into account as a first order correction the impact of line tension on the contact angle of sessile droplets of varying sizes. The analysis yields a negative line tension with a value between -10^{-10} and -10^{-11} N/m. This value and, in particular, the molecular dimension (≈ 1.4 nm) of the much less error-sensitive, more directly derived characteristic length scale, τ/γ_{LV} , agree well with theoretical predictions. The negative sign of the line tension leads to a lower stability limit for droplets of less than ≈ 10 nm contact area radius. On the other hand, the experimental data indicate that smaller, stable 2-dimensional surface aggregates (terraces) could conceivably exist. These 2-D terraces are possibly stabilized by a positive second-order curvature effect, which compensates the negative first order line tension contribution.

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- [22] Each sample preparation results in a distribution of sessile droplet sizes that are grown under identical conditions and are thus comparable. The presented data are derived from many (> 10) different preparations over a period of months. In addition, the data are the result of different experimental runs (preparation plus analysis) performed independently by two experimentalists (JKB and CW).
- [23] It appears as if the irregularly shaped larger aggregates consist of a conglomeration of smaller aggregates. See supplementary material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.105.076103>.
- [24] Errors are an estimation combined from instrumental (noise) and measurement (deformation) contributions: instrumental: $z: \pm 0.15$ nm, $x, y: \pm 1$ nm; measurement $x, y, z: \pm 0.1$ nm.
- [25] Approximating the droplets shape by a spherical cap shape and identifying the extrapolated slope as a measure of Θ agrees with the thermodynamic definition of Θ . It is consistent with Eq. (1) and avoids any ambiguities for Θ due to local modifications of the contact line section caused by real effects or by measurement artifacts (See Fig. 1). To minimize artifacts in determining the optimum spherical drop shape, an average of several cross sections per droplet, rotated by 45° to each other, was used for the analysis.
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