



Review article

Line tension and its influence on droplets and particles at surfaces



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ABSTRACT

In this review we examine the influence of the line tension τ on droplets and particles at surfaces. The line tension influences the nucleation behavior and contact angle of liquid droplets at both liquid and solid surfaces and alters the attachment energetics of solid particles to liquid surfaces. Many factors, occurring over a wide range of length scales, contribute to the line tension. On atomic scales, atomic rearrangements and reorientations of submolecular components give rise to an atomic line tension contribution τ_{atom} (~ 1 nN), which depends on the similarity/dissimilarity of the droplet/particle surface composition compared with the surface upon which it resides. At nanometer length scales, an integration over the van der Waals interfacial potential gives rise to a mesoscale contribution $|\tau_{vdW}| \sim 1$ –100 pN while, at millimeter length scales, the gravitational potential provides a gravitational contribution $\tau_{grav} \sim +1$ –10 μ N. τ_{grav} is always positive, whereas, τ_{vdW} can have either sign. Near wetting, for very small contact angle droplets, a negative line tension may give rise to a contact line instability. We examine these and other issues in this review.

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1. Introduction

Two bulk phases, i and j , intersect at a surface. This surface possesses an associated surface tension, or, energy per unit area σ_{ij} . Similarly, three bulk phases meet at a line, the three-phase contact line. This contact line possesses an associated line tension, or, energy per unit length τ . In this review we summarize our views on the line tension associated with a three-phase contact line. Thus, the ideas in this review are directly applicable to liquid droplets at a solid (Fig. 1a) or liquid (Fig. 1b) surface, particles at a liquid surface (Fig. 1c), as well as, thin films or foams in contact with a bulk liquid phase (Fig. 1d). The term “line tension” is also used to describe the two-dimensional surface discontinuity for an (insoluble) surface monolayer at a liquid surface [1,2] (Fig. 1e), however, this review is restricted solely to the line tension at three-phase contact lines (Fig. 1a–d).

The line tension plays an important role in governing the statics, dynamics, and stability of numerous soft matter systems. For example, the line tension determines droplet contact angles around fibers [3], at liquid [4], solid [5], and heterogeneous solid [6,7] surfaces, as well as, strongly influencing droplet behavior in the vicinity of wetting transitions [8–12]. When considering surface nucleation [13–17] and vaporization [18] phenomena, line tension contributions should be included. Surface dynamics, such as, droplet spreading [19,20] and droplet fragmentation [21,22] are both influenced by line tension effects. The stability of films [23], foams [24,25], liquid filaments [26,27], spherical droplets [28,29], and nanobubbles [30] are all governed by line tension effects. Line tension contributions are important in determining the depletion interaction between nanoparticles adsorbed at liquid surfaces [31], as well as, nanoparticle adsorption to [32] and detachment from [33,34] these surfaces. Hence, the line tension plays a role in mineral separation via the flotation process [35].

Despite the importance that the line tension plays in many surface related phenomena, line tension studies have often proven controversial. This controversy stems mainly from discrepancies in the line tension *magnitude* between mean field theories ($|\tau_{theory}| \sim 10^{-12}$ – 10^{-10} N), computer simulations ($|\tau_{MD}| \sim 10^{-12}$ – 10^{-11} N), and experimental measurements ($|\tau_{expt}| \sim 10^{-12}$ – 10^{-6} N) [36,37]. The experimental range for the line tension magnitude is very broad where, although a number of experiments agree with theory and computer simulations, there are many other experiments (usually for large millimeter-sized liquid droplets at surfaces [38]) which differ by many orders of magnitude from mean field theoretical predictions. An added complication, originally pointed out by Gibbs [39], is that the line tension may be of either sign and, in fact, both positive and negative line tensions have been determined via theory, computer simulations, and experiment. Thus, the line tension has sometimes been characterized as being ill-defined, both in magnitude and in sign, where the reliability of many experimental measurements have been called into question. This has led to the rather unfortunate situation where the concept of the line tension is sometimes completely ignored in situations where it plays an important role. The origin of the wide range in experimental line tension magnitudes $|\tau_{expt}|$ is addressed in a number of sections in this review (Sections 2.3, 3.1.1, 4, and 5).

There are other less contentious controversies in this field, some of which have now been resolved, while others are still generating significant discussion. In the partial wetting region a droplet on a solid surface will possess a finite, non-zero contact angle ($\theta > 0^\circ$) where the three-phase solid-liquid-vapor contact line (Fig. 1a) possesses an associated line tension τ . As a wetting transition is approached (eg. by increasing the temperature) the contact angle θ decreases and becomes equal to zero at and above the wetting transition. The solid surface is now covered by a thick wetting film. Thus, the three-phase contact line disappears at a wetting transition. This disappearance of the three-phase contact line gives rise to many questions. What is the functional behavior of the line tension as the wetting transition is approached? Is the line tension zero, finite, or infinite at the wetting transition? If the line tension is finite at the wetting transition, what is the sign of the line tension? Questions such as these generated significant theoretical discussion where differing groups arrived at differing answers. Much of this debate now appears to have been resolved [8]. The answers depend upon the order of the wetting transition (first or second order), as well as, the range of the surface interactions. These issues, including the origin of the sign of the line tension, will be discussed briefly in Section 2.3.

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