drops on a surface. If vapour, liquid and solid phases are present, as in the case of the system liquid/vapour, solid/liquid and solid/vapour interfaces coexist. The system tends to minimize the total surface energy, and in this way determines the value of the contact angle and the formation of a spherical cap (similar to that shown in Fig. 1). But molecules in the vicinity of the contact line have an additional special energy, because their environment is different from that in the bulk or at the surface. We therefore expect the existence of a line energy (an idea proposed by Gibbs) proportional to the length of this line, that is, to the number of molecules along it

Orders of magnitude are very useful at this point. The surface tension $\gamma$ is a typical intermolecular potential $V$ divided by the square of a molecular size $a$ ($\gamma \sim V/a^2$), which yields some tens of mN m$^{-1}$ for a generic liquid or solid (only interacting through van der Waals forces). On the other hand, a line tension $\tau$ should be of the order of $V/a$, and thus of about $10^{-11}$ N for similar systems. Note that here we cannot predict the sign of $\tau$, which depends on the nature of the different phases around the line.

The existence of a line tension could modify the contact angle. But whereas the line energy scales as $\tau r$ (where $r$ is the drop size), the surface energy scales as $\gamma r^2$. Thus we expect that the contact angle should deviate from its macroscopic value for small drops — the analysis of the deviation providing a measurement of $\tau$. A positive $\tau$ should tighten the molecules in the droplet against each other, causing an increase in the contact angle and a rounding up of the shape of the drop. The opposite should happen for a negative $\tau$. Most deviations have indeed been interpreted as resulting from $\tau$, but values deduced from these deviations spanned over seven orders of magnitude (between $10^{-12}$ and $10^{-5}$ N), and even the sign of $\tau$ was not clear for measurements performed on very similar systems. If we come back to our naive scaling arguments, we would expect these deviations to be relevant only for drops of nanoscopic size, hence much smaller than those observed experimentally.
Checco and colleagues explored the change in contact angle with decreasing drop size by condensing a vapour of alkane on a well-defined solid. The shape of the drop was analyzed using an AFM in true non-contact mode, from which the value of the contact angle could be precisely deduced. The authors observed that for drop sizes between 2 µm and 200 nm, the smaller the drop, the smaller the angle. The precision of the experiments together with the amplitude of the range explored allowed the authors to conclude, surprisingly but definitely, that the contact-angle deviation could not be fitted by the classical correction of \( \tau \). Trying to fit the correction on small portions of the experimental curves would not provide a fixed value for \( \tau \), but one that changed depending on the drop size. Besides, as stressed above, these corrections should not hold for such 'large' drops.

To explain these results, Checco and colleagues built a very simple model, which is likely to be relevant for most experiments performed to date for the same purpose. A solid (even if very carefully prepared) always has inhomogeneities (physical or chemical) at its surface. This can be revealed by AFM mapping, or macroscopically by the fluctuation in the values of contact angle of a macroscopic drop (of very small amplitude in Checco's case, yet measurable). Tiny drops appear preferentially on the most wettable spots, acting as nucleators for the condensation — which explains the small values of the contact angle for small drops. As the drop size increases, the contact angle increases, because such drops explore a domain larger than the size of the heterogeneities. Minimizing the surface energy of the drop on this heterogeneous substrate (a method first proposed by Cassie and Baxter and improved by Swain and Lipowsky) allowed Checco and colleagues to deduce a variation of the contact angle as a function of the drop size. Using AFM mapping of the surfaces, the authors could calculate contact angles for each drop size, which provides very convincing fits of the data on the whole range of sizes.

Although simple, the model of Checco and colleagues is important because it settles an old question, explains experimental observations, old and new, and shows that previous interpretations of decreasing contact angle with decreasing size based solely on the line tension argument were irrelevant at microscopic scales.

**References**